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# Phonons in complex oxides

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## Résumé

Les oxydes complexes sont une classe de matériaux céramiques combinant atomes de métaux, terres rares et oxygène dans des formulations aussi bien stœchiométriques que non-stœchiométriques. Ces oxydes sont connus pour présenter des propriétés physiques extraordinaires dues le plus souvent à des interactions fortes, dirigées, et ordonnées entre charges, spins, orbitales, liées à la dynamique du réseau cristallin et, dans les cas étudiés dans cette thèse, à la structure distordue des octaèdres  $MO_6$ . En effet la plupart de ces composés sont du type structural pérovskite. Ainsi, la nature de la liaison cation-oxygène détermine en partie leurs propriétés électroniques et magnétiques particulières. On peut citer comme exemples d'oxydes complexes : ZnO, un semi-conducteur à large gap luminescent et à grande mobilité électronique ; LaMnO<sub>3</sub>, antiferromagnétique et isolant de Mott, mais aussi un composé à magnétorésistance géante sous dopage ; les composés métalliques comme SrRuO<sub>3</sub> ; les supraconducteurs à haute température critique (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>) ; des ferroéléctriques (BaTiO<sub>3</sub>) ; des composés multiferroïques (TbMnO<sub>3</sub>) ; des matériaux « spinice » frustrés conduisant dans certains cas à l'observation de quasi-monopoles magnétiques (Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>).

Le sujet de cette thèse concerne des mesures de diffusion Raman sur une nombreuse série ou grande variété d' oxydes complexes de type pérovskite : monocristaux de YCrO<sub>3</sub>, YMnO<sub>3</sub>, *RBO*<sub>3</sub> (*R* – terre rare, *B* – Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ga), Sc<sub>3</sub>CrO<sub>6</sub>, et Sc<sub>2</sub>O<sub>3</sub>, et des poudres de sesquioxydes de terres rares du type  $R_2O_3$  avec *R* – Sc, Lu, Er , Y, Ho, Gd, Eu, Sm, et Nd. Ces résultats sont discutés en détail par l'analyse des modes Raman, la simulation ou prédiction des spectres, complétés par une étude systématique des modes « mous » dans les pérovskites *ABO*<sub>3</sub>. Les propriétés physiques intéressantes de quelques uns de ces oxydes sont décrites très brièvement ci-dessous.

 $YCrO_3$  existe sous forme monoclinique et orthorhombique. La dernière variété est faiblement ferromagnétique sous  $T_N = 140$  K. Cette phase est aussi antiferromagnétique cantée avec des propriétés multiferroïques. De même, le composé orthorhombique  $YMnO_3$  est une manganite multiferroïque à basses températures, présentant une faible polarisation due à une brisure de symétrie induite par frustration magnétique, avec  $T_c < T_N$  au dessous de 50 K.

 $Sc_2O_3$  appartient à la classe des sesquioxydes de terres rares (comme  $Y_2O_3$  et  $Lu_2O_3$ ). Ce composé est une céramique optiquement transparente pouvant être utilisée comme scintillateur afin de convertir une radiation ionisante de haute énergie en photons de l'UV-visible. Cet oxyde possède également un haut index de réfraction (1.90 à 400 nm) et coupe l'UV à 215 nm ce qui en fait un candidat à des applications en photonique et optoélectronique. Il a de plus une conductivité thermique élevée, appropriée pour une utilisation dans les lasers solides de forte puissance.

Pratiquement tous les oxydes décrits dans ce travail ont été étudiés structuralement par la diffraction X et la microscopie électronique que ce soit dans cette thèse ou ailleurs, et certaines de leurs propriétés électroniques, magnétiques et optiques ont été mises en évidence dans la littérature comme nous l'avons indiqué plus haut. Cependant une étude exhaustive de leurs propriétés vibrationnelles restait à accomplir en relation avec leur structure complexe. La dynamique de réseau de ces matériaux et plus spécialement l'analyse de leurs spectres de diffusion Raman nécessitaient une approche globale basée sur une comparaison avec de très nombreuses données de la littérature concernant les pérovskites. C'était l'objectif de cette thèse : le travail relaté dans ce mémoire a permis d'élucider les relations existant entre les distorsions structurales qui sont essentielles dans les propriétés physiques de ces matériaux et les marqueurs spécifiques que sont les bandes Raman atypiques (modes quasi-mous ou autres) observées au cours de l'étude.

Le premier Chapitre de la thèse examine les spectres Raman des cristaux orthorhom-

biques de type ABO<sub>3</sub> suivants : le composé YCrO<sub>3</sub> et les cristaux maclés de YMnO<sub>3</sub>. On montre en premier lieu que la structure réelle observée de groupe *Pnma* est le résultat de quatre type de distorsions structurales affectant la structure idéale cubique  $Pm\bar{3}m$ . Ces structures distordues ont les symétries Imma, P4/mbm, et Cmcm, correspondant respectivement aux distorsions de tilt des octaèdres BO<sub>6</sub> le long des directions cubiques [101], [010], à la distorsion de Jahn-Teller, et au décalage de l'atome A (A-shift). La symétrie des bandes Raman est déterminée par des mesures de polarisation sous différentes configurations de diffusion. Par comparaison avec des études antérieures déjà publiées sur YCrO<sub>3</sub>, nous trouvons deux nouvelles bandes Raman de type  $B_{1g}$  et  $B_{2g}$  à 556 et 611 cm<sup>-1</sup>. Sur ce matériau il n'y a pas d'effets de résonance et cela est vérifié avec quatre excitations laser différentes. Des calculs de dynamique de réseau (LDC) basés sur le formalisme d'un modèle empirique à coquille permettent d'attribuer les bandes observées à des vibrations atomiques spécifiques. Comme anticipé, les deux composés isostructuraux traités dans ce chapitre présentent des modes de vibrations proches, mais les intensités des bandes Raman diffèrent notablement. L'interprétation de ce résultat s'appuie sur le modèle structural proposé par Abrashev et coll. qui ont montré que l'intensité des pics Raman dépend des quatre distorsions structurales précitées. La forte intensité de deux modes  $B_{1q}$  et  $B_{2q}$  dans YMnO<sub>3</sub> est expliquée par une distorsion de Jahn-Teller (JT) importante. Cependant, la faible intensité des autres pics dans YMnO<sub>3</sub> par rapport à celle des pics correspondants de YCrO<sub>3</sub> ne peut être expliquée par ce modèle. Cette intensité diminuée est certainement due à un fin maclage des cristaux de manganite résultant d'un ordre de IT.

Cette notion de modes « mous » dans les manganites est étendue ensuite à plusieurs pérovskites distordues RBO<sub>3</sub> dans le Chapitre 2 où R est une terre rare et B – Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ga. Ces perovskites présentent une rotation des octaèdres BO<sub>6</sub>. L'analyse systématique des données existant dans la littérature sur la structure et les spectres Raman de ces composés montre que dans chaque famille la fréquence des modes mous est proportionnelle à l'angle de tilt  $\alpha'$  des octaèdres distordus de la structure orthorhombique *Pnma*. Les modes mous sont associés à des instabilités anti-ferrodistortives. La distance B - 0 moyenne pour tous les membres d'une famille RBO3 donnée ne varie pas et constitue un paramètre structural de meilleure qualité avec une meilleure précision que le rayon ionique employé usuellement. Le coefficient de proportionnalité  $\varkappa$  entre la fréquence du mode « mou » et l'angle de tilt octaédrique dépend de la distance moyenne  $\langle B-0 \rangle$ . Cette dépendance peut- être approximée avec la même précision en utilisant différentes fonctions (puissance, linéaire et exponentielle). Toutes ces fonctions prédisent avec la même précision la fréquence des modes « mous » dans ces perovskites, qui peut ensuite être utilisée dans l'analyse des structures et des spectres Raman. Ainsi l'angle de tilt des octaèdres dans ces structures peut être directement déduit des spectres Raman, ce qui au final s'avère très utile puisque ces tilts déterminent leurs propriétés électroniques et magnétiques.

Le Chapitre 3 est consacré à l'étude de la LDC de l'oxyde complexe ternaire  $Sc_3CrO_6$ . Pour cette partie des monocristaux de  $Sc_3CrO_6$  sont élaborés par « croissance à haute température en solution », et comme pour les autres cristaux caractérisés par rayons X, analysés sous microscope électronique en EDX, et en spectroscopie micro-Raman. Nous confirmons que la composition chimique de ce matériau n'est pas stœchiométrique avec une formulation :  $Sc_3Cr_1Cr_{1-x}Sc_xO_{12}$ , x = 0.08, composition qui résulte de l'existence deux octaèdres différents  $Cr1O_6$  et  $(Cr,Sc)2O_6$ . Cette observation est en accord avec la structure affinée du cristal  $R\bar{3}$ . Les spectres Raman polarisés sont enregistrés à température ambiante pour différentes configurations géométriques, qui nous permettent de déterminer la symétrie des modes actifs en Raman contenus dans la représentation  $9A_g + 9E_g$ . Les fréquences et la symétrie des modes de vibrations calculés par dynamique de réseau sont en bon accord avec les fréquences expérimentales. Les modes calculés sont discutés par une approche moléculaire qui prédit la séparation des modes en groupes de fréquences proches. Ces regroupements peuvent être expliqués par : a) la présence de deux octaèdres différents dans la maille élémentaire, et b) par

le fait que la structure rhomboédrique est très proche d'une structure cubique avec un angle de maille  $\alpha = 91.97^{\circ}$ . En effet, cette hypothèse est justifiée par le calcul LDC de huit modes de haute fréquence provenant des élongations internes de l'octaèdre  $CrO_6$ . En plus des mesures à température ambiante, nous avons également acquis des spectres Raman dans la gamme de températures  $20 - 600^{\circ}$ C. Lorsque la température d'observation croît, l'intensité des pics  $A_g$  décroît par rapport à celle des autres pics ce qui suggère une transition de la structure  $R\bar{3}$  vers une structure  $R\bar{3}c$ .

Le dernier Chapitre présente une caractérisation cristallographique et Raman complète de monocristaux  $Sc_2O_3$ . La diffraction des rayons X confirme que les échantillons sont cubiques et cristallisent dans le groupe d'espace  $Ia\bar{3}$  ce qui les classe dans le type C des sesquioxydes de terre rare. La théorie des groupes prévoit donc les modes actifs en Raman suivants :  $4A_g + 4E_g + 14F_g$ . Tous les modes  $A_g$ ,  $E_g$ , et 11 modes  $F_g$  sur les 14 prévus sont observés expérimentalement, et leur symétrie est obtenue par des mesures Raman en lumière polarisée. Pour ce cristal, les résultats expérimentaux sont en très bon accord avec des calculs DFT de dynamique de réseau.

Cette étude est étendue à une analyse comparative des modes actifs en Raman dans les types C d'oxydes de terre rare  $R_2O_3$  dont les propriétés vibrationnelles n'ont été que peu étudiées en raison du fait qu'ils se présentent sous forme de poudres, rendant très difficiles des mesures Raman précises en lumière polarisée. Nous montrons que la grande différence de masse entre les ions oxygène et de terre rare conduit à la séparation des phonons en deux groupes : les vibrations des atomes d'oxygène à hautes fréquences, et les vibrations de terre rare à basses fréquences. Un calcul LDC dans un modèle à coquille montre un bon accord entre les fréquences expérimentales et calculées et confirme l'origine des modes. Lorsque R = Eu, on observe un amollissement systématique des fréquences intermédiaires de vibration des atomes d'oxygène. Cette anomalie est sans doute due à la présence de lacunes d'oxygène dans la structure cristalline qui rendent celle-ci non stœchiométrique.

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## Introduction

#### Goals of the thesis

The major goal of our research is to study different complex oxides using Raman spectroscopy as a main experimental technique, supplemented by x-ray diffractometry and lattice dynamical calculations. Many of these materials exhibit strong relationships between charge, spin and orbital degrees of freedom. From this, there can arise a variety of phenomena. Most importantly for our research, many of these properties are conjugated with specific structural transitions, which can be regarded as distortions of the idealized perovskite structure. Therefore, we are interested in Raman spectroscopy of complex oxides as it is very sensitive to vibrations of the light atoms (like the oxygen atoms), since the frequency and the selection rules of the atomic vibrations depend on the local atomic coordination and symmetry.

First we want to find good overall correspondence between modes in the two isostructural compounds - YCrO<sub>3</sub> and YMnO<sub>3</sub> and to show, that the difference of the intensities of corresponding modes could be explained within the framework of a simple structural model, where the real orthorhombic *Pnma* structure is described as a combination of four basic structural distortions and each of the Raman modes is activated by at least one of these distortions. Moreover, we want to expand our studies over series of ABO<sub>3</sub> perovskites with orthorhombic *Pnma* structure and to show that the frequencies of the Raman modes, which have the same symmetry as the BO<sub>6</sub> octahedral tilts [rotation around [101] and [010] cubic axis] will scale with the angle of these tilts, like the soft mode does in the case of the rhombohedral  $R\bar{3}c$  structure. Further, we will determine the exact structure of  $Sc_3CrO_6$  and its optical phonons to check if this structure can be considered as distorted more simple cubic structure and to find the correspondence between the phonons in both structures. In addition, we want to show that if we study in details the Raman spectra of a single crystals, by polarized and temperature measurements and lattice dynamical calculations, a phase transition to higher symmetry structure could be predicted. Even more, we could unambiguous determine the symmetry of the Raman modes for each compound of a given series from nonpolarized measurement of powders (in our case  $R_2O_3$  sesquioxides, R – rare-earth).

### Crystal structure of cubic perovskite

The perovskite family consists of a large class of inorganic compounds with same type of crystal structure as the mineral perovskite –  $CaTiO_3$ . The vast majority of chemical elements, which adopts the perovskite structure, their ability to form cation- or anion-deficient structures, as well as distorted perovskite-like structures, results in broad diversity of physical properties and phenomena such as high- $T_c$  superconductivity, ferroelectricity, colossal magnetoresistance, spin, charge and orbital ordering, insulator-metal transition, large thermoelectric power at low temperature, etc. All this makes these compounds very attractive to the researchers for decades.

The perovskite oxides have the general formula ABO<sub>3</sub>. The crystal structure of an ideal

perovskite can be described as corner shearing  $BO_6$  octahedra [see Figure 1 (a)] and A cation, occupying the center of a 12-fold oxygen coordination vicinities, formed by eight adjacent octahedra [see Figure 1 (b)], so it can be regarded as a superstructure of  $ReO_3$  with A cation incorporated in the center of the cube. Perovskites with ideal cubic structure (space group  $Pm\bar{3}m$ ) are not very common, even the mineral  $CaTiO_3$  is slightly distorted. These deviations of the idealized structure can be a result of:

- size effects concerning the ionic radius of the *A* and *B* elements;<sup>[1,2]</sup>
- different *B* 0 bond length in the *B*O<sub>6</sub> octahedron (Jahn-Teller effect);
- ordering in solid solutions of  $(A_x A'_{1-x})BO_3$  or  $A(B_x B'_{1-x})O_3$  types;
- oxygen deficiency or ordering of the vacancies  $(A_n B_n O_{3n-x})$  and others.

In most cases the distortion of a certain perovskite is a combination of two or more of the above effects. In the ionic crystals (like the perovskites) the atoms are touching one another and the interatomic distances are equal to the sum of the ionic radii (of the touching ions), <sup>[3]</sup> so the lattice parameter of the cubic perovskite *a* is equal to  $\sqrt{2}(r_A + r_0)$ , on the other hand it can be described with the following expression:  $2(r_B + r_0)$ , where  $r_A$ ,  $r_B$  and  $r_0$  are the ionic radii of ions in *A*-, *B*-site and the oxygen, respectively. Goldschmidt<sup>[4]</sup> introduced the ratio

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

known as *tolerance factor* and it is used as a measure of the deviation from the ideal situation. As it is seen for the idealized cubic structure t = 1. For t > 1, A cation is too big or B cation is too small, the structure is hexagonal (i.e. BaNiO<sub>3</sub><sup>[5]</sup>), beyond the hexagonal region, a cubic bixbyite structure is formed. For t in the interval (0.9, 1) the structure is still cubic (i.e. BaTiO<sub>3</sub> and SrTiO<sub>3</sub>), whereas for 0.71 < t < 0.9 – small A cation, the  $BO_6$  will tilt in order to fill space and this will lower the symmetry to orthorhombic *Pnma* [see Figure 2 (a)] or rhombohedral  $R\bar{3}c$  [see Figure 2 (b)].

#### Raman spectroscopy as an experimental method

Briefly here we give the outline for the nature, advantages and disadvantages of Raman spectroscopy as the main experimental method used in this thesis, for the characterization of the studied samples.

#### Inelastic scattering of light

Simply stated the Raman effect can be described as inelastic scattering of light by inhomogeneities of the medium. Defects/imperfections (i.e. dislocations) in the solid, leads to elastic scattering, where no frequency shift of the incoming radiation is observed. However, modulation of the inhomogeneities due to atomic vibrations in the medium, leads to a shift of the frequency of scattered light. Inelastic scattering of light by acoustic phonons was predicted by Léon Brillouin in 1922<sup>[6]</sup> (independent theoretical studies were made by Leonid Mandelstam in 1918, nevertheless he published his results four years later in 1926<sup>[7]</sup>). After that, inelastic scattering of light by molecular vibrations was reported by C. V. Raman<sup>[8,9]</sup> in 1928,



**Figure 1.** Crystal structure of the ideal cubic  $ABO_3$  perovskite, with space group  $Pm\bar{3}m$ , where the Wyckoff notations for the different ions are A - 1b (1/2, 1/2, 1/2), B - 1a (0, 0, 0) and 0 - 3d (1/2, 0, 0). (a) Visualization as corner sharing  $BO_6$  octahedra showing the six-fold oxygen coordination of the *B* cation. (b) The *A* cation occupy the center of the vicinity which is created by 8 octahedra, giving the *A* cation a 12-fold oxygen coordination.



**Figure 2.** As a result of the  $BO_6$  octahedral tilt from the ideal cubic perovskite can be obtained superstructures with lower symmetry. (a) Unit cell of GdFeO<sub>3</sub>-type structure with space group *Pnma*. (b) Rhombohedral unit cell, in this case the real structure of LaAlO<sub>3</sub> with  $R\bar{3}c$  symmetry. For comparison the unit cell of the cubic perovskite is also given, as well as the relative orientation of the basis vectors in the different structures. The indices c, o and r stand for cubic, orthorhombic and rhombohedral basis, respectively.

later in 1930, Raman received the Nobel Prize in Physics "for his work on the scattering of light and for the discovery of the effect named after him".

According to the classical theory, when plane electromagnetic wave with frequency  $\omega_i$ and wave vector  $\mathbf{k}_i$ ,

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_{i}(\mathbf{k}_{i},\omega_{i})\cos{(\mathbf{k}_{i}\cdot\mathbf{r}-\omega_{i}t)},$$

propagates in an infinite, isotropic medium with electric susceptibility  $\chi$ , it is induced a polarization **P**(**r**, *t*)

$$\mathbf{P}(\mathbf{r},t) = \mathbf{P}_{i}(\mathbf{k}_{i},\omega_{i})\cos{(\mathbf{k}_{i}\cdot\mathbf{r}-\omega_{i}t)},$$
(1)

with the same frequency and wave vector as the incoming wave, and amplitude depending on the susceptibility  $\chi$  as

$$\mathbf{P}_{i}(\mathbf{k}_{i},\omega_{i}) = \chi \mathbf{E}_{i}(\mathbf{k}_{i},\omega_{i})$$
<sup>(2)</sup>

The atomic vibrations in solids are quantized into phonons. At non-zero temperatures the electric susceptibility is modified by thermally excited phonons with atomic displacements,  $\mathbf{Q}(\mathbf{r}, t)$ , described as plane waves

$$\mathbf{Q}(\mathbf{r},t) = \mathbf{Q}(\mathbf{q},\omega_{\rm ph})\cos\left(\mathbf{q}\cdot\mathbf{r}-\omega_{\rm ph}t\right)$$

with wave vector **q** and frequency  $\omega_{\rm ph}$ . These displacements will slightly modify the susceptibility, and since their magnitudes, **Q**(**q**,  $\omega_{\rm ph}$ ), are small in comparison with the lattice constant, one can expand  $\chi$  in a Taylor series of **Q** 

$$\chi(\mathbf{k}_{i},\omega_{i},\mathbf{Q}) = \chi_{0}(\mathbf{k}_{i},\omega_{i}) + \left(\frac{\partial\chi}{\partial\mathbf{Q}}\right)_{\mathbf{Q}=0} \mathbf{Q}(\mathbf{r},t) + \cdots, \qquad (3)$$

where  $\chi_0$  is the electric susceptibility at equilibrium position, and the second therm in Equation (3) represents the derivative of susceptibility with respect to **Q**, again at equilibrium position. Substituting Equations (3) and (2) into (1) yields to the following expression for the polarization of the medium

$$\mathbf{P}(\mathbf{r}, t, \mathbf{Q}) = \mathbf{P}_0(\mathbf{r}, t) + \mathbf{P}_{\text{ind}}(\mathbf{r}, t, \mathbf{Q}),$$

where

$$\mathbf{P}_{0}(\mathbf{r},t) = \chi_{0}(\mathbf{k}_{i},\omega_{i})\mathbf{E}_{i}(\mathbf{k}_{i},\omega_{i})\cos{(\mathbf{k}_{i}\cdot\mathbf{r}-\omega_{i}t)}$$

describes the oscillations of the induced dipole moment, with the same frequency as of the incident light. This process is elastic Rayleigh scattering, whereas

$$\mathbf{P}_{\text{ind}}(\mathbf{r}, t, \mathbf{Q}) = \left(\frac{\partial \chi}{\partial \mathbf{Q}}\right)_{\mathbf{Q}=0} \mathbf{Q}(\mathbf{r}, t) \mathbf{E}_{i}(\mathbf{k}_{i}, \omega_{i}) \cos\left(\mathbf{k}_{i} \cdot \mathbf{r} - \omega_{i}t\right)$$
(4)

is the induced polarization, modulated by the atomic vibrations.

We can find out the frequency and the wave vector of  $\mathbf{P}_{ind}$  by substituting  $\mathbf{Q}(\mathbf{r}, t)$  in Equa-4 tion (4), and by using that  $\cos \alpha \cos \beta = \frac{1}{2} [\cos (\alpha - \beta) + \cos (\alpha + \beta)]$  Equation (4) yields

$$\mathbf{P}_{ind}(\mathbf{r}, t, \mathbf{Q}) = \left(\frac{\partial \chi}{\partial \mathbf{Q}}\right)_{0}^{0} \mathbf{Q}(\mathbf{q}, \omega_{ph}) \cos\left(\mathbf{q} \cdot \mathbf{r} - \omega_{ph}t\right) \mathbf{E}_{i}(\mathbf{k}_{i}, \omega_{i}) \cos\left(\mathbf{k}_{i} \cdot \mathbf{r} - \omega_{i}t\right)$$

$$= \frac{1}{2} \left(\frac{\partial \chi}{\partial \mathbf{Q}}\right)_{0}^{0} \mathbf{Q}(\mathbf{q}, \omega_{ph}) \mathbf{E}_{i}(\mathbf{k}_{i}, \omega_{i}) \cos\left[(\mathbf{k}_{i} - \mathbf{q}) \cdot \mathbf{r} - (\omega_{i} - \omega_{ph})t\right]$$

$$+ \frac{1}{2} \left(\frac{\partial \chi}{\partial \mathbf{Q}}\right)_{0}^{0} \mathbf{Q}(\mathbf{q}, \omega_{ph}) \mathbf{E}_{i}(\mathbf{k}_{i}, \omega_{i}) \cos\left[(\mathbf{k}_{i} + \mathbf{q}) \cdot \mathbf{r} - (\omega_{i} + \omega_{ph})t\right].$$
(5)

So, with this simple classical approach for description of the interaction of plane electromagnetic wave with infinite isotropic medium we could qualitatively evaluate the mechanism of Rayleigh and Raman scattering. The first one can be considered as a consequence of oscillations with frequency  $\omega_i$  induced by the electric field of the incoming wave, whereas the second one is consequence of oscillations with frequency  $\omega_i \pm \omega_{ph}$ , as a result of the modulation of the incident light by the atomic vibrations with frequency  $\omega_{ph}$ . As it is seen from Equation (5),  $\mathbf{P}_{ind}$ , is a superposition of two waves: Stokes shifted with frequency  $\omega_s = \omega_i - \omega_{ph}$  and wave vector  $\mathbf{k}_s = (\mathbf{k}_i - \mathbf{q})$ , and anti-Stokes shifted with frequency and wave vector  $\omega_s = \omega_i + \omega_{ph}$  and  $\mathbf{k}_s = (\mathbf{k}_i + \mathbf{q})$ ,<sup>(1)</sup> respectively. The difference between frequency of the incident and the scattered light gives the Raman shift. The dependence of the scattered light intensity on the Raman shift is the Raman spectra.

Actually, the Raman process is a quantum-mechanics interaction and it can be described as follows: when an incident photon with frequency  $\omega_i$  interact with a medium it is either



**Figure 3.** Conservation of the momentum in Raman scattering process.  $\mathbf{k}_i$ ,  $\mathbf{k}_s$  and  $\mathbf{q}$  are the wave vectors of the incident/scattered light and the phonon, respectively. (a) Stokes process:  $\mathbf{k}_i = \mathbf{k}_s + \mathbf{q}$ . (b) Anti-Stokes process:  $\mathbf{k}_i = \mathbf{k}_s - \mathbf{q}$ .

annihilated and creates a phonon with frequency  $\omega_{\rm ph}$  and a Stokes photon with frequency  $\omega_{\rm s} = \omega_{\rm i} - \omega_{\rm ph}$  [Figure 3 (a)], or together with a phonon is annihilated and creates anti-

<sup>&</sup>lt;sup>(1)</sup>The index s in  $\omega_s$  and  $\mathbf{k}_s$  stand for scattered light.

Stokes photon with frequency  $\omega_s = \omega_i + \omega_{ph}$  [Figure 3 (b)]. The intensity of the scattered light depends on the temperature as the intensity ratio of the two lines is given by

$$I_{\rm s}(\omega_{\rm i}+\omega_{\rm ph})/I_{\rm s}(\omega_{\rm i}-\omega_{\rm ph}) = \exp\left(-\hbar\omega_{\rm ph}/k_{\rm B}T\right)$$

It is seen that anti-Stokes lines vanishes at  $T \rightarrow 0$ , because there are no available phonons to be annihilated in ground state.

During these processes of scattering, the energy and momentum have to be conserved. The magnitude and the orientation of **q** depends on the geometry of the experiment. Since  $k_i \approx k_s$  the magnitude of the phonon can be written as

$$q = 2k_{\rm i}\sin\frac{\theta}{2} \tag{6}$$

where  $\theta$  is the scattering angle. Even in backscattering geometry ( $\theta = 180^\circ$ )  $q_{\text{max}}$  cannot exceed  $2k_i$ , therefore, only phonons from the center of the Brillouin zone ( $\Gamma$ -point) can be probed, since typically used excitation sources are in the visible or near infrared region and  $k_i \ll$  Brillouin zone boundary.

#### Raman tensor and selection rules

So far we saw that phonon can contribute to the Raman effect only if it change the electric susceptibility –  $(\partial \chi / \partial \mathbf{Q})_0 \neq 0$ , but it rather depends on the symmetry of the vibration. We will call a phonon *Raman-active* if it changes the susceptibility, and will call it *infrared-active* if there is a change in dipole moment during the vibration. Obviously, a vibration could be both Raman- and infrared-active, but it is not the case if the crystal has inversion symmetry where the two types are mutually excluded. In addition it is also possible to have inactive modes, we will call these modes *silent*.

For evaluation of the intensity of the scattered light lets proceed analogously to Equation (3), but now, instead of the scalar  $\chi$ , we will introduce the electric susceptibility as second rank tensor –  $\hat{\chi} = {\chi_{ij}}$ . The components of this tensor can be expanded as a Taylor series with respect to the normal coordinates *Q* 

$$\chi_{ij} = (\chi_{ij})_0 + \sum_k \left(\frac{\partial \chi_{ij}}{\partial Q_k}\right)_0 Q_k + \sum_{k,l} \left(\frac{\partial^2 \chi_{ij}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots,$$

where the summation is over all normal coordinates Q. The term  $(\partial \chi_{ij}/\partial Q_k)_0$ , usually multiplied by some numeric constant, represents a component of another tensor, the so-called *Raman tensor* –  $\hat{\mathcal{R}}$ . The components of this tensor has three indices, *i*, *j* and *k*, whereas the first two of them take values from 1 to 3 (corresponding to the *x*, *y* and *z* coordinates) the last one runs over the 3N - 3 normal coordinates, where *N* is the number of the atoms in the unit cell. In other words *k* runs over all optical modes for which  $\mathbf{q} = 0$ . For the Raman-active phonons the Raman tensor is a symmetrical  $3 \times 3$  matrix with elements proportional to the derivatives of  $\hat{\chi}$ .

The intensity of the Raman lines is proportional to the time-averaged power of radiation by the induced polarization  $\mathbf{P}_{ind}$ , and it depends on the polarization of the incident and scat-

tered light,  $\mathbf{e}_{i}$  and  $\mathbf{e}_{s}$ , respectively. Therefore, the intensity will be

$$I_{\rm s} \propto |\mathbf{e}_{\rm i} \cdot \hat{\mathcal{R}} \cdot \mathbf{e}_{\rm s}|^2. \tag{7}$$

Depending on the crystal structure, some of the components of the Raman tensor could be equal to zero, and the relations between the other non-zero components have been already obtained for all crystal classes. So, using Equation (7) it can be determined whether Ramanactive mode is observed under specific geometrical configuration or it is not. These selection rules can help us to find the symmetry of a particular Raman mode, by polarized measurements, if we compare its relative intensity in different scattering geometries. The opposite is also possible, if we know the symmetry of the mode we could orientate a single crystal along different crystallographic directions. However, for samples like polycrystalline films or powders, the information from polarized measurements is much more limited. In this case, usually, it is used the *depolarization ratio* for a particular mode

$$\rho = \frac{I_{\rm s}(\mathbf{e}_{\rm i} \perp \mathbf{e}_{\rm s})}{I_{\rm s}(\mathbf{e}_{\rm i} \parallel \mathbf{e}_{\rm s})},\tag{8}$$

which is the ratio of the  $I_s$  intensities, measured for perpendicular and parallel relative orientation of the polarizations of incident and scattered light. The value of the depolarization ratio depends on the symmetry of the mode. In general, for  $0 < \rho < 3/4$  the vibration can be considered to be symmetrical, and it is called *polarized*, whereas the bands with  $\rho = 3/4$  are non-symmetrical, and they are called *depolarized*.

#### Porto's notation

For description of the orientation of a single crystal in particular Raman experiment it is often used a notation proposed by Porto.<sup>[10]</sup> It consist of four symbols A(BC)D, where:

- *A* the direction of the propagation of the incident light (**k**<sub>i</sub>);
- *B* the direction of the polarization of the incident light (**e**<sub>i</sub>);
- *C* the direction of the polarization of the scattered light (**e**<sub>s</sub>);
- *D* the direction of the propagation of the scattered light (**k**<sub>s</sub>).

All Raman spectra, further shown in this thesis, are collected in backscattering geometry (where  $\mathbf{k}_i = -\mathbf{k}_s$ ), with linearly polarized laser light. An example of this configuration is shown in Figure 4 (a). In some cases capital letter *H* and *V* are used to describe the relative orientation of the polarizer and the analyzer: *H* stands for *horizontal*, and *V* for *vertical*. For example, *HV* means that the incident light is polarized horizontally, whereas the scattered light is polarized vertically.

#### **Experimental setup**

An experimental setup required to obtain a Raman spectrum can vary a lot, but typically the following is required:

• a light source;



**Figure 4.** Example of Porto's notation (a) in backscattering geometry, where  $\mathbf{k}_i = -\mathbf{k}_s$ , and (b) right angle scattering geometry, where  $\mathbf{k}_i \perp \mathbf{k}_s$ . In the case of linearity polarized light  $\mathbf{k}_i \perp \mathbf{e}_i$  and  $\mathbf{k}_s \perp \mathbf{e}_s$ .

- a collection optics;
- a monochromator;
- a detector.

Although, the idea is very simple, the Raman effect is extremely weak, which impose some restrictions on the light source, usually a continuous wave laser is enough powerful and give a narrow spectral linewidth. On the other hand the Raman scattering is accompanied by the Rayleigh scattering, which is up to  $10^6$  times stronger and have to be rejected. Double and triple monochromators reduce this light to an acceptable level and permit Raman measurements below  $50 \text{ cm}^{-1}$ . But they are very inefficient, due to the multiple dispersive elements and spatial filters their optical throughput is just about 3 - 10%. An alternative to the multistage spectrometers are the holographic notch filters, which selectively rejects a narrow band of light, and passes the light outside of this region, thus the Stokes and anti-Stokes line can be observed simultaneously which is not possible with the cheaper, but more durable dielectric edge filters. Most of the modern instrumentations employs multichannel CCD array as detectors, due to their high sensitivity and rapid spectral acquisition.

As it was mentioned before, all the Raman spectra were collected in backscattering geometry with linearly polarized lasers. For this purpose it was used micro-Raman spectrometer HORIBA JOBIN YVON LABRAM HR800 VISIBLE in Laboratory "Spectroscopy of crystals", Faculty of Physics, University of Sofia. Figure 5 shows schematically the laser beam path, of the used apparatus, toward the spectrometer. It is equipped with internal He-Ne laser (wavelength 633 nm), as well as an external Ar<sup>+</sup> COHERENT INNOVA 305 laser with three available wavelengths – 458, 488 and 515 nm. To focus the laser beam over the sample it is used an optical microscope Olympus BX41 with objectives with magnification  $\times 10$ ,  $\times 20$ ,  $\times 50$  and  $\times 100$ , respectively. Moreover, the objective is used to collect the scattered light, thus the Rayleigh signal should be rejected. In our case it was used edge filter which is attached to adjustable angle stand, so with an appropriate angle, the laser beam is completely reflected, and up to 85% of the Raman scattered light is forwarded to the spectrometer and detector. Main disadvantage of these kind of filters is that the anti-Stokes (or Stokes) shifted lines cannot be observed, as well lines which are very close to the laser line ( $< 90 \text{ cm}^{-1}$ ). After the Raman signal is separated from the laser beam it is forwarded to the spectrograph, which is of Czerny-Turner type. There the first spherical mirror of the spectrograph (800 mm focal length) re-



**Figure 5.** Scheme of micro-Raman spectrometer HORIBA JOBIN YVON LABRAM HR800 VISIBLE.

flects a parallel beam onto the grating. The second mirror is used to focus the dispersed light from the grating onto the  $1024 \times 256$  px CCD detector. As the spectral resolution depends on the grating and excitation wavelength, two gratings, mounted on interchangeable holders, are available – 600 g/mm and 1800 g/mm. The higher groove density grating covers smaller scanning range, thus the resolution is higher, however, a drawback of this grating is the less intense spectrum. To get better signal-to-noise ratio the CCD detector is Peltier cooled down to -70 °C. In addition with LABRAM HR800 could be used a heating/cooling stage LINKAM TH600, suitable in the range from room temperature up to 600 °C. In this case to prevent damage of the lens' coating of standard objectives it is used an objective with long working distance and magnification  $\times 50$ .

Raman spectroscopy have many advantages compared to other experimental methods, depending on the purpose of the analysis.

- non-contact and non-destructive method (in fact the later depends on the laser power);
- no special sample preparation;
- in most cases the acquisition time is very short;

- could be used for liquid and solid samples;
- confocal Raman microscope provides high spatial resolution and give the ability to collect data from very small volume of the sample;
- Polarization measurements can give information about crystal orientation, etc.

Despite its many benefits, Raman spectroscopy has also drawbacks like:

- cannot be used for a study of metals;
- not suitable for absolutely unknown crystals (not so good data base for comparison of the spectra);
- sometimes the interpretation of the spectra is not trivial and cannot be automated, because usually the number of experimentally observed lines is not equal to the theoretical predictions;
- it could be observed scattering from other quasi-particles, rather than phonons, which makes the interpretation of the spectrum very difficult;
- secondary phases could have more intense spectrum than the main phase;
- Raman effect is very weak, this require very sensitive detector and well optimized instrumentation.

## Other characterization techniques

Micro-Raman spectroscopy has been employed to study three different types of single crystals, namely YCrO<sub>3</sub> and YMnO<sub>3</sub>, Sc<sub>3</sub>CrO<sub>6</sub>, and Sc<sub>2</sub>O<sub>3</sub>. Except Raman spectroscopy, used as main experimental technique in this thesis, for the characterization of the samples it was used also:

- scanning electron microscopy (SEM) for elemental analysis and chemical characterization of all the samples, the measurements were carried out with SEM; TESCAN LYRA equipped with energy-dispersive x-ray spectrometer (EDX; BRUKER), by Assoc. Prof. Dr. S. Rusev, and Assist. Prof. Dr. G. Tsutsumanova at Faculty of Physics, University of Sofia, Bulgaria;
- single-crystal diffractometry for crystallographic description of the samples, the measurements were carried out with AGILENT DIFFRACTION SUPERNOVA DUAL four-circle diffractometer equipped with ATLAS CCD detector, by Assoc. Prof. Dr. R. Nikolova and Assoc. Prof. Dr. B. Shivachev at Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences (BAS), Sofia, Bulgaria;

## Crystal growth from solution

Solution crystal growth is widely used method for the growth of a variety of crystals, especially when the starting materials are unstable or decompose at the melting point. It is a highly complex process and depends on various parameters, such as solubility of solute in the solvent. For a given solute, there may be different solvents. Apart from high-purity starting materials it is very important to choose a suitable solvent to make a saturated solution at a desired temperature. In general there are two methods used for solution crystal growth:<sup>[11-13]</sup>

- low temperature solution growth,
- high temperature solution growth (HTS).

The advantage of using crystal growth from solution, rather than from melt is the solvent, which purpose is to lower the crystallization temperature. Thus, the parameters of the growth can be easily controlled and the quality of the grown crystal is better with respect to dislocations and point defects. High temperature solution growth is especially preferred when the grown materials:<sup>[11]</sup>

- which are incongruently melting,
- melt at very high temperatures,
- undergo phase transition below the crystallization temperature,
- have very high vapour pressure at melting point.

There are several techniques related to this method, such as *flux growth*, in which the solvent (flux) can be metals, oxides, hydroxides, salts or a combination of these. Crystallization occurs as the solution (homogeneous mixture of the solute in the solvent) becomes critically supersaturated, for the purpose everything is sealed in a crucible, and the temperature is increased until components of the solution are completely dissolved.

The major drawbacks of the solution crystal growth method are presence of impurities, substitution of ions from the crystal with those from the solvent, and relatively slow growth rate (in comparison with growth from melt). Nevertheless, the crystals will have less defects, such as vacancies and dislocations, furthermore, the most popular materials grown from high-temperature solution are oxides, crystallized from molten salts.<sup>[11]</sup>

In this thesis the studied single crystals of  $YCrO_3 Sc_3 CrO_6$  and  $Sc_2O_3$  were grown by Prof. DSc M. Gospodinov (Institute of Solid State Physics, BAS, Sofia, Bulgaria) and Assoc. Prof. Dr. V. Marinova (Institute of Optical Materials and Technologies, BAS, Sofia, Bulgaria), and single crystals of  $YMnO_3$  were grown by Dr. Y.-Q. Wang (Texas Center for Superconductivity at University of Houston, USA). All the crystals described below are grown by HTS method in platinum crucible, except  $YMnO_3$ .

#### Single crystals of YCrO<sub>3</sub> and YMnO<sub>3</sub>

As starting materials for growth of YCrO<sub>3</sub> single crystals were used  $Y_2O_3$  and  $Cr_2O_3$ . A solid phase synthesis of stoichiometric powder YCrO<sub>3</sub> was performed at 1100 °C in an oxygen atmosphere for 48 hours. PbF<sub>2</sub> : KF : B<sub>2</sub>O<sub>3</sub> in ratio 0.75 : 0.23 : 0.02 were used as solvents. The ratio of the ground material YCrO<sub>3</sub> to the solvents was determined according to the phase diagrams<sup>[14,15]</sup> of the system  $Y_2O_3$ ,  $Cr_2O_3$ , and PbF<sub>2</sub>. This ratio varies from 1/3 to 1/4. About 600 g of the mixture were semi-hermetically closed in the crucible with a cover in order to prevent the evaporation of PbF<sub>2</sub> and KF, which have a high vapor pressure at the growth process temperature. The temperature of the mixture was increased at a rate of 50 °C/h to 1200 °C. To completely dissolve the components of the materials and to achieve a homogeneous solution, the temperature of 1200 °C was maintained for 48 hours. Then the crucible was slowly cooled at a rate of 0.5 °C/h to 920 °C. At the final temperature the crucible was taken out of the furnace, the cover was drilled through and the solvent was poured out. The obtained crystals remained on the ground and the walls of the crucible.

Orthorhombic single crystals of YMnO<sub>3</sub> were synthesized by solid state reaction

$$Y_2O_3 + Mn_2O_3 \rightarrow 2YMnO_3$$
.

The starting material were mixed and preheated at 900 °C to 1200 °C in oxygen atmosphere for 16 hours followed by sintering at 1140 °C to 1170 °C for one day (again in oxygen atmosphere). As a result YMnO<sub>3</sub> crystallizes in the hexagonal  $P6_3cm$  structure. The hexagonal samples were resintered in a high pressure furnace under 35 kbar at 1015 °C to 1030 °C for 5 h. Under these conditions the hexagonal phase was completely transformed into the metastable orthorhombic structure.<sup>[16]</sup> The chemical composition of the final samples was confirmed using scanning electron microscope equipped with energy-dispersive x-ray spectrometer. The SEM-EDX observations revealed that both type of crystals had a homogeneous composition of Y : B = 1 : 1 (B = Cr, Mn) without any impurities.

#### Single crystals of Sc<sub>3</sub>CrO<sub>6</sub>

Sc<sub>3</sub>CrO<sub>6</sub> crystals were successfully grown by Sc<sub>2</sub>O<sub>3</sub> of 99.99%, Cr<sub>2</sub>O<sub>3</sub> of 99.995%, and PbF<sub>2</sub> and KF of 99.999% purity. Solid phase synthesis of Sc<sub>3</sub>CrO<sub>6</sub> powder was performed at 1100 °C in oxygen atmosphere for 48 h. The complete reaction between the starting materials was controlled by x-ray powder diffractometry. As solvent were used a mixture of PbF<sub>2</sub> and KF in 1 : 4 ratio. The Sc<sub>3</sub>CrO<sub>6</sub> : *solvent* ratio varied from 1 : 7 to 1 : 10. This mixture with a mass of 600 g was quasi-hermetically closed in the crucible with a cover in order to prevent the evaporation of PbF<sub>2</sub>. The temperature of the crucible was increased at a rate of 50 °C/h to 1150 °C. To completely dissolve the components of the materials and to achieve a homogeneous solution, the temperature of 1150 °C was maintained for 48 h and then subsequently lowered at a rate of 1 °C/h to 900 °C. At this temperature the crucible was taken out of the furnace and the solvent was poured out. The Sc<sub>3</sub>CrO<sub>6</sub> crystals remain in the crucible.

#### Single crystals of Sc<sub>2</sub>O<sub>3</sub>

To grow single crystals of  $Sc_2O_3$  were used  $Sc_2O_3$  powder of 99.995% purity and PbF<sub>2</sub> and NaF with purity of 99.999% purity as starting materials. The ratio of the PbF<sub>2</sub> and NaF solvents was 1 : 1, while the  $Sc_2O_3$  : *solvents* ratio was 1 : 10. About 500 g of this mixture were closed in the crucible in order to prevent the evaporation of the solvents. The temperature was increased at a rate of 50 °C/h to 1200 °C. To achieve a homogeneous solution, the temperature of 1200 °C was maintained for 24 h and then lowered at a rate of 0.5 °C/h to 900 °C. After that the solvent was poured out and the  $Sc_2O_3$  crystals remained on the bottom and walls of the crucible.

## Lattice dynamical calculations

Often the number of experimentally observed peaks in the Raman spectrum, for a particular material, is different than the theoretically predicted one (from factor group analysis). In this case the assignment of the peaks to definite atomic vibrations is ambiguous and difficult task. Even if it is possible to collect polarized Raman spectra, and the symmetry of the lines is determined, it does not solve the problem entirely. In this case, a comparison of the Raman spectra with such of other well-known isostructural compound could be made, but it is also not always possible, thus the analysis can be accomplished by *lattice dynamical calculations* – LDC.

#### Shell model

The *rigid ion model*, developed by Kellermann for calculation of the phonon dispersion curves in ionic crystals,<sup>[17]</sup> treats the ions as point charges interacting with long-range Coulomb forces and short-range forces, restricted only to the nearest neighbours, gives good values for the acoustic and *transverse optical* (TO) modes.<sup>(2)</sup> However, no electronic screening is accounted ( $\varepsilon_{\infty} = 1$ ) and the frequency of the *longitudinal optical* (LO) mode<sup>(3)</sup> is overestimated. To overcome the limitations of this model, the lattice dynamical calculations were performed within the framework of the *shell model*. This simple model, introduced by Dick and Overhauser,<sup>[18]</sup> properly accounts the predominant ionicity of the transition metal oxides and it is widely used for calculation of different crystal properties. In this model the ion is divided into a *core*, which represent the nucleus and the inner electrons of the ion and has all of its mass, and a massless *shell* representing the valence electrons. The core and the shell are coupled by harmonic spring with spring constant *k*. The interatomic potential, as in the case of the rigid ion model, is a combination of a long-range Coulomb potential and short-range potential to model the repulsions and van der Waals forces between electron charge clouds. The interaction between two ions are shown schematically in Figure 6. When an electric field is



**Figure 6.** Schematic representation of the interactions in the shell model. In order to account the ionic polarizability, the cores are linked to the shells by harmonic spring with spring constant *k*. The long-range forces acting between all cores and shell are also drawn as springs.

applied (i.e. field of the surrounding ions) the shell retains its spherical charge distribution, but it is displaced with respect to the core. Thus, the ionic polarizability of a free ion,  $\alpha$ , is taken into account by means of the displacement,  $\delta r_i$ , of the shell with charge  $q_i$  from the

<sup>&</sup>lt;sup>(2)</sup>Vibrations perpendicular to the direction of **q**.

<sup>&</sup>lt;sup>(3)</sup>Vibrations along the direction of **q**.

core, and it is given by

$$\alpha_i = \frac{q_i^2}{4\pi\varepsilon_0 k}$$

The energy corresponding to this interaction is

$$U_i^{\rm spring} = \frac{1}{2} k \delta r_i^2. \tag{9}$$

Since the Coulomb forces act between all cores and shells, except for the cores and shells on the same ion, the electrostatic energy of interaction between the *i*-th and *j*-th ions is given by

$$U_{i}^{\text{electr.}} = \sum_{j}^{N} \frac{q_{i}q_{j}}{4\pi\varepsilon_{0}|\mathbf{r}_{\text{s}i} - \mathbf{r}_{\text{s}j}|} + \sum_{j}^{N} \frac{q_{i}Q_{j}}{4\pi\varepsilon_{0}|\mathbf{r}_{\text{s}i} - \mathbf{r}_{\text{c}j}|} + \sum_{j}^{N} \frac{Q_{i}q_{j}}{4\pi\varepsilon_{0}|\mathbf{r}_{\text{c}i} - \mathbf{r}_{\text{s}j}|} + \sum_{j}^{N} \frac{Q_{i}Q_{j}}{4\pi\varepsilon_{0}|\mathbf{r}_{\text{c}i} - \mathbf{r}_{\text{c}j}|},$$
(10)

where  $i \neq j$ , N is the number of atoms,  $q_{i,j}$  and  $Q_{i,j}$  are the charges and  $\mathbf{r}_{si,j}$ , and  $\mathbf{r}_{ci,j}$  are the radius vectors of the shells and cores, respectively.

Normally, it is assumed that the short-range forces act only between the nearby shells, and the most commonly used analytical function to describe these interactions is the Buckingham potential – linear combination of Born-Mayer and van der Waals potentials

$$U_i^{\text{short}} = \sum_j^N \left[ A \exp\left(-\frac{|\mathbf{r}_{si} - \mathbf{r}_{sj}|}{\rho}\right) - \frac{C}{|\mathbf{r}_{si} - \mathbf{r}_{sj}|^6} \right],\tag{11}$$

where A,  $\rho$  and C are specific parameters for each pair of shells i and j ( $i \neq j$ ). The first term describes the strong repulsion due to the exponential decay of the overlapped wavefunctions of the ions with increasing the distance from the nucleus. The second term constitute the attractive part and describes the cohesion of the system. Using Equations (9), (10) and (11) for the energy of the system we can write

$$U = \frac{1}{2} \sum_{i}^{N} \left( U_{i}^{\text{electr.}} + U_{i}^{\text{short}} + 2U_{i}^{\text{spring}} \right).$$

This energy can be minimized with respect to the cores' positions, and this was achieved with the GULP code – General utility lattice program.<sup>[19]</sup>

The main problem of this approach for calculations is transferability of the parameters A,  $\rho$ , C and k used for the Buckingham potential. The most common way to adjust the parameters is a least-squares fit to different physical properties of the studied material. Most of the parameters used in this thesis are taken from the work of Lewis and Catlow.<sup>[20]</sup> Where it was necessary they were refined in order to obtain better agreement between the optimised structural parameters and the experimental ones. Another criterion for the quality of the fit was the difference between the calculated  $\Gamma$ -point mode frequencies from one side and the experimental Raman frequencies on the other side. The *force constant matrix* was used to

calculate the phonon frequencies, it is derived from the second derivatives of the internal energy of the system with respect to the atomic coordinates. Then it is converted into the *dynamical matrix*, after the diagonalization of the latter, the eigenvalues give the frequencies of the phonons, whereas the eigenvectors give the normalized atomic displacements.<sup>(4)</sup> Analyzing the eigenvectors, the symmetry of the modes is determined and assignment of the experimentally observed lines to a definite atomic vibration can be done.

#### **Density functional theory**

The shell model significantly increases the agreement between experiment and theory in comparison to the rigid ion model. Further improvements can be achieved within the formalism of the *breathing shell model* proposed by Schröder,<sup>[21]</sup> where the compressibility of the ions is taken into consideration. However, such kind of "extension" of the model just adds more fitting parameters without any particular physical meaning. Furthermore, all these empirical models does not treat correctly compounds with covalent bonding, where the valence electrons are not rigidly attached to the ions, rather than they are shared in the bonds between them. To avoid the drawbacks of the empirical methods it can be used *ab initio* or *first principles* approach based on the *density functional theory* – DFT. The starting point of *ab initio* calculations is the solution of the time-independent, non-relativistic Schrödinger equation

$$\hat{\mathcal{H}}\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N,\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_M) = E\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N,\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_M)$$

where  $\hat{\mathcal{H}}$  is the Hamiltonian of a system consisting of *M* nuclei and *N* electrons,

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 \right) + \sum_{I=1}^{M} \left( -\frac{\hbar^2}{2M_I} \nabla_I^2 \right) + V(\mathbf{r}, \mathbf{R}).$$
(12)

The arguments of the wave function  $\Psi$ ,  $\mathbf{x}_i$  stands for  $(\mathbf{r}_i, s_i)$ , where  $s_i$  is the spin of the electron,  $\mathbf{r}_i = (x_i, y_i, z_i)$  is its position, and  $\mathbf{R}_I$  is the position of the nucleus. The first two terms in Equation (12) describes the kinetic energy of the *i*-th electron (of mass *m*) and the *I*-th nucleus (of mass  $M_I$ ), where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Since  $\mathbf{x} \equiv (\mathbf{r}, s)$  is a combined variable, further integration over  $\mathbf{x}$  will be defined as

$$\int d\mathbf{x} \stackrel{\text{\tiny def}}{=} \sum_{S} \int d\mathbf{r} \quad \text{where} \quad \int d\mathbf{r} \stackrel{\text{\tiny def}}{=} \iiint dx dy dz,$$

for particles without spin **x** should be considered as **r**.

Back to Equation (12), where the third term represents the Coulombic attraction between the electrons and the nuclei and the repulsive potential due to the electron-electron and

<sup>&</sup>lt;sup>(4)</sup>Detailed description of the procedures used for the structure optimization, lattice dynamical calculations, treatment of the potentials, optimization of the calculation time and etc. can be found in the GULP manual.

nucleus-nucleus interactions

$$V(\mathbf{r},\mathbf{R}) = \frac{1}{4\pi\varepsilon_0} \left( \sum_{i=1}^N \sum_{I=1}^M \frac{-e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^N \sum_{j\neq i}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^M \sum_{J\neq I}^M \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \right),$$

here  $Z_I$  is the atomic number of nucleus *I*.

Within the Born-Oppenheimer approximation<sup>[22,23]</sup> the heavier nuclei are much slower than the fast moving and much lighter electrons, thus the nuclear kinetic energy is negligible, their potential energy is constant and the electrons are considered to move in the field of fixed nuclei. This means that the total energy of the system is a function of the positions  $\mathbf{R}_I$  of the nuclei, which represent stationary eigenvalue problem for any given configuration of  $\mathbf{R}_I$ , however, we will be interested from the lowest energy solution,  $E_0$ , called the *ground state*. Considering the above approximation the wavefunction can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \longrightarrow \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N),$$

now it depends on 3N spatial coordinates  $\mathbf{r}_i$ , and N spin coordinates  $s_i$  of the electrons. Since the wavefunction itself has no physical meaning, rather than its square modulus,  $|\Psi|^2$ , interpreted as a probability density to find N electrons in volume  $d\mathbf{x}_1 \cdots d\mathbf{x}_N$ , thus  $\Psi$  should be normalized, and has to satisfy

$$\int \cdots \int |\Psi|^2 d\mathbf{x}_1 \cdots d\mathbf{x}_N = 1.$$
<sup>(13)</sup>

Considering this, the Hamiltonian from formula (12) takes the form

$$\hat{\mathcal{H}} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} \sum_{I=1}^{M} \frac{-e^2 Z_I}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{R}_I|} = \hat{T} + \hat{E}_{ee} + \hat{E}_{eN}, \quad (14)$$

where  $\hat{T}$  is the operator of the kinetic energy of the electrons,  $\hat{E}_{ee}$  is the electron-electron repulsion energy operator, and  $\hat{E}_{eN}$  is the operator of the electron-nucleus attraction energy, thus the total energy of the electron system is

$$E = T + E_{\rm ee} + E_{\rm eN}.$$

Any potential acting on the electrons, which is not related to electron-electron interaction is considered as external potential, in this case  $\sum_i V_{\text{ext}}(\mathbf{r}) \equiv E_{\text{eN}}$ , but it also can include other electric or magnetic fields. Furthermore, for *N*-electron system, the external potential fixes the Hamiltonian and the ground state properties are determined by *N* and  $V_{\text{ext}}$ .

A variational principle<sup>[22,23]</sup> can be introduced according to which for a given state with wavefunction  $\Psi$ , satisfying Equation (13), the energy  $E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$  will be an upper bound to the energy of the ground state  $E_0 = \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle$ . In other words, to find the ground state energy and wavefunction we have to minimize the *functional*  $E[\Psi]$  with respect to all allowed

N-electron wavefunctions

$$E_0 = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | \hat{T} + \hat{E}_{ee} + \hat{E}_{eN} | \Psi \rangle.$$
(15)

Here, by functional we understand a rule, which assigns a number to a function, like

$$A[\Psi] = \langle \hat{A} \rangle = \int \cdots \int \Psi^* \hat{A} \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_N \equiv \langle \Psi | \hat{A} | \Psi \rangle,$$

usually the square brackets are used to distinguish a functional from a function.

So far we saw that for the electronic system described by the Hamiltonian (14), in principle, the ground state energy can be derived from minimization of the energy functional  $E[\Psi]$ , but in practice it is challenging task, since the wavefunction still depends on 4*N* coordinates, and the systems of interest usually consist of many atoms and much more electrons.

Hohenberg and Kohn<sup>[24]</sup> showed that instead of the wavefunction  $\Psi$ , it is convenient to use the electron density,  $\rho(\mathbf{r})$ , which depends only on three spatial variables, as a basic variable in the DFT. For electrons in position  $\mathbf{r}_1$  it is defined by

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N.$$

On the other hand, the external potential  $V_{\text{ext}}(\mathbf{r})$  is a unique functional of  $\rho(\mathbf{r})$ , apart from a trivial additive constant. Since  $\rho$  determines N as

$$\int \rho(\mathbf{r}) d\mathbf{r} = N$$

it also determines the ground state wavefunction and therefore all other electronic properties of the system. Thus for a given external potential Equation (15) can be rewritten as

$$E_{0} = \min_{\rho} E[\rho] = \min_{\rho} \langle \Psi | \hat{T} + \hat{E}_{ee} + \hat{E}_{eN} | \Psi \rangle$$
  
$$= \min_{\rho} \left( \langle \Psi | \hat{T} + \hat{E}_{ee} | \Psi \rangle + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right)$$
  
$$= \min_{\rho} \left( F[\rho] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right), \qquad (16)$$

where in general  $F[\rho] = T[\rho] + E_{ee}[\rho]$  is universal functional of the density and it is independent of the external potential,  $V_{ext}$ .

A step further was made by Kohn and Sham,<sup>[25]</sup> as they suggested to calculate the kinetic energy,  $T_s$ , of a noninteracting electrons system with the same density as the real system of interacting electrons, thus the universal functional  $F[\rho]$  takes the form

$$F[\rho] = T_{\rm s}[\rho] + E_{\rm H}[\rho] + E_{\rm xc}[\rho],$$

where  $E_{\rm H}[\rho]$  is the classic electrostatic (Hartree) energy of the electrons,

$$E_{\rm H}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

and  $E_{\rm xc}$  is the so-called *exchange-correlation energy*, which contains the difference between T and  $T_{\rm s}$  as well as all non-classical contribution to the electron-electron interaction: self-interaction correction, exchange and correlation. In other words  $E_{\rm xc}$  contains everything that is unknown.

Now instead of one equation for *N* electrons we have *N* one-electron equations and for complex systems with increasing the number of electrons only the number of equations to be solved increases. Although the Kohn and Sham approach is considered to give an exact solutions for the ground state density  $\rho_0$  and the ground state energy  $E_0$ , the real  $E_{xc}$  functional remains unknown. The most simple approximation is the so-called *local density approximation* (LDA), based on the exact exchange energy for an uniform electron gas, where the functional depends only on the density at particular point **r**,

$$E_{\rm xc}^{\rm LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{\rm xc}(\rho(\mathbf{r})) d\mathbf{r}.$$

Here,  $\epsilon_{xc}(\rho(\mathbf{r}))$  is the exchange-correlation energy per particle of the uniform electron gas of density  $\rho(\mathbf{r})$ . In order to account for the non-homogeneity of the true electron density it can be used more sophisticated functional such as a *generalized gradient approximation* (GGA):

$$E_{\rm xc}^{\rm GGA}[\rho] = \int f(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\mathbf{r},$$

where *f* depends on gradients of the density as well as the density itself.

All these methods and approximations are implemented in the CASTEP<sup>[26]</sup> code, used for the simulation of the Raman spectrum of  $Sc_2O_3$  shown in Section 4.2. The calculations were performed on facilities provided by Le centre de calcul intensif des Pays de la Loire (CCIPL), Nantes, France.

# **1.** Comparative Raman study of isostructural YCrO<sub>3</sub> and YMnO<sub>3</sub>: Effects of the structural distortions and the twinning

Polarized Raman spectra of isostructural orthorhombic  $YCrO_3$  and  $YMnO_3$  single crystals were collected at same conditions using different laser excitation in the visible range. The symmetry of the observed lines was determined and they were assigned to definite atomic vibrations based on lattice dynamical calculations. The frequencies of the lines of the same origin in both compounds are close, however, their intensities differ significantly. While the different intensity of the modes, activated by the Jahn-Teller distortion, can be explained by the different magnitude of this distortion in the two compounds, the cause of the reduced intensity of other lines in low frequency region in the Raman spectra of  $YMnO_3$  is likely due to the fine twinning of the crystal.

The interest in the transition-metal perovskite-like oxides  $ABO_3$  continues for decades because of many attractive phenomena observed in these compounds. Among them are structural second-order phase transitions, high- $T_c$  superconductivity, colossal magnetoresistance, charge- and orbital-ordering, complex magnetic properties, etc. As a rule the structural, electrical and magnetic properties of these compounds are strongly correlated. They can be tuned through the change of the mismatch of the A - O and B - O bond lengths, expressed by the tolerance factor  $t = (r_A + r_0)/\sqrt{2}(r_B + r_0)$ , where  $r_0$ ,  $r_A$  and  $r_B$  are the ionic radii of the oxygen and atoms in the A- and B-positions, respectively. Depending on the value of t, most of these compounds crystallize in superstructures of the ideal cubic perovskite (space group  $Pm\bar{3}m$ ) with  $R\bar{3}c$  or Pnma symmetry. Using the model proposed by Glazer<sup>[27]</sup>, treating the  $BO_6$  octahedra as rigid ones, the superstructures can be obtained from the ideal cubic perovskite through some tilts (rotations) of the octahedra around the main cubic crystallographic directions. According to Glazer 23 tilt systems are possible (see Table 1.1), which cover 15

Nº	Symbol	Lattice centering	Relative pseudocubic subcell parameters	Space group
Thre	ee-tilt systems			
1	$a^{+}b^{+}c^{+}$	Ι	$a_{\rm c} \neq b_{\rm c} \neq c_{\rm c}$	<i>Immm</i> (№ 71)
2	$a^{+}b^{+}b^{+}$	Ι	$a_{\rm c} \neq b_{\rm c} = c_{\rm c}$	<i>Immm</i> (№ 71)
3	$a^{+}a^{+}a^{+}$	Ι	$a_{\rm c} = b_{\rm c} = c_{\rm c}$	<i>Im</i> 3 (№ 204)
4	$a^{+}b^{+}c^{-}$	Р	$a_{\rm c} \neq b_{\rm c} \neq c_{\rm c}$	<i>Pmmm</i> (№ 59)
5	$a^{+}a^{+}c^{-}$	Р	$a_{\rm c} = b_{\rm c} \neq c_{\rm c}$	<i>Pmmm</i> (№ 59)
				(Continued)

**Table 1.1.** Complete list of possible simple tilt systems, as defined in Ref. [27] by Glazer.

N⁰ Symbol Lattice Relative pseudocubic Space group centering subcell parameters  $a^{+}b^{+}b^{-}$ Р 6  $a_{\rm c} \neq b_{\rm c} = c_{\rm c}$ Pmmm (№ 59)  $a^{+}a^{+}a^{-}$ 7 Р  $a_{\rm c} = b_{\rm c} = c_{\rm c}$ *Pmmm* (№ 59)  $a^+b^-c^$  $a_c \neq b_c \neq c_c, \alpha \neq 90^\circ$ 8 Α A2<sub>1</sub>/m11 (№ 11)  $a_c = b_c \neq c_c, \alpha \neq 90^\circ$ 9  $a^{+}a^{-}c^{-}$ A2<sub>1</sub>/m11 (№ 11) Α  $a^{+}b^{-}b^{-}$  $a_c \neq b_c = c_c, \alpha \neq 90^\circ$ 10 Α *Pnma* (№ 62)  $a^{+}a^{-}a^{-}$  $a_{\rm c} = b_{\rm c} = c_{\rm c}, \alpha \neq 90^{\circ}$ *Pnma* (№ 62) 11 Α  $a_{\rm c} \neq b_{\rm c} \neq c_{\rm c}, \alpha \neq \beta \neq \gamma \neq 90^{\circ}$ 12  $a^{-}b^{-}c^{-}$ F *F*1 (№ 2)  $a_c \neq b_c = c_c, \alpha \neq \beta \neq \gamma \neq 90^\circ$ *I*2/*a* (№ 15) 13  $a^{-}b^{-}b^{-}$ F  $a_{\rm c} = b_{\rm c} = c_{\rm c}, \alpha = \beta = \gamma \neq 90^{\circ}$ 14  $a^{-}a^{-}a^{-}$ F *R*3*c* (№ 167) Two-tilt systems  $a^{0}b^{+}c^{+}$ 15 Ι  $a_{\rm c} < b_{\rm c} \neq c_{\rm c}$ *Immm* (№ 71)  $a^{0}b^{+}b^{+}$ 16 Ι  $a_{\rm c} < b_{\rm c} = c_{\rm c}$ *I*4/*m* (№ 78)  $a^{0}b^{+}c^{-}$  $a_{\rm c} < b_{\rm c} \neq c_{\rm c}$ 17 В *Bmmb* (№ 63)  $a^{0}b^{+}b^{-}$  $a_c < b_c = c_c$ *Bmmb* (№ 63) 18 В  $a^0b^-c^$  $a_{\rm c} < b_{\rm c} \neq c_{\rm c}, \alpha \neq 90^{\circ}$ 19 F F2/m11 (№ 12)  $a^{0}b^{-}b^{-}$  $a_{\rm c} < b_{\rm c} = c_{\rm c}, \alpha \neq 90^{\circ}$ 20 F *Imcm* (№ 74) One-tilt systems  $a^{0}a^{0}c^{+}$ 21  $a_{\rm c} = b_{\rm c} < c_{\rm c}$ С C4/mmb (№ 127)  $a^{0}a^{0}c^{-}$ 22 F  $a_{\rm c} = b_{\rm c} < c_{\rm c}$ *F*4/*mmc* (№ 140) Zero-tilt system  $a^{0}a^{0}a^{0}$ 23 Р  $a_{\rm c} = b_{\rm c} = c_{\rm c}$ *Pm3m* (№ 221)

Table 1.1. (Continued)

space groups. In Table 1.1 the symbols in the second column are following the notation:

- the position of each letters corresponds to tilt along the [100], [010] and [001] directions of the cubic cell [i.e. first letter means tilt along [100]];
- the superscript takes values 0 to indicate zero-tilt around an axis, + or for in-phasetilt or anti-phase-tilt of adjacent octahedra along this direction;
- letters are repeated to indicate the same amplitude of tilt.

Raman spectroscopy is a powerful experimental technique for study of perovskite-like oxides. Due to the fact that there are no Raman-active modes in the ideal cubic perovskite, all observed lines in the one-phonon region of the Raman spectra of the real perovskites have to be related to some deviations of the real structure from the ideal one. For example, as shown in the pioneering work of Scott, <sup>[28]</sup> one of the Raman-active modes in the rare-earth aluminates with  $R\bar{3}c$  structure consists in a rigid octahedral tilt around [111] direction. This mode can be considered as a "soft mode" and its frequency goes to zero as the temperature approaches the critical temperature of the structural second-order phase transition. Iliev *et al.*<sup>[29]</sup> have shown that in the case of rare-earth manganites with orthorhombic *Pnma* structure, two of the observed lines in the Raman spectra originate from modes with a shape of the two static octahedral tilts, existing in the structure. Although that these compounds do not undergo second order transition to higher symmetry phase, the frequency of these lines directly scales the octahedral tilts as it is proportional to the tilt angle.



**Figure 1.1.** Illustration of the distortion for the MnO<sub>6</sub> octahedra in YMnO<sub>3</sub> as a consequence of the Jahn-Teller effect.

However, the model of rigid octahedra is inappropriate when the *B* ion is a Jahn-Teller (JT) ion (as the  $Mn^{3+}$ ). In manganites the JT effect results in presence of two pairs of Mn - 0 bonds of significantly different length and strongly deformed  $MnO_6$  octahedra (see Figure 1.1). For this reason one can propose a structural model to explain the relationship between the intensity of the Raman lines and the structural distortions in orthorhombic manganites. In this model the real *Pnma* structure can be derived from the ideal cubic *Pm* $\bar{3}m$  with only four basic distortions.<sup>[30]</sup>

Following the notations in Ref. [30] the first basic distortion,  $D_{[101]}$ , is a rotation (tilt) of the MnO<sub>6</sub> octahedra around the cubic [101]. As a result of this rotation the new structure is orthorhombic with space group *Imma*. The second basic distortion  $D_{[010]}$  again represent rotation of the MnO<sub>6</sub> octahedra but now it is around the cubic [010] axis. In this case the derived structure is tetragonal with space group *P4/mbm*. The quantitative measure of these distortions is the angle of rotation (tilt angle) defined as

$$D_{[101]} = \arctan\left(2|x_{02} - z_{02}|\right)$$
 and (1.1)

$$D_{[010]} = \arctan\left(\frac{2\sqrt{2}|z_{01}| + 4\sqrt{2}|y_{02}|}{2}\right), \qquad (1.2)$$

where  $x_{02}$ ,  $z_{02}$ ,  $z_{01}$  and  $y_{02}$  are the deviations of the fractional coordinates of oxygen atoms

O1 and O2 in the ideal structure (without the distortion).<sup>[30]</sup>

The third distortion,  $D_{\rm JT}$ , is deformation of the MnO<sub>6</sub> octahedra in which two of the Mn – O2 bonds are both elongated, and the other two are shortened, so the Mn(O2)<sub>4</sub> square becomes a rhomb (see Figures 1.1 and 1.2). As in the previous case the resulting structure is tetragonal with space group *P4/mbm*. The quantitative measure of  $D_{\rm JT}$  is defined as the relative difference of the two Mn – O2 bonds,  $\Delta d_{\rm Mn-O2}/\langle d_{\rm Mn-O2} \rangle$ . If the distortion is small, in orthorhombic *Pnma* basis, it is equal to

$$D_{\rm JT} = 2|x_{02} + z_{02}|. \tag{1.3}$$

The sift of the *A*-type atoms from their positions in the ideal perovskite in *x* directions (in *Pnma* basis) is defined as the fourth basic distortion. The new structure is also orthorhombic with space group *Cmcm*. The quantitative measure is

$$D_{A-\mathrm{shift}} = 2x_A. \tag{1.4}$$

All four structures, obtained from only one of the basic distortions, as well as the real *Pnma* structure are shown in Figure 1.2.

Within the framework of the latter model, it can be concluded that the intensities of 20 out of the all 24 Raman-active modes in the GdFeO<sub>3</sub>-type structure are connected with only one of the above mentioned distortions and the change of the intensities reflects the change of the structural distortions. Using this model it was possible to explain the significant difference of the relative intensity of the  $B_{2a}(1)$  mode, activated by the JT distortion in the spectra of CaMnO<sub>3</sub> (containing non-JT Mn<sup>4+</sup> ion) and YMnO<sub>3</sub> (containing JT Mn<sup>3+</sup> ion). Unfortunately, the strong dependence of the intensity of many of the remaining lines in the Raman spectra of CaMnO<sub>3</sub> on the excitation photon energy (i.e. the resonance effects) hampers the proof of the model in this case. In addition, the different charges of the A and B ions in  $Y^{3+}Mn^{3+}O_3$ and Ca<sup>2+</sup>Mn<sup>4+</sup>O<sub>3</sub> impede the comparison of the Raman spectra of these two compounds. For this reason we present parallel Raman study of  $YBO_3$  (B = Cr, Mn). The isostructural orthorhombic *Pnma* compounds have close lattice parameters as well as close values of three of the four structural distortions, as defined in Ref. [30]. The only difference is the presence of the JT distortion in  $Mn^{3+}O_6$  octahedra, leading to their strong deformation, whereas the  $Cr^{3+}O_6$  ( $Cr^{3+}$  is not a JT ion) octahedra are symmetric with nearly equal Cr - 0 bonds. The polarized Raman spectra of each compound, collected using laser excitation with different photon energy in the visible region, are practically identical, which shows that the resonance effects are negligible. It is worth noting here that this could not be concluded from the previous works<sup>[29,31-35]</sup> because the spectra were obtained with a single laser line. Indeed, several papers on orthorhombic YMnO<sub>3</sub> report polarized <sup>[29,32,35]</sup> or nonpolarized <sup>[33,34]</sup> Raman spectra, obtained with either 515 nm or 633 nm laser excitation. For YCrO<sub>3</sub> there is only one early paper<sup>[31]</sup> on the polarized Raman spectra using 515 nm. In this work we show that there is a significant difference in the intensity of  $B_{2g}(1)$  line (activated by the JT distortion) in YCrO<sub>3</sub> and YMnO<sub>3</sub>. Surprisingly, the intensity of other lines in low frequency region is strongly suppressed in YMnO<sub>3</sub>, despite the close values of the activating structural distortions in both compounds. A comparison with the Raman spectra of other isostructural rare-earth perovskites



**Figure 1.2.** The real *Pnma* structure (GdFeO<sub>3</sub>-type) and the four more simple structures as a result of the basic distortions.

leads to the conclusion that this is a result of a fine twinning of YMnO<sub>3</sub> single crystals.

Polarized Raman spectra were obtained in backscattering geometry from several scattering configurations: xx, yy, zz, xz and yx'. In this notations the first and the second letter shows the polarization of the incident and the scattered light, respectively, and x, y, z and x' are parallel to the orthorhombic [100], [010], [001] and [101] crystal directions. It is not trivial to identify the orthorhombic (100) crystal directions. To do this we use the fact that all quasi-cubic perovskites have good cubic cleavage. This leads to almost perfect cubic shape of their microcrystals with the naturally grown surfaces of cubic {100} type, see Figure 1.3. Additionally preliminary measurements of polarized Raman spectra in special configurations according these surface could be made. Only the orthorhombic [010] direction [(010)<sub>0</sub> surface] is perpendicular to {010}<sub>c</sub> plane, so it can easily be identified. However, in (010)<sub>0</sub> surface the [100]<sub>0</sub> and [001]<sub>0</sub> directions are parallel to the diagonals (in the case of rhomb-like surface) of the parallelogram-shaped surface. Because the lattice parameter  $a_0 > c_0$ , it follows that [100]<sub>0</sub> direction must be along the longer diagonal, see Figure 1.3. The comparison of the angle between (101)<sub>0</sub> and ( $\overline{101}_{0}$  planes (that can be calculated from the published structural data<sup>[36]</sup>) with the measured angle between the crystal edges *AO* and *BO* on the photo in Figure 1.3 is excellent, so we can distinguish *x* and *z* directions.



**Figure 1.3.** (a) Sketch of the unit cell of YCrO<sub>3</sub>. (b) Optical image of (010) surface of YCrO<sub>3</sub> single crystal. The notations used for the crystallographic directions are also given. Comparison of the calculated angle between the vertical (101) and ( $\overline{1}01$ ) orthorhombic surfaces (the crystal edges *AO* and *BO* on the photo) from the structural data<sup>[36]</sup> and measured angle directly from the image is done. The last helps us to distinguish *x* and *z* directions.

The measurements were carried out using micro-Raman spectrometer LABRAM HR800 VISIBLE at room temperature. An objective ×100 was used both to focus the incident laser beam and to collect the scattered light. To check the presence of resonance effects in the Raman spectra, He-Ne (633 nm) and Ar<sup>+</sup> (514 and 458 nm) lasers were used as excitation sources. A small set of preliminary measurements, in which the product *laser power* × *acquisition time* remains constant, has been done to find out the appropriate power for which the overheating of the samples is negligible. Thus, for both types of crystals and all laser lines the laser power used was about 2 mW. Due to the fine twinning of the YMnO<sub>3</sub> crystals, their nominally *xx* and *zz* spectra are identical. In contrast, the YCrO<sub>3</sub> crystals are twin-free, as *xx* and *zz* spectra are significantly different (see Figure 1.4).

To facilitate the assignment of the Raman lines we performed shell-model lattice dynamical calculations based on interatomic potentials. The calculations were carried out using the GULP code.<sup>[19]</sup> The parameters of the Born-Mayer potential, *Z*, *Y*, *k*, *A*,  $\rho$  and *C* are listed in Table 1.2. The cell parameters and atomic positions of YMnO<sub>3</sub> and YCrO<sub>3</sub>, used in the calcula-

Atom	Z ( e )	Y ( e )	k (eV/Ų)
Y	2.90		
Mn	0.30	2.80	51.20
Cr	0.30	2.80	49.50
O <sub>Mn</sub>	0.82	-2.82	53.72
O <sub>Cr</sub>	0.82	-2.82	36.70
Atomic pair	<i>A</i> (eV)	ρ (Å)	$C (eV \times Å^6)$
Y – 0	1345.1	0.3491	0.000
Mn – 0	715.8	0.3464	0.000
Cr – 0	1763.0	0.2960	0.000
0 - 0	22764.3	0.1490	27.879

**Table 1.2.** Parameters of the potentials of the shell-shell and core-shell interactions. Due to different values of k for the oxygen in YMnO<sub>3</sub> and YCrO<sub>3</sub> it is marked as O<sub>Mn</sub> and O<sub>Cr</sub>, respectively. All the potentials are taken from Ref. [20], except the one for Cr – O pair which is from Ref. [37].

tions, are taken from Ref. [38] and Ref. [36].

The orthorhombic YBO<sub>3</sub> (B = Cr, Mn) crystals have GdFeO<sub>3</sub>-type structure <sup>[36,38]</sup> (space group *Pnma*, Z = 4,  $a_o \approx c_o \approx \sqrt{2}a_c$ ,  $b_o \approx 2a_c$ , where  $a_c$  is the lattice parameter of the ideal cubic perovskite). The group theory predicts  $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$  Raman-active modes from the  $\Gamma$ -point of the Brillouin zone. <sup>[39,40]</sup> The selection rules for these modes as well the symmetry-allowed directions of motion of the atoms, participating in them, are given in Table 1.3 and Figure 1.5. Polarized Raman spectra, obtained from (010) and (101) surfaces of a YCrO<sub>3</sub> crystal with 515 nm laser excitation are shown in Figure 1.4.

**Table 1.3.** Selection rules for Raman-active modes in *Pnma* structure in specific scattering configurations. *a*, *b*, *c*, *d*, *e*, and *f* are non-zero components of the Raman tensors

Mode	xx	уу	ZZ	xz	yx'
$A_g$	a <sup>2</sup>	$b^2$	$c^2$	0	0
$B_{1g}$	0	0	0	0	$d^{2}/2$
$B_{2g}$	0	0	0	<i>e</i> <sup>2</sup>	0
$B_{3g}$	0	0	0	0	$f^{2}/2$

It is seen in spectra with xx, yy and zz polarization that seven lines, observed at 152, 185, 281, 342, 426, 492, and 564 cm<sup>-1</sup>, have  $A_g$  symmetry and they correspond to the predicted  $7A_g$  modes. We observe an additional broad line near 530 cm<sup>-1</sup> having also  $A_g$  symmetry. The width of this line is more than two times larger than the width of the other  $A_g$  lines. Its irregular shape is not of Lorentz type and differs in xx, yy and zz scattering configura-



**Figure 1.4.** Polarized Raman spectra of YCrO<sub>3</sub> single crystal, obtained from (010) and (101) surfaces with 515 nm laser line. For better comparison  $z'(yx')\bar{z}'$  spectrum is multiplied by five, and the other spectra are shifted along vertical axis for clarity.

tions. Therefore we suppose that it does not originate from one-phonon Raman-allowed scattering, rather it has two-phonon origin. In the *xz*-spectrum of YCrO<sub>3</sub> only four out of seven the Raman-allowed  $B_{2g}$  lines are observed. Comparison of *yy*- and *xz*-spectra of YCrO<sub>3</sub> and YMnO<sub>3</sub> (where all  $7B_{2g}$  are seen), obtained with 633, 515, and 458 nm laser excitation is made in Figure 1.6 and Figure 1.7, respectively. Their assignment to definite atomic vibrations, based on LDC, is also given. Due to the fact that the all faces of the naturally grown YCrO<sub>3</sub> crystals are with quasi-cubic {100} orientation, it was impossible to measure *yx* or *yz* spectra, where  $B_{1g}$  and  $B_{3g}$  lines could be observed separately. For this reason in Figure 1.4 we present a spectrum with *yx'* polarization [obtained from  $(\bar{1}01)_0 \equiv (100)_c$  surface], which contains both  $B_{1g}$  and  $B_{3g}$  lines. However, using the data, presented by Udagawa *et al.*<sup>[31]</sup>, as well as our LDC results, the symmetry of these line also can be determined. In Table 1.4 are summarized the frequencies of the observed lines and the calculated ones by LDC in this work, as well previously published data [Ref. [31] for YCrO<sub>3</sub>, Ref. [32] for YMnO<sub>3</sub> ].

It is seen that the experimental results for YMnO<sub>3</sub> are practically identical. In the previously published papers<sup>[29,32,35]</sup>, the Raman spectra of YMnO<sub>3</sub> were obtained only with 633 nm laser excitation. As it can be seen from Figures 1.6 and 1.7 the relative intensity of the observed lines does not depend on the photon excitation energy. Comparing the results for YCrO<sub>3</sub> presented in Ref. [31] and here, because of the much better quality of our spectra, two more weak lines are detected (the line at 611 cm<sup>-1</sup> of  $B_{2g}$  symmetry, and the line at 556 cm<sup>-1</sup> that based on LDC is a  $B_{1g}$  line). The lack of resonance effects holds also for



**Figure 1.5.** The shape of the Raman allowed phonon modes for the  $ABO_3$  compounds with *Pnma* structure. Only  $A_g$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $B_{3g}$  modes with pure oxygen vibrations are shown. The rest modes with these symmetries corresponds to mixed rare-earth – oxygen vibrations.<sup>[32]</sup>

the spectra of YCrO<sub>3</sub>. On the other hand, from Figures 1.6 and 1.7 it is seen that the relative intensity for lines, corresponding to one and the same mode in both compounds, is very different. For example, the most intensive lines at 618 ( $B_{2g}$ ) and 497 cm<sup>-1</sup> ( $A_g$ ) in the YMnO<sub>3</sub> are very weak in YCrO<sub>3</sub>, where they correspond to the lines at 611 and 492 cm<sup>-1</sup>. In contrast, the most intensive lines in YCrO<sub>3</sub> (219 cm<sup>-1</sup>–  $B_{2g}$  and 281 and 342 cm<sup>-1</sup>–  $A_g$ ) are very weak in YMnO<sub>3</sub>. In general, the intensity of a line in a Raman spectrum in specific geometrical configuration is a complex function of the electronic structure of the compound, the energy of the incident photons, the specifics of the crystal structure and the geometrical configuration.



**Figure 1.6.** Raman spectra with  $z'(yy)\bar{z}'$  polarization (where only  $A_g$  lines are allowed), obtained from (101) surfaces of YMnO<sub>3</sub> and YCrO<sub>3</sub> single crystals using different laser excitation. For better comparison some of the spectra are multiplied by a number, indicated on the figure. The assignment of the corresponding lines, based on the LDC, is also given.

However, in our case of  $YBO_3$  (B = Cr, Mn) there is no dependence of the relative intensity of a line on the exciting photon energy. Therefore, it is plausible to assume that this intensity is determined mainly by the structural distortion. In the model, proposed in Ref. [30], and adapted for this type of structure, it is concluded that the intensity of the most (20 out of 24) Raman-active lines is governed mainly by only one basic structural distortion and it will monotonously increases with its value. The assignment of the Raman-active modes and the structural distortion, activating them are shown in Table 1.4. The numbering of the modes in the table and Figures 1.6 and 1.7 follows the notations from Ref. [30].

**Table 1.4.** Comparison between experimental and calculated frequencies of the Raman-active lines in YCrO<sub>3</sub> and YMnO<sub>3</sub>. The symmetry of the lines, the assignment (based on LDC) to the definite atomic vibrations, and the activating distortions [according Ref. [30]] are also given.

Symmetry	YCrO <sub>3</sub>			YMnO <sub>3</sub>			Assign-	Activating
	Ref. [31]	Expt.	Calc.	Ref. [32]	Expt.	Calc.	ment	distortion
$A_g$	156	152	152	151	150	165	7	A-shift
$A_g$	188	185	185	188	187	217	5	[010]
								(Continued)
Symmetry	Y	′Cr0 <sub>3</sub>		YMnO <sub>3</sub>			Assign-	Activating
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_	Ref. [31]	Expt.	Calc.	Ref. [32]	Expt.	Calc.	ment	distortion
$A_g$	282	281	229	288	289	265	6	A-shift
$A_g$	346	342	298	323	324	302	2	[010], JT
$A_g$	429	426	384	396	398	373	4	[101]
$A_g$	492	492	429	497	497	483	1	[010], JT
$A_g$	566	564	493	518	519	498	3	[101]
$B_{2g}$			160	151	152	179	7	A-shift
$B_{2g}$	223	219	209	220	222	234	5	[101]
$B_{2g}$			274	317	318	297	4	[101]
$B_{2g}$	318	313	339	341	342	351	6	A-shift
$B_{2g}$			444	481	481	497	3	[101]
$B_{2g}$	502	502	461	537	539	523	2	[010]
$B_{2g}$		611	611	616	618	618	1	JT
$B_{1g}$			193	205	205	226	5	A-shift
$B_{1g}$	272	266	267	284	285	269	4	[010], JT
$B_{1g}$	413	408	329	383	382	327	3	[101]
$B_{1g}$		556	466			414	2	[101]
$B_{1g}$			611			647	1	A-shift
$B_{3g}$	176	174	152	178	179	184	5	[101]
$B_{3g}$			308	336	337	332	4	[010], JT
$B_{3g}$	487	485	440			410	3	[101]
$B_{3g}$	569	567	482			491	2	[101]
$B_{3g}$			619			642	1	[101]

Table 1.4. (Continued)

In Table 1.5 are given the calculated from structural data values of the four structural distortions for some perovskites. The values of the distortions are calculated according the formulas (1.1) – (1.4). As seen from Table 1.5, the values of  $D_{[101]}$ ,  $D_{[010]}$  and  $D_{A-\text{shift}}$  distortions in YMnO<sub>3</sub> and YCrO<sub>3</sub> are close, whereas the value of  $D_{\text{JT}}$  is by a factor of six larger in YMnO<sub>3</sub> compared to YCrO<sub>3</sub>. Only the  $B_{2g}(1)$  mode (in-phase stretching vibration of O2 atoms) is activated solely by  $D_{\text{JT}}$ . Indeed, the line, corresponding to this mode in YMnO<sub>3</sub>, is the most intensive one, while in YCrO<sub>3</sub> it is very weak. Moreover, the second in intensity  $A_g(1)$  line in YMnO<sub>3</sub> is also activated by  $D_{\text{JT}}$ . On the other hand, in the Raman spectra of  $ABO_3$  perovskites, containing non-JT ion in *B*-position (or an JT-ion, which does not produce large difference in the B - O2 distances, as is the case of Ti<sup>3+</sup>), the  $B_{2g}(1)$  line is either weak or even not detectable (see, e.g.,  $B = Al^{[46]}$ , Sc<sup>[47,48]</sup>, Ti<sup>[49,50]</sup>, V<sup>[51]</sup>, Fe<sup>[52,53]</sup>, Ni<sup>[54]</sup>). Therefore, it appears that the intensity of the  $B_{2g}(1)$  line can be used as a measure of the JT-distortion of the  $BO_6$  octahedra.

The intensity of other  $A_g$  and  $B_{2g}$  lines in the low frequency range (below 350 cm<sup>-1</sup>) in



**Figure 1.7.** Raman spectra with  $y(xz)\bar{y}$  polarization (where only  $B_{2g}$  lines are allowed), obtained from (101) surfaces of YMnO<sub>3</sub> and YCrO<sub>3</sub> single crystals using different laser excitation. For better comparison some of the spectra are multiplied by a number, indicated on the figure. The assignment of the corresponding lines, based on the LDC, is also given.

Table 1.5	. The values of the	structural distortions	of several YBO <sub>3</sub>	compounds ( $B =$
Al, Ti, V, Cı	r, Mn) and $NdBO_3$	(B = Sc, Ni).		

Compound	D <sub>[101]</sub> (deg)	$D_{[010]}$ (deg)	D <sub>JT</sub>	D <sub>A-shift</sub>	Ref.
YAlO <sub>3</sub>	13.7	10.3	0.0000	0.1062	[41]
NdScO <sub>3</sub>	17.5	12.1	0.0054	0.1064	[42]
YTiO <sub>3</sub>	18.5	13.4	0.0020	0.1458	[43]
YVO <sub>3</sub>	17.6	12.8	0.0102	0.1388	[44]
YCrO <sub>3</sub>	16.7	12.2	0.0084	0.1324	[36]
YMnO <sub>3</sub>	16.8	14.2	0.0542	0.1710	[38]
NdNiO <sub>3</sub>	11.8	8.0	0.0070	0.0700	[45]

the spectra of YCrO<sub>3</sub> are rather strong compared to the corresponding lines in the spectra of YMnO<sub>3</sub> [except for the  $A_g(5)$  line, which has comparable intensity in both compounds]. This is somewhat puzzling as both compounds have comparable values of the three other structural distortions, responsible for the intensity. Moreover, the comparison of the polarized Raman spectra (in particular those with yy polarization) of other isostructural compounds shows that all seven  $A_g$  lines have a relative intensity <sup>[48,51]</sup> similar to that of YCrO<sub>3</sub>. The reasonable

question is why the intensity of these lines in YMnO<sub>3</sub> is so different? It seems that the reason is not in the large value of the JT distortion but rather in the twinning of the crystal. It can be found that practically all synthesized and investigated single crystals from the type  $A^{3+}B^{3+}O_3$ ( $A^{3+}$  – rare-earth ion), except the manganites, are not twinned, whereas all single crystals of manganites are twinned in the (010) plane (the same plane where the JT orbital ordering holds). Actually, there is only one report<sup>[55]</sup> on untwinned LaMnO<sub>3</sub> single crystal, but in that paper Raman spectroscopy was not used. In this case the untwinned crystal has been found by chance among the majority of twinned crystals in the ingot and probably it has been naturally detwinned by appropriately oriented uniaxial stress in a small region in the crucible during the cooling. Due to the fact that the size of the twin domains is much smaller than 1  $\mu$ m (the diameter of the laser beam used), a considerable part of atoms in the structure are close to a twin boundary and therefore they have incoherent and variable atomic environment, leading to depressing of the corresponding Raman lines. This hypothesis can be proved in a parallel Raman study of twinned and detwinned manganite crystals.

In summary, single crystals of YCrO<sub>3</sub> and finely twinned crystals of YMnO<sub>3</sub> were studied by micro-Raman spectroscopy in backscattering geometry at room temperature with different scattering configurations. The symmetry of the observed lines was determined from the polarized spectra. In comparison to a previous paper<sup>[31]</sup> for YCrO<sub>3</sub> two new lines,  $B_{1g}$  and  $B_{2g}$  at 556 and 611 cm<sup>-1</sup>, are registered. Based on performed lattice dynamical calculations the observed lines are assigned to definite atomic vibrations. The lines in the spectra of YCrO<sub>3</sub> and YMnO<sub>3</sub>, corresponding to same modes, have close frequencies, but significantly different relative intensities. The large intensity of two of the lines [ $B_{2g}(1)$  and  $A_g(1)$ ] in YMnO<sub>3</sub> is explained by the presence of large Jahn-Teller distortion. The low intensity of the rest lines in the spectra of YMnO<sub>3</sub>, if compared to these in YCrO<sub>3</sub>, cannot be explained accounting for the structural distortions. It is concluded that the reduced intensity of these lines is caused by the fine twinning of the manganite crystals related to the JT ordering.

# **2.** Frequency dependence of the quasi-soft Raman-active modes in rotationally distorted $R^{3+}B^{3+}O_3$ perovskites, R – rare-earth, B – Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Ga

The structural data and Raman spectra of distorted  $R^{3+}B^{3+}O_3$  perovskites ( $R^{3+}$  – rare-earth,  $B^{3+}$  – Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Ga) with  $BO_6$  octahedral tilts were critically reviewed in order to obtain the frequency ( $\omega$ ) vs  $BO_6$  tilt angle ( $\alpha$ ) dependence of the quasi-soft vibrational modes. It was found that the relation  $\omega = \varkappa \alpha$  is satisfied in a good approximation for each  $RBO_3$  family with fixed B atom, despite of different spatial tilt orientation for compounds of the same series with either orthorhombic *Pnma* or rhombohedral  $R\bar{3}c$  structure. The dependence of the proportionality coefficient  $\varkappa$  on the averaged  $\langle B-O \rangle$  octahedral distance can be described using different functions (power, linear and exponential ones). The established dependencies can be used for analysis of Raman data and heuristic prediction of structural second-order transitions.

Among the numerous compounds with perovskite-like structure, the group of  $R^{3+}B^{3+}O_3$ oxides ( $R^{3+}$  – rare-earth,  $B^{3+}$  – transition metal) is one of most intensively studied because of the richness of phenomena that have been observed changing the temperature, pressure or upon doping through chemical substitution. Following the model of Glazer,<sup>[27]</sup> the crystal structure of these compounds can be obtained from the ideal cubic perovskite tilting the  $BO_6$ octahedra (treated as rigid species) around one or more crystallographic directions. For most members of this family, depending on the type of  $R^{3+}$  and  $B^{3+}$  atoms the crystal structure at room temperature is either orthorhombic *Pnma* [Glazer notation  $a^-b^+a^-$ , two octahedral tilts around [101] and [010] cubic directions, see Figure 2.1] or rhombohedral  $R\bar{3}c$  [Glazer notation  $a^-a^-a^-$ , one octahedral tilt around [111] cubic direction].<sup>[56]</sup>

With the increase of the temperature<sup>[28]</sup> or the pressure<sup>[57]</sup> structural second-order phase transition from rhombohedral  $R\bar{3}c$  to cubic  $Pm\bar{3}m$  structure is observed. The order parameter in this case is the tilt angle and the corresponding soft phonon mode can be described as rotations of the  $BO_6$  octahedra around [111] cubic direction. This mode is of  $A_{1g}$ symmetry and it is Raman-active. This allows to use Raman spectroscopy to study the dependence of its frequency  $\omega$  on temperature and/or pressure. Experimentally it has been found that  $\omega$  depends on the temperature T as  $\omega^2 \propto (T_c - T)$ , where  $T_c$  is the temperature of the structural phase transition,<sup>[28]</sup> as it is expected from the Landau theory of second-order phase transitions.<sup>[58]</sup> Similar dependence  $\omega^2 \propto (p_c - p)$  has been observed with increasing the pressure<sup>[57]</sup> ( $p_c$  is the pressure of the phase transition). The tilt angle  $\alpha$  also depends on the pressure as  $\alpha^2 \propto (p_c - p)$ .<sup>[59]</sup> Therefore, for one compound the soft mode frequency  $\omega$ is expected to be proportional to the tilt angle  $\alpha$ . Such a rough *frequency – tilt angle* proportionality has been noticed even for isostructural rhombohedral compounds with different chemical content.<sup>[60,61]</sup>

With the increase of the temperature, the orthorhombic  $RBO_3$  perovskites do not undergo second-order phase transition. They either undergo first-order phase transition to



**Figure 2.1.** The crystal structure of orthorhombically distorted *Pnma RBO*<sub>3</sub> perovskite (the real structure of LaGaO<sub>3</sub>). (a) View along [100] direction. The  $\alpha_{[101]}$  tilt angle is clearly visible. (b) View along [010] direction. The  $\alpha_{[010]}$  tilt angle is clearly visible.

rhombohedral  $R\bar{3}c$  or keep their orthorhombic *Pnma* structure up to very high temperatures.<sup>[62]</sup> However, the lattice dynamical calculations for *Pnma* structure predict that two out of the 7 $A_g$  Raman-active modes have the shape of the two octahedral tilts<sup>[32]</sup> and therefore it is plausible to expect that their frequencies will be indicative for the values of the two tilt angles. Because of this, we can regard these two modes as quasi-soft ones. Investigating the Raman spectra of  $RMnO_3$  (R – La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Y), Iliev *et al.*<sup>[29]</sup> have shown that the frequencies of these rotational modes are proportional to the tilt angles with proportionality coefficient  $\varkappa = 23.5$  cm<sup>-1</sup>/deg. Somewhat smaller value of  $\varkappa$  (20.0 cm<sup>-1</sup>/deg) has been reported in Ref. [48] after comparison with the corresponding lines in the Raman spectra of  $RScO_3$  (the ionic radius of Sc<sup>3+</sup> is larger than the one of Mn<sup>3+</sup>).

In this work we derive a rather general relationship between the frequency of the soft (or quasi-soft) modes (for both  $R\bar{3}c$  and Pnma structures), the corresponding tilt angle and the type of the *B* atom for  $R^{3+}B^{3+}O_3$  oxides ( $R^{3+}$  – rare-earth,  $B^{3+}$  – Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Ga) using structural and Raman data available in the literature . We note here that the tilt angles can be determined from the fractional coordinates of the oxygen atoms in the unit cell. In the case of  $R\bar{3}c$  structure the relation is simple,

$$\alpha_{[111]} = \arctan\left[\sqrt{3}(1-2x_0)\right].^{[60]}$$

For the *Pnma* structure, however, the quantitative definition of the values of the two [101] and [010] octahedral tilts is not trivial, because strictly speaking, spatial orientation of the rigid octahedra can be reproduced by three consecutive rotations (e.g. using Euler angles). For small tilt angles, however, the description with two commutative rotations around [101] and [010] cubic directions is satisfactory. We have already defined the formulae for these

angles in Chapter 1 Equations (1.1) and (1.2), in other words

$$\alpha_{[101]} \equiv D_{[101]}$$
 and  $\alpha_{[010]} \equiv D_{[010]}$ 

An alternative approach is proposed in Ref. [63] but there it is assumed that all B-O distances in the  $BO_6$  octahedra are equal, which obviously is not the case for some  $RBO_3$  perovskites (e.g.  $RMnO_3$ , containing  $Mn^{3+}$  Jahn-Teller ion).



**Figure 2.2.** Frequency  $\omega$  vs tilt angle  $\alpha$  dependence for the quasi-soft modes of the *RBO*<sub>3</sub> families. The proportionality coefficient  $\varkappa$  for each *RBO*<sub>3</sub> family is also given.

The extraction of the quasi-soft mode frequencies from the available Raman data may be challenging in some cases. Indeed, in some studies, <sup>[28,29,37,46,48,50,60,64-67]</sup> a complete analysis of the Raman spectra has been done, including determination of the symmetry of the observed lines and their assignment to definite atomic vibrations based on LDC or other empirical dependencies. In other cases, however, <sup>[47,49,51,53,68–76]</sup> it is difficult and somewhat ambiguous to determine which lines correspond to the quasi-soft modes. The reason is that in the *Pnma* structure there are 24 Raman-active modes  $(7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g})$  and either non-polarized spectra were measured or the symmetry of the lines were determined from the polarized spectra without any discussion of their origin. The careful observation of published polarized Raman spectra leads to the conclusion that the  $A_a$  and some of the  $B_{2a}$ lines are the most intense.<sup>[67]</sup> To identify the lines corresponding to the quasi-soft modes, we applied the approach verified earlier on the example of  $RMnO_3$ <sup>[29]</sup> and  $RScO_3$ <sup>[48]</sup> series. It has been found in the latter studies that the frequency of the Raman lines assigned to either internal stretching oxygen vibrations or to mixed rare-earth – oxygen vibrations varies weakly on the type of the rare-earth ion [for the classification of the Raman-active modes in Pnma structure, see Table 1.4 and Figure 1.5 in Chapter 1 and Refs. [30,32]]. The lines with stronger frequency shift within a  $RBO_3$  family with fixed B atoms appear to be the quasi-soft

modes. The dependence of the frequency of these rotational-like modes on the static octahedral tilt is given in Figure 2.2 (used frequencies, structural data and their sources are given on Table 2.1).

As it follows from Figure 2.2 for each series of  $RBO_3$  oxides the quasi-soft mode frequency  $\omega$  is proportional to the value of the static tilt  $\alpha$ . Moreover, the proportionality coefficient  $\varkappa$  is practically independent on the direction of the rotation axis [[111] for the rhombohedral structures and [101] or [010] for orthorhombic structures]. The coefficient  $\varkappa$ , however, varies from 20.8 cm<sup>-1</sup>/deg for the scandates to 28.9 cm<sup>-1</sup>/deg for the aluminates.

**Table 2.1.** List of the experimentally observed frequencies ( $\omega_{expt}$ ) of the quasi-soft modes and the tilting angle  $\alpha$ , used in Figure 2.2. The four- and five-digit numbers in the column "Ref.  $\alpha$ " indicate the reference code of the structural data in the ICSD (Inorganic Crystal Structure Database, FIZ Karlsruhe<sup>[77]</sup>). The calculated frequencies using power ( $\omega_P$ ), linear ( $\omega_L$ ) and exponential ( $\omega_E$ ) functions (approximating the *frequency* – *tilt angle* dependence) and the corresponding  $\Delta \omega = \omega - \omega_{expt}$  are also given (see the text below).  $\omega$  and  $\Delta \omega$  are in cm<sup>-1</sup>.

Compound	$\alpha$ (deg)	$\omega_{\mathrm{expt}}$	$\omega_{ m P}$	$\omega_{ m L}$	$\omega_{\mathrm{E}}$	$\Delta \omega_{ m P}$	$\Delta \omega_{ m L}$	$\Delta \omega_{ m E}$	Ref. $\omega_{\mathrm{exp}}$	t Ref. α
LaAlO <sub>3</sub>	$\alpha_{[111]} = 4.94$	123	143	141	142	20	18	19	[60]	[62]
PrAlO <sub>3</sub>	$\alpha_{[111]} = 8.41$	214	243	240	242	29	26	28	[28]	90558
NdAlO <sub>3</sub>	$\alpha_{[111]} = 9.25$	241	267	264	266	26	23	25	[28]	90572
SmAlO <sub>3</sub>	$\alpha_{[101]} = 10.53$	291	304	300	303	13	9	12	[64]	10334
SmAlO <sub>3</sub>	$\alpha_{[010]} = 6.12$	175	177	175	176	2	0	1	[64]	10334
GdAlO <sub>3</sub>	$\alpha_{[101]} = 11.87$	315	342	338	341	27	23	26	[76]	[62]
GdAlO <sub>3</sub>	$\alpha_{[010]} = 7.94$	233	229	226	228	-4	-7	-5	[76]	[62]
YAlO <sub>3</sub>	$\alpha_{[101]} = 13.32$	403	384	380	383	-19	-23	-20	[46]	83027
YAlO <sub>3</sub>	$\alpha_{[010]} = 9.66$	265	279	276	278	14	11	13	[46]	83027
YbAlO <sub>3</sub>	$\alpha_{[101]} = 14.75$	464	426	421	425	-38	-43	-39	[70]	[62]
YbAlO <sub>3</sub>	$\alpha_{[010]} = 11.25$	361	325	321	324	-36	-40	-37	[70]	[62]
NdScO <sub>3</sub>	$\alpha_{[101]} = 17.50$	380	359	354	357	-21	-26	-23	[48]	[42]
NdScO <sub>3</sub>	$\alpha_{[010]} = 12.05$	227	247	243	246	20	16	19	[48]	[42]
SmScO <sub>3</sub>	$\alpha_{[101]} = 18.61$	400	381	376	380	-19	-24	-20	[48]	[42]
SmScO <sub>3</sub>	$\alpha_{[010]} = 12.43$	233	255	251	254	22	18	21	[48]	[42]
GdScO <sub>3</sub>	$\alpha_{[101]} = 19.22$	418	394	388	392	-24	-30	-26	[48]	[42]
GdScO <sub>3</sub>	$\alpha_{[010]} = 12.84$	248	263	259	262	15	11	14	[48]	[42]
DyScO <sub>3</sub>	$\alpha_{[101]} = 20.05$	434	411	405	409	-23	-29	-25	[48]	[42]
DyScO <sub>3</sub>	$\alpha_{[010]} = 13.25$	254	271	268	270	17	14	16	[48]	[42]
LaTiO <sub>3</sub>	$\alpha_{[101]} = 13.00$	296	296	298	297	0	2	1	[50]	[43]
LaTiO <sub>3</sub>	$\alpha_{[010]} = 9.59$	252	219	219	219	-33	-33	-33	[50]	[43]
NdTiO <sub>3</sub>	$\alpha_{[101]} = 15.06$	345	343	344	343	-2	-1	-2	[49]	82008
SmTiO <sub>3</sub>	$\alpha_{[101]} = 16.23$	365	370	371	370	5	6	5	[49]	51180
GdTiO <sub>3</sub>	$\alpha_{[101]} = 17.11$	385	390	391	390	5	6	5	[49]	8149
YTiO <sub>3</sub>	$\alpha_{[101]} = 18.62$	417	424	426	424	7	9	7	[65]	[78]
	-								(0	ontinued)

Table 2.1. (Continued)

Compound	$\alpha$ (deg)	$\omega_{\mathrm{expt}}$	$\omega_{ m P}$	$\omega_{ m L}$	$\omega_{\mathrm{E}}$	$\Delta \omega_{ m P}$	$\Delta \omega_{ m L}$	$\Delta \omega_{ m E}$	Ref. $\omega_{\mathrm{expt}}$	Ref. α
YTiO <sub>3</sub>	$\alpha_{[010]} = 13.19$	273	301	302	301	28	29	28	[65]	[78]
LaVO <sub>3</sub>	$\alpha_{[101]} = 11.90$	283	286	287	286	3	4	3	[51]	86554
NdVO <sub>3</sub>	$\alpha_{[101]} = 14.36$	339	345	347	345	6	8	6	[51]	63522
YV0 <sub>3</sub>	$\alpha_{[101]} = 17.57$	427	422	424	422	-5	-3	-5	[75]	95579
YV0 <sub>3</sub>	$\alpha_{[010]} = 12.76$	337	306	308	307	-31	-29	-30	[75]	95579
YbVO <sub>3</sub>	$\alpha_{[101]} = 18.44$	441	443	445	443	2	4	2	[75]	97783
YbVO <sub>3</sub>	$\alpha_{[010]} = 13.31$	344	320	321	320	-24	-23	-24	[75]	97783
LaCrO <sub>3</sub>	$\alpha_{[101]} = 10.85$	256	274	276	274	18	20	18	[37]	[79]
LaCrO <sub>3</sub>	$\alpha_{[010]} = 5.26$	104	133	134	133	29	30	29	[37]	[79]
YCrO <sub>3</sub>	$\alpha_{[101]} = 16.71$	426	422	424	423	-4	-2	-3	[67]	[36]
YCrO <sub>3</sub>	$\alpha_{[010]} = 12.21$	342	309	310	309	-33	-32	-33	[67]	[36]
LaMnO <sub>3</sub>	$\alpha_{[111]} = 11.17$	236	262	264	262	26	28	26	[60]	[80]
LaMnO <sub>3</sub>	$\alpha_{[101]} = 12.08$	284	283	285	284	-1	1	0	[29]	[38]
LaMnO <sub>3</sub>	$\alpha_{[010]} = 9.20$	198	216	217	216	18	19	18	[29]	[38]
PrMnO <sub>3</sub>	$\alpha_{[101]} = 13.47$	324	316	318	316	-8	-6	-8	[29]	[38]
PrMnO <sub>3</sub>	$\alpha_{[010]} = 11.56$	232	271	273	272	39	41	40	[29]	[38]
NdMnO <sub>3</sub>	$\alpha_{[101]} = 14.11$	332	331	333	331	-1	1	-1	[29]	[38]
NdMnO <sub>3</sub>	$\alpha_{[010]} = 11.83$	245	278	279	278	33	34	33	[29]	[38]
SmMnO <sub>3</sub>	$\alpha_{[101]} = 15.34$	353	360	362	360	7	9	7	[29]	95491
SmMnO <sub>3</sub>	$\alpha_{[010]} = 13.12$	266	308	309	308	42	43	42	[29]	95491
EuMnO <sub>3</sub>	$\alpha_{[101]} = 15.36$	361	361	362	361	0	1	0	[29]	[81]
$GdMnO_3$	$\alpha_{[101]} = 16.14$	371	379	381	379	8	10	8	[29]	95493
$GdMnO_3$	$\alpha_{[010]} = 13.38$	310	314	316	314	4	6	4	[29]	95493
TbMnO <sub>3</sub>	$\alpha_{[101]} = 16.23$	378	381	383	381	3	5	3	[29]	[38]
$TbMnO_3$	$\alpha_{[010]} = 13.74$	315	323	324	323	8	9	8	[29]	[38]
$DyMnO_3$	$\alpha_{[101]} = 16.79$	386	394	396	394	8	10	8	[29]	[38]
DyMnO <sub>3</sub>	$\alpha_{[010]} = 14.01$	320	329	331	329	9	11	9	[29]	[38]
YMnO <sub>3</sub>	$\alpha_{[101]} = 16.79$	398	394	396	394	-4	-2	-4	[29]	[38]
YMnO <sub>3</sub>	$\alpha_{[010]} = 14.15$	325	332	334	332	7	9	7	[29]	[38]
HoMnO <sub>3</sub>	$\alpha_{[101]} = 17.14$	396	402	404	403	6	8	7	[29]	[38]
HoMnO <sub>3</sub>	$\alpha_{[010]} = 14.23$	324	334	336	334	10	12	10	[29]	[38]
LaFeO <sub>3</sub>	$\alpha_{[101]} = 11.04$	280	264	266	264	-16	-14	-16	[66]	93611
LaFeO <sub>3</sub>	$\alpha_{[010]} = 9.43$	190	225	227	226	35	37	36	[66]	93611
PrFeO <sub>3</sub>	$\alpha_{[101]} = 13.95$	335	334	335	334	-1	0	-1	[74]	63645
PrFeO <sub>3</sub>	$\alpha_{[010]} = 9.64$	205	230	232	231	25	27	26	[74]	63645
DyFeO <sub>3</sub>	$\alpha_{[101]} = 16.97$	409	406	408	406	-3	-1	-3	[53]	27280

(Continued)

Table 2.1. (Continued)

Compound	$\alpha$ (deg)	$\omega_{\mathrm{expt}}$	$\omega_{ m P}$	$\omega_{ m L}$	$\omega_{\mathrm{E}}$	$\Delta \omega_{ m P}$	$\Delta \omega_{ m L}$	$\Delta \omega_{ m E}$	Ref. $\omega_{\mathrm{expt}}$	Ref. α
DyFeO <sub>3</sub>	$\alpha_{[010]} = 12.61$	332	302	303	302	-30	-29	-30	[53]	27280
HoFeO <sub>3</sub>	$\alpha_{[101]} = 17.36$	425	415	418	416	-10	-7	-9	[53]	27281
HoFeO <sub>3</sub>	$\alpha_{[010]} = 12.71$	340	304	306	304	-36	-34	-36	[53]	27281
ErFeO <sub>3</sub>	$\alpha_{[101]} = 17.89$	424	428	430	428	4	6	4	[52]	27282
ErFeO <sub>3</sub>	$\alpha_{[010]} = 12.94$	345	309	311	310	-36	-34	-35	[52]	27282
TmFeO <sub>3</sub>	$\alpha_{[101]} = 18.18$	434	435	437	435	1	3	1	[53]	27283
TmFeO <sub>3</sub>	$\alpha_{[010]} = 12.95$	346	310	312	310	-36	-34	-36	[53]	27283
LuFeO <sub>3</sub>	$\alpha_{[101]} = 19.05$	450	455	458	456	5	8	6	[72]	27285
LuFeO <sub>3</sub>	$\alpha_{[010]} = 13.26$	350	317	319	317	-33	-31	-33	[72]	27285
SmCoO <sub>3</sub>	$\alpha_{[101]} = 12.86$	358	354	352	353	-4	-6	-5	[71]	90969
SmCoO <sub>3</sub>	$\alpha_{[010]} = 9.20$	280	253	252	253	-27	-28	-27	[71]	90969
DyCoO <sub>3</sub>	$\alpha_{[101]} = 14.84$	407	408	407	408	1	0	1	[71]	[82]
DyCoO <sub>3</sub>	$\alpha_{[010]} = 11.60$	330	319	318	319	-11	-12	-11	[71]	[82]
NdNiO <sub>3</sub>	$\alpha_{[101]} = 11.82$	305	316	316	316	11	11	11	[47]	[45]
NdNiO <sub>3</sub>	$\alpha_{[010]} = 8.03$	250	214	214	214	-36	-36	-36	[47]	[45]
SmNiO <sub>3</sub>	$\alpha_{[101]} = 13.50$	335	360	361	360	25	26	25	[47]	90959
SmNiO <sub>3</sub>	$\alpha_{[010]} = 10.09$	265	269	269	269	4	4	4	[47]	90959
LaGaO <sub>3</sub>	$\alpha_{[111]} = 10.79$	252	271	272	271	19	20	19	[69]	[62]
LaGaO <sub>3</sub>	$\alpha_{[101]} = 11.04$	255	277	278	277	22	23	22	[69]	51285
LaGaO <sub>3</sub>	$\alpha_{[010]} = 4.80$	138	120	121	121	-18	-17	-17	[69]	51285
PrGaO <sub>3</sub>	$\alpha_{[101]} = 12.82$	320	322	323	322	2	3	2	[73]	73766
PrGaO <sub>3</sub>	$\alpha_{[010]} = 8.58$	185	215	216	215	30	31	30	[73]	73766
NdGaO <sub>3</sub>	$\alpha_{[101]} = 13.85$	343	348	349	348	5	6	5	[68]	[68]
NdGaO <sub>3</sub>	$\alpha_{[010]} = 9.74$	218	244	245	244	26	27	26	[68]	[68]
NdGaO <sub>3</sub>	$\alpha_{[101]} = 13.69$	336	343	345	344	7	9	8	[69]	[69]
NdGaO <sub>3</sub>	$\alpha_{[010]} = 9.10$	214	228	229	228	14	15	14	[69]	[69]

Further we are looking for structural explanation of the dependence of  $\varkappa$  on the type of the B atom. It is naturally to expect that a suitable structural parameter could be the ionic radius  $r_B$  of the  $B^{3+}$  ion in 6-fold oxygen coordination. The values of these radii have been given by Shannon.<sup>[3]</sup> Unfortunately, the attempt to establish a reliable dependence of  $\varkappa$  on  $r_B$  was not very successful. To our opinion this was partly due to the fact that the Shannon radii  $r_B$  have been defined with relatively low accuracy ( $\pm 0.01$  Å). An additional problem is that for some ions (e.g. Co<sup>3+</sup>, Ni<sup>3+</sup>, Mn<sup>3+</sup> and Fe<sup>3+</sup>)  $r_B$  strongly varies with the spin state. For this reason, instead of  $r_B$ , we tried using another parameter well-known from the structural chemistry <sup>[83]</sup> – the averaged B–0 octahedral distance – (B–0). The averaging over the three different pairs of B–0i (i = 1, 2, 3) is necessary only for the *Pnma* structure, whereas in  $R\bar{3}c$  structure all six B–0 distances are equal due to the crystal symmetry. We use arithmetic mean, because the

difference between values of different means [arithmetic, quadratic (related to the moment of inertia of the  $BO_6$  octahedra) or geometric (related to the volume of the  $BO_6$  octahedra)] is smaller than 0.001 Å (even in the case of strongly distorted  $BO_6$  octahedra in manganites). The calculated values of  $\langle B-O \rangle$  for several  $RBO_3$  families are displayed in Figure 2.3 (all used values and their sources are given on Table 2.3).



**Figure 2.3.** The averaged *B*–O distance for the  $BO_6$  octahedra in various  $RBO_3$  perovskites. The full symbols correspond to the materials with rhombohedral  $R\bar{3}c$  structure, whereas the empty symbols are for structures with orthorhombic *Pnma* symmetry. The horizontal lines represent the averaged  $\langle B-O \rangle$  distance over each  $RBO_3$ family.

Figure 2.3 illustrates that for most compounds within a given  $RBO_3$  series, the deviation of an individual  $\langle B-O \rangle$  from the averaged  $\langle B-O \rangle$  distance over the whole series is less than 0.005 Å and it is comparable with the differences of  $\langle B-O \rangle$ , calculated using different structural data for one and the same compound. The accuracy of the so obtained over-family-

<i>B</i> – atom	$\overline{\langle B-0\rangle}$ (Å)	<i>B</i> – atom	$\overline{\langle B-0\rangle}$ (Å)
Al	1.905	V	2.008
Со	1.931	Fe	2.011
Ni	1.948	Mn	2.021
Cr	1.979	Ti	2.038
Ga	1.983	Sc	2.102

**Table 2.2.** The averaged  $\langle B-0 \rangle$  distance for each  $RBO_3$  family.

averaged  $\langle B-0 \rangle$  value (see Table 2.2) is an order of magnitude better than the one calculated using the Shannon radii of  $B^{3+}$  and  $O^{2-}$  ions. The deviation is significant only for the rhombohedral  $R\bar{3}c$  LaMnO<sub>3</sub> (the calculated  $\langle B-0 \rangle$  is much smaller compared to the ones from the same series). This implies that the proposed rhombohedral structural model poorly de-

scribes the real crystal structure, at least because it does not account for the Jahn-Teller MnO<sub>6</sub> octahedral distortions. As evident from Figures 2.2 and 2.3 largest  $\varkappa$  corresponds to *RBO*<sub>3</sub> series with smallest  $\overline{\langle B-O \rangle}$  distance and *vice versa*. Therefore one can search for a monotonically decreasing function of  $\varkappa$  versus the averaged  $\langle B-O \rangle$ .

Compound	⟨ <i>B</i> −0⟩ (Å)	Reference	Compound	⟨ <i>B</i> −0⟩ (Å)	Reference
LaAlO <sub>3</sub>	1.900	[62]	TbMnO <sub>3</sub>	2.022	[38]
PrAlO <sub>3</sub>	1.895	90558	DyMnO <sub>3</sub>	2.024	[38]
NdAlO <sub>3</sub>	1.893	90572	YMnO <sub>3</sub>	2.014	[38]
SmAlO <sub>3</sub>	1.898	10334	HoMnO <sub>3</sub>	2.013	[38]
EuAlO <sub>3</sub>	1.916	[62]	ErMnO <sub>3</sub>	2.013	[38]
GdAlO <sub>3</sub>	1.905	[62]	LaFeO <sub>3</sub>	2.007	93611
TbAlO <sub>3</sub>	1.911	84422	PrFeO <sub>3</sub>	2.013	63645
DyAlO <sub>3</sub>	1.908	[62]	NdFeO <sub>3</sub>	2.003	78587
YAlO <sub>3</sub>	1.901	83027	SmFeO <sub>3</sub>	2.013	27276
HoAlO <sub>3</sub>	1.907	39606	EuFeO <sub>3</sub>	2.013	27277
ErAlO <sub>3</sub>	1.912	[62]	GdFeO <sub>3</sub>	2.012	27278
YbAlO <sub>3</sub>	1.909	[62]	DyFeO <sub>3</sub>	2.012	27280
LuAlO <sub>3</sub>	1.909	[62]	YFeO <sub>3</sub>	2.012	80865
NdScO <sub>3</sub>	2.103	[42]	HoFeO <sub>3</sub>	2.010	27281
SmScO <sub>3</sub>	2.103	[42]	ErFeO <sub>3</sub>	2.011	27282
EuScO <sub>3</sub>	2.128	4128	TmFeO <sub>3</sub>	2.011	27283
GdScO <sub>3</sub>	2.101	[42]	YbFeO <sub>3</sub>	2.011	27284
DyScO <sub>3</sub>	2.100	[42]	LuFeO <sub>3</sub>	2.010	27285
LaTiO <sub>3</sub>	2.039	[43]	LaCoO <sub>3</sub>	1.932	201763
NdTiO <sub>3</sub>	2.039	82008	PrCoO <sub>3</sub>	1.930	[82]
SmTiO <sub>3</sub>	2.035	51180	NdCoO <sub>3</sub>	1.930	82078
GdTiO <sub>3</sub>	2.039	8149	SmCoO <sub>3</sub>	1.927	90969
YTiO <sub>3</sub>	2.040	[78]	TbCoO <sub>3</sub>	1.933	[82]
YTiO <sub>3</sub>	2.039	[43]	DyCoO <sub>3</sub>	1.933	[82]
LaVO <sub>3</sub>	2.002	86554	YCoO <sub>3</sub>	1.933	84720
CeVO <sub>3</sub>	2.000	63521	HoCoO <sub>3</sub>	1.932	[82]
NdVO <sub>3</sub>	2.014	63522	ErCoO <sub>3</sub>	1.932	[82]
GdVO <sub>3</sub>	2.010	40391	TmCoO <sub>3</sub>	1.931	[82]

**Table 2.3.** (B-O) distance for  $RBO_3$  perovskites (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu; <math>B = Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ga).

(Continued)

Compound	⟨ <i>B</i> −0⟩ (Å)	Reference	Compound	⟨ <i>B</i> −0⟩ (Å)	Reference
DyVO <sub>3</sub>	2.008	40392	YbCoO <sub>3</sub>	1.931	[82]
ErVO <sub>3</sub>	2.015	40393	LuCoO <sub>3</sub>	1.930	[82]
YVO <sub>3</sub>	2.011	95579	LaNiO <sub>3</sub>	1.935	93919
YbVO <sub>3</sub>	2.008	97783	PrNiO <sub>3</sub>	1.942	67721
LaCrO <sub>3</sub>	1.972	[79]	NdNiO <sub>3</sub>	1.944	[45]
NdCrO <sub>3</sub>	1.977	38022	SmNiO <sub>3</sub>	1.954	90959
GdCrO <sub>3</sub>	1.974	38023	EuNiO <sub>3</sub>	1.955	88039
DyCrO <sub>3</sub>	1.991	16505	GdNiO <sub>3</sub>	1.956	88040
YCrO <sub>3</sub>	1.982	[36]	DyNiO <sub>3</sub>	1.960	88041
ErCrO <sub>3</sub>	1.977	28487	HoNiO <sub>3</sub>	1.938	24876
LaMnO <sub>3</sub> <sup>(1)</sup>	1.971	[80]	LaGaO <sub>3</sub>	1.975	51285
LaMnO <sub>3</sub> <sup>(2)</sup>	2.018	[38]	CeGaO <sub>3</sub>	1.977	[62]
PrMnO <sub>3</sub>	2.024	[38]	PrGaO <sub>3</sub>	1.983	73766
NdMnO <sub>3</sub>	2.024	[38]	NdGaO <sub>3</sub>	1.985	[68]
SmMnO <sub>3</sub>	2.030	95491	NdGaO <sub>3</sub>	1.984	[69]
EuMnO <sub>3</sub>	2.025	[81]	SmGaO <sub>3</sub>	1.989	[62]
GdMnO <sub>3</sub>	2.028	95493	EuGaO <sub>3</sub>	1.982	[62]
			GdGaO <sub>3</sub>	1.990	492

**Table 2.3.** (Continued)

Figure 2.4 shows the dependence of the proportionality coefficient  $\varkappa$  on the averaged  $\langle B-0 \rangle$  distance. Due to the limited range of the known values for  $\varkappa$  and  $\overline{\langle B-0 \rangle}$  different functions can relatively well approximate the dependence. We fitted the dependence using power, linear and exponential functions. The obtained parameters from the power fit ( $\varkappa = a \overline{\langle B-0 \rangle}^n$ ) are  $a = 271.1 \text{ cm}^{-1}/(\deg \text{Å}^n)$  and n = -3.5. For the linear fit ( $\varkappa = b \overline{\langle B-0 \rangle} + c$ ) the parameters are  $b = -42.3 \text{ cm}^{-1}/(\deg \text{Å})$  and  $c = 109.1 \text{ cm}^{-1}/\deg$ . For the exponential fit [ $\varkappa = d \exp(-\overline{\langle B-0 \rangle}/f)$ ] the parameters are  $d = 798.2 \text{ cm}^{-1}/\deg$  and f = 0.6 Å. The use of an exponential function is plausible, as it could be deduced from the exponential fall-off of the repulsive Born-Meyer potential, which describes fairly well the lattice dynamics of ionic compounds. Using this formulae we have calculated the frequencies of the quasi-soft modes for the investigated compounds and we have compared them with the experimentally observed ones (see Table 2.1). The averaged deviation for the best approximation (the power fit) is  $|\overline{\omega_{calc} - \omega_{expt}|}| = 15.5 \text{ cm}^{-1}$  (or  $|\overline{\omega_{calc} - \omega_{expt}|/\omega_{expt}} = 6.0\%$ ). It is comparable with the accuracy of the LDC for this type of compounds [see, e.g. Refs. [84–86]] and in most cases it is sufficient to identify the two quasi-soft modes out of the seven  $A_q$  lines in the Raman spec-

<sup>&</sup>lt;sup>(1)</sup>Rhombohedral  $R\bar{3}c$  structure.

<sup>&</sup>lt;sup>(2)</sup>Orthorhombic *Pnma* structure.



**Figure 2.4.** Dependence of the *frequency* – *tilt angle* proportionality coefficient  $\varkappa$  on the averaged  $\langle B$ –O $\rangle$  distance. The continuous, dashed and dotted lines represent the proposed power, linear and exponential dependencies with parameters shown in the figure.

tra of orthorhombic *Pnma* perovskites. Therefore, these formulae can be very useful for the initial assignment of the observed lines in Raman spectra of these compounds.

In some cases, however, the difference between the calculated and experimental frequency is quite large. We will comment in details here only the RMnO<sub>3</sub> family because there are most Raman data available for it. One finds that the largest differences of 39, 33, and 42 cm<sup>-1</sup> occur for the quasi-soft mode, corresponding to the  $\alpha_{[010]}$  tilt for R = Pr, Nd and Sm, respectively. The change of the  $\alpha_{[010]}$  tilt angle value, that increases from 9.20 deg (for R = La) to 14.23 deg (for R = Ho), should results in an increase of the frequency of the corresponding quasi-soft mode by about 50%. There is, however, another mode of the same symmetry ( $A_g$  bending vibration of O1<sup>[29]</sup>) in the same frequency region, which depends only weakly on the type of the rare-earth. The frequencies of these two modes are very close in the case of R = Pr, Nd and Sm, resulting in their strong mixing. Therefore, the calculated by our formula frequency in this case can be considered as "naked" (unmixed) one.

On the other hand, the obtained averaged  $\langle B-O \rangle$  distances (shown in Figure 2.3 and tabulated in Table 2.2) can be independently used for a quick check of a structural model proposed for other perovskites belonging to this group. Deviations of more than 0.02 Å from the overfamily-averaged values with great certainty could be a sign for incorrect structural model.

In summary, the systematic analysis of the available structural and Raman data leads to the conclusion that for each  $RBO_3$  family (with fixed *B*-atom) the frequency of the quasi-soft modes is proportional to the angle of the corresponding static tilt. The comparison of the averaged *B*–O distance for all members of a  $RBO_3$  family, shows that this distance practically does not vary over the family and it is a suitable structural parameter, that can be defined with better accuracy than the widely used ionic radius. The quasi-soft mode *frequency – tilt angle* 

proportionality coefficient dependence on the averaged  $\langle B-0 \rangle$  distance can be approximated with equal accuracy with different functions (power, linear and exponential). The found functions predict with satisfying accuracy the frequency of the soft (quasi-soft) mode(s) in the *RBO*<sub>3</sub> perovskites, which can be used for analysis of structural and Raman spectroscopy data.

## **3.** Raman spectroscopy and lattice dynamical calculations of Sc<sub>3</sub>CrO<sub>6</sub> single crystals

Single crystals of Sc<sub>3</sub>CrO<sub>6</sub> were grown by high temperature solution growth method. They were studied using x-ray single crystal diffractometry, scanning electron microscopy (SEM) with x-ray microprobe analysis and micro-Raman spectroscopy. The crystal structure was refined as rhombohedral one with space group  $R\bar{3}$ , which confirms that it belongs to the Mg<sub>3</sub>TeO<sub>6</sub> – structural type family. In the polarized Raman spectra collected at room temperature all  $9A_g + 9E_g$  Raman-allowed phonon modes were observed. The experimentally determined frequencies are compared to the results of lattice dynamical calculations using a shell model. The Raman spectra, obtained with increasing temperature up to 600 °C, do not provide direct indication for structural phase transition. The decrease with increasing temperature of the relative intensity of five  $A_g$  lines compared to the rest ones, however, suggests a possible structural phase transition from  $R\bar{3}$  to  $R\bar{3}c$  above the investigated temperature region.

The detailed study of the phase diagrams  $A_2O_3$ - $B_2O_3$  (A and B – rare-earths or transition metals) often leads to identification of new ternary oxides.<sup>[87]</sup> Although, the Sc<sub>2</sub>O<sub>3</sub>- $B_2O_3$  phase diagram is poorly investigated, it is known, that under high pressure ScAlO<sub>3</sub><sup>[88]</sup> and ScCrO<sub>3</sub><sup>[89]</sup> perovskites (with GdFeO<sub>3</sub>-type, *Pnma* structure) can be obtained in the Sc<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> systems, respectively. At ambient pressure the compound Sc<sub>3</sub>AlO<sub>6</sub>, which belongs to the Mg<sub>3</sub>TeO<sub>6</sub> structural type<sup>[90-92]</sup> could be synthesized.<sup>[93]</sup> Due to the difference in the structures of Sc<sub>2</sub>O<sub>3</sub> (bixbyite type) and Cr<sub>2</sub>O<sub>3</sub> (corundum type), it is reasonable to expect in the Sc<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> system existence of new ternary compound, Sc<sub>3</sub>CrO<sub>6</sub>,<sup>[87]</sup> instead of the solid solution Sc<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub>.

The mixed transition metal – rare-earth oxides are interesting, because changing the temperature and pressure complex structural<sup>[94]</sup> and magnetic<sup>[95,96]</sup> phase diagrams can be observed. On the other side they were extensively studied because of their broad technological significance. They can be used for low-temperature synthesis of ceramics, as phase stabilizers<sup>[97]</sup> and references therein as well as scintillator materials in nuclear engineering.<sup>[98]</sup>

Figure 3.1 (a) shows the  $Sc_3CrO_6$  single crystals visualized using scanning electron microscope (SEM; TESCAN LYRA) equipped with energy-dispersive x-ray spectrometer (EDX; BRUKER). The crystals look quasi-cubic with the largest crystal surfaces being of {100}, {110}, and {111} type. The Sc : Cr atomic ratio was determined by EDX analysis as 3.31 : 1 which corresponds to non-stoichiometric compound with chemical content  $Sc_6Cr_1Cr_{1-x}Sc_xO_{12}$ , x = 0.08 (assuming that only Cr2 position is partially occupied by Sc, as discussed further in the text).

The crystallographic characterization of as-grown  $Sc_3CrO_6$  was carried out by x-ray single crystal diffractometry. A single crystal was mounted on a glass capillary and diffraction data were collected at room temperature by  $\omega$ -scan technique, on an AGILENT DIFFRACTION SUPERNOVA DUAL four-circle diffractometer equipped with ATLAS CCD detector. A mirrormonochromatized Mo K $\alpha$  radiation from micro-focus source was used ( $\lambda = 0.7107$  Å). The



**Figure 3.1.** A photo of set of  $Sc_3CrO_6$  single crystals as grown (before cleaning) obtained by scanning electron microscopy – (a). The three types of crystal surfaces, the quasi-cubic {100}, {110}, and {111} ones, are clearly seen. Rhombohedral unit cell of  $Sc_3CrO_6$ : (b) the two different  $Cr1O_6$  and  $(Cr,Sc)2O_6$  octahedra and (c) the edge shared  $Sc1O_6$  octahedra are drawn.

determination of the cell parameters, data integration, scaling and absorption correction were carried out using the CRYSALISPRO program package.<sup>(1)</sup> The structure was solved by direct methods (SHELXS-97)<sup>[99]</sup> and refined by full-matrix least-square procedures on  $F^2$ . The results are listed in Table 3.1.<sup>(2)</sup>

<b>Table 3.1.</b> Structural data of $Sc_3CrO_6$ : atomic labels, Wyckoff notation, occupancy and
atomic positions are tabulated. The space group of the crystal is refined as $R\bar{3}$ (Nº 148),
$Z = 2, a = 6.1188 \text{ Å}, a = 91.97^{\circ}$ (rhombohedral cell).

Atom	Wyckoff notation	Occupancy	x	у	Ζ
Cr1	1 <i>a</i>	1.00	0	0	0
Cr2	1b	0.74	1/2	1/2	1/2
Sc2	1b	0.26	1/2	1/2	1/2
Sc1	6 <i>f</i>	1.00	0.24661	0.42868	0.93725
01	6 <i>f</i>	1.00	0.19058	0.42498	0.58550
02	6 <i>f</i>	1.00	0.30779	0.09363	0.96179
		Interator	nic distances		
Atomic pair	Bond length (Å)	Atomic pair	Bond length (Å)	Atomic pair	Bond length (Å)
Cr1 - 01	1.974	Sc - 01	2.055	Sc - 02	2.099
Cr2 – 02	2.023	Sc - 01	2.167	Sc - 02	2.106
(Sc - 0)	2.125	Sc - 01	2.185	Sc - 02	2.139

The Raman measurements were carried out using micro-Raman spectrometer LABRAM

<sup>&</sup>lt;sup>(1)</sup>CRYSALISPRO, Agilent Technologies UK Ltd., 2010

<sup>&</sup>lt;sup>(2)</sup>Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, CSD number 424191

HR800 VISIBLE. At room temperature an objective ×100 was used both to focus the incident laser beam and to collect the scattered light. To check the presence of resonance effects in the Raman spectra, He-Ne (633 nm) and Ar<sup>+</sup> (514 and 458 nm) lasers were used as excitation sources. For the high temperature measurements a heating stage LINKAM TH600 and a long working distance ×50 objective were used. To find out the origin of the Raman lines we performed shell-model lattice dynamical calculations. The parameters for the Born-Mayer potential – *Z*, *Y*, *k*, *A*,  $\rho$ , and *C* are listed in Table 3.2.

Atom	Z ( e )	Y ( e )	$k (eV/Å^2)$
Sc	2.97		
Cr	0.30	2.80	49.5
0	0.82	-2.82	96.2
Atomic pair	<i>A</i> (eV)	ρ (Å)	$C (eV \times Å^6)$
Sc – 0	1326.5	0.3211	0.000
Cr – 0	1763.0	0.2960	0.000
0 - 0	22764.3	0.1490	27.879

**Table 3.2.** Parameters of the potentials of the shell-shell and core-shell interactions used for LDC. The values for Cr and O are taken from Ref. [67].

The crystal structure of Sc<sub>3</sub>CrO<sub>6</sub>, as determined by x-ray single crystal diffractometry, has space group  $R\bar{3}$ , [Nº 148, Z = 2, see Figure 3.1 (b) and (c)]. Due to the smaller Cr1 – O1 distance compared to the Cr2 – O2 one, it is plausible to propose that as in the case of Sc<sub>3</sub>AlO<sub>6</sub><sup>[93]</sup> the 1*a* Wyckoff position (in the rhombohedral cell) is occupied by Cr1 atoms, whereas the 1*b* Wyckoff position is occupied randomly by Cr2 and Sc2. This is confirmed by the structure refinement where 74% of the 1*b* position is occupied by Cr2 and 26% by Sc2 atoms. The

**Table 3.3.** Wyckoff position and site symmetry of the atoms in the rhombohedral unit cell of Sc<sub>3</sub>CrO<sub>6</sub>. The irreducible representations of the  $\Gamma$ -point phonon modes are  $\Gamma_{\text{Total}} = 9A_g + 9E_g + 11A_u + 11E_u$ .

Atom	Wyckoff notation	Site symmetry	Irreducible representations
Cr1	1 <i>a</i>	S <sub>6</sub>	$A_u + E_u$
(Cr,Sc)2	1 <i>b</i>	S <sub>6</sub>	$A_u + E_u$
Sc1	6 <i>f</i>	$C_1$	$3A_g + 3A_u + 3E_g + 3E_u$
01	6 <i>f</i>	$C_1$	$3A_g + 3A_u + 3E_g + 3E_u$
02	6 <i>f</i>	C <sub>1</sub>	$3A_g + 3A_u + 3E_g + 3E_u$

atoms at these positions do no take part in Raman-active vibrations. The rest Sc1 atoms and the O1 and O2 oxygen atoms occupy general 6*f* Wyckoff positions, so the total number of the Raman-active modes is  $9A_g + 9E_g$ <sup>[39,40,100]</sup> (see Table 3.3). The Raman tensors of these modes in an orthogonal basis with two axes coinciding with two of the axes of the hexagonal

basis of  $R\bar{3}$  are

$$A_{g} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},$$
$$E_{g}^{(1)} = \begin{bmatrix} c & d & e \\ d & -c & f \\ e & f & 0 \end{bmatrix} \text{ and } E_{g}^{(2)} = \begin{bmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & 0 \end{bmatrix}.$$

At first glance it looks easy to distinguish the lines in the Raman spectra with either  $A_g$  or  $E_g$  symmetry. However, all polarized Raman spectra (in parallel or crossed polarization), collected from the  $\{100\}_{cub}$  crystal surfaces (which are easiest to recognize) contain eighteen lines with rather arbitrary intensity, depending on the orientation of the polarization of the incident laser beam (parallel or at 45 deg) according to the edge of the surface. The separation of the lines by symmetry into two groups can be done from the polarized Raman spectra, collected in some special geometrical configurations.

If x, y and z is a orthogonal basis, where z is parallel to the  $z_{hex}$  axis and x and y are two arbitrary directions in  $(001)_{hex}$  plane, then in zz spectrum only lines with  $A_g$  symmetry can be seen, whereas in zx spectrum only  $E_g$  lines are allowed. These spectra can be obtained from any  $(mn0)_{hex}$  plane. In the Raman spectra, collected from a  $(001)_{hex}$  plane, the  $E_g$  lines must be seen with equal intensity in xx and xy polarizations. In contrast, the  $A_g$  lines can be seen only in xx polarization (see Table 3.4). It is not easy to identify these types of planes



**Figure 3.2.** (a) Quasi-cubic crystal with eight  $\{111\}_{cub}$  surfaces. Only two of them (in grey) coincide with the  $\{001\}_{hex}$  ones. (b) Quasi-cubic crystal with twelve  $\{110\}_{cub}$  surfaces. Only six of them (in grey) contain the  $[001]_{hex}$  direction. (c) A sketch of the real rhombohedral Sc<sub>3</sub>CrO<sub>6</sub> crystal with three  $\{110\}_{cub}$  surfaces. The calculated angles between the edges of a  $\{110\}_{cub}$  surface, containing the  $[001]_{hex}$  direction, are shown.

among the crystal surfaces of the quasi-cubic single crystals. From Figure 3.2 it can be seen that among the eight  $\{111\}_{cub}$  crystal surfaces only two are  $(001)_{hex}$  ones, whereas six out of the 12  $\{110\}_{cub}$  crystal surfaces have an edge, parallel to the  $[001]_{hex}$  direction. Moreover, the  $\{110\}_{cub}$  crystal surface edge, parallel to the  $[001]_{hex}$  direction, can be recognized by the specific angles between it and adjacent surface edges [see Figure 3.2 (c)]. Rolling the single crystals, we have succeed to find the surfaces with the appropriate orientations. The Raman spectra, collected from these two types of surfaces are shown in Figure 3.3. In *zz* spectrum eight out of the nine allowed  $A_g$  lines are seen at 222, 259, 331, 405, 445, 458, 668, and

Mode	$xx \equiv yy$	$xy \equiv yx$	ZZ	$xz \equiv zx$
$\overline{A_g}$	$a^2$	0	$b^2$	0
$E_g$	$c^{2} + d^{2}$	$c^{2} + d^{2}$	0	$e^2 + f^2$

**Table 3.4.** Selection rules for Raman-active modes in  $R\bar{3}$  structure, where x and y are two arbitrary directions in  $(001)_{hex}$  plane and z is parallel to the  $z_{hex}$  axis

698 cm<sup>-1</sup>. Their intensity in this spectrum is proportional to the square of the *b* component of the Raman tensor. The ninth  $A_g$  line can be seen only in xx and AA spectra at 343 cm<sup>-1</sup>. In these spectra the intensity of the  $A_g$  lines is proportional to the square of the *a* component of the Raman tensor. In zx spectrum only  $E_g$  lines are allowed and they are positioned at 243, 277, 319, 372, 393, 426, 519, 573, and 638 cm<sup>-1</sup>.

The  $E_g$  intensity in the *zx* spectrum is proportional to  $e^2 + f^2$  (*e* and *f* are components of the  $E_g$  Raman tensor). In the *AA* and *BA* [*A* and *B* are two arbitrary perpendicular directions in the (001)<sub>hex</sub> plane] spectra the  $E_g$  lines must be of equal intensity, proportional to  $c^2 + d^2$  (*c* and *d* are components of the  $E_g$  Raman tensor). As it is seen from the *AA* and *BA* spectra, nine

**Table 3.5.** List of the frequencies of the  $9A_g + 9E_g$  modes, experimentally observed ( $\omega_{expt}$ ) in the Raman spectra and calculated by LDC ( $\omega_{calc}$ ).

Mode	$\omega_{\mathrm{expt}}~(\mathrm{cm}^{-1})$	$\omega_{\rm calc}~({\rm cm}^{-1})$	Mode	$\omega_{\mathrm{expt}}~(\mathrm{cm}^{-1})$	$\omega_{\rm calc}~({\rm cm}^{-1})$
$A_g(1)$	222	222	$E_{g}(1)$	243	225
$A_{g}(2)$	259	248	$E_{g}(2)$	277	274
$A_g(3)$	331	316	$E_{g}(3)$	319	296
$A_g(4)$	343	328	$E_{g}(4)$	372	335
$A_g(5)$	405	430	$E_{g}(5)$	393	407
$A_g(6)$	445	466	$E_{g}(6)$	426	423
$A_g(7)$	458	520	$E_{g}(7)$	519	518
$A_g(8)$	668	669	$E_{g}(8)$	573	578
$A_{g}(9)$	698	697	$E_{g}(9)$	638	646

lines obey this rule at the same positions as the lines observed in *zx* spectrum. The results are summarized in Table 3.5. Additionally from the spectra, shown in Figure 3.3, except the symmetry of the eighteen Raman-allowed lines, also the ratio of the values of the non-zero components of the Raman tensors of the allowed lines can be evaluated.

In Figure 3.4 are shown the  $y(xx)\bar{y}$  polarized Raman spectra obtained with three different laser lines. It is seen that the relative intensity of all lines observed practically does not depend on the energy of the exciting photons. It means that there are no resonance effects influencing on the intensity of the lines. Therefore, if an intensity change is observed (e.g. with the temperature, see below), it is most likely connected to some special features of the crystal structure.

Figure 3.5 shows non-polarized Raman spectra obtained from  $(mn0)_{hex}$  surface with 514 nm laser excitation in the temperature range 20 – 600 °C. The changes of the parameters of the Raman lines are monotonous, a sign for a lack of structural phase transition in



**Figure 3.3.** Polarized Raman spectra of  $Sc_3CrO_6$ , collected from  $(mn0)_{hex}$  and  $(001)_{hex}$  planes with  $\lambda_L = 458$  nm excitation at room temperature. The lines, indicated with wavenumber (in cm<sup>-1</sup> colored in blue for the  $A_g$  and black for the  $E_g$  ones), are allowed for the corresponding geometrical configuration. The lines, marked with filled circles, are forbidden for the given configuration.

this temperature region. However, the careful comparison of the spectra shows that the intensity of five  $A_g$  lines (marked with empty circles in Figure 3.5) decreases with increasing temperature. We fitted the intensities of all lines in the spectra at different temperatures. Plot of the normalized ratio of the intensity of each of these five  $A_g$  lines and the intensity of the nearest to it non-vanishing line, versus the temperature T is shown in Figure 3.6. It is seen that this ratio decreases with the temperature monotonically. Extrapolating this behavior to higher temperatures, it appears that at  $T \approx 1000$  °C these five lines must disappear in the Raman spectra. To explain such behavior we look for arguments in specific features of the crystal structure. Generally speaking, the symmetry of the real rhombohedral structure ( $\alpha = 91.97^\circ$ ) can be increased in two ways: (a) if the Cr10<sub>6</sub> and (Cr,Sc)20<sub>6</sub> octahedra become identical or (b) the structure becomes cubic. The rhombohedral structure with identical octahedra has  $R\bar{3}c$  symmetry, the cubic structure with different octahedra has  $Pm\bar{3}$  symmetry, and the cubic structure with identical octahedra has  $Pm\bar{3}n$  symmetry.



**Figure 3.4.**  $y(xx)\bar{y}$  polarized Raman spectra of Sc<sub>3</sub>CrO<sub>6</sub>, obtained with three different laser lines 458, 514, and 633 nm.

The analysis of vibrational modes in the real structure could be done in different ways. Due to the fact that the structure contains different types of octahedra ( $CrO_6$  and  $ScO_6$ ) with different length of the Cr - 0 and Sc - 0 bonds, a molecular approach for description of the structure and analysis of the vibrational modes can be applied. This approach was used to assign the modes observed in the isostructural Mg<sub>3</sub>TeO<sub>6</sub><sup>[101]</sup>. In Ref. [101], however, it has been plausible to use it because of the large charge difference of the Mg<sup>2+</sup> and Te<sup>6+</sup> ions. In that case the crystal structure can be regarded as containing isolated TeO<sub>6</sub> octahedra and Mg ions between them. If so, the type of vibrations for the high frequency modes can be determined as their shape will be typical one for an isolated TeO<sub>6</sub> octahedron [*XY*<sub>6</sub> molecule, see Ref. [102]].

The results using the molecular approach for  $Sc_3CrO_6$  are given in Table 3.6. A single  $XY_6$  molecule has six internal modes ( $v_i$ , i = 1..6, see Figure 3.7), one triply degenerated rotational mode [ $F_{1g}$  (rot)] and one triply degenerated translational mode [ $F_{1u}$  (tr)]. Constructing a cubic  $Pm\bar{3}n$  crystal structure with two identical  $XY_6$  molecules in the primitive cell, the number of  $\Gamma$ -point modes for this structure are two times larger than the number of the octa-



**Figure 3.5.** Non-polarized Raman spectra obtained from  $(mn0)_{hex}$  surface in the temperature range 20 – 600 °C. The  $E_g$  lines are marked with triangles and the  $A_g$  lines are marked with circles. Upon the increase of the temperature, the five  $A_g$  lines, which intensity decreases in comparison to the intensity of the other lines, are marked with empty circles.

hedral modes due to the presence of Davydov's pairs [pair of modes that are identical for each octahedron but differ by the phase of vibration for the two octahedra, see Refs. [103,104]]. Lowering the symmetry of this hypothetical cubic crystal to rhombohedral  $R\bar{3}c$  one, the triply

**Table 3.6.** Correlation between vibrational modes of a  $XY_6$  molecule (CrO<sub>6</sub> octahedron) and modes in hypothetical  $Pm\bar{3}n$ ,  $R\bar{3}c$  and the real  $R\bar{3}$  crystal structure of Sc<sub>3</sub>CrO<sub>6</sub>.

$O_{h}^{(1)}$	$T_{h}^{(2)}$	$O_h^3 (Pm\bar{3}n)^{(3)}$	$D_{3d}^{6} (R\bar{3}c)^{(3)}$	$C_{3i}^2 \equiv S_6^2 (R\bar{3})^{(3)}$
Irreducibi	le represer	ntations for the CrO	, octahedra	
$A_{1a}(v_1)$	$A_{a}$	$A_{1a} + A_{2a}$	$A_{1a} + A_{2a}$	$2A_{a}$
$E_g(v_2)$	$E_g$	$2E_g$	$2E_g$	$2E_g$
-	-	-	-	(Continued)

$O_{h}^{(1)}$	$T_{h}^{(2)}$	$O_h^3  (Pm\bar{3}n)^{(3)}$	$D_{3d}^{6} (R\bar{3}c)^{(3)}$	$C_{3i}^2 \equiv S_6^2  (R\bar{3})^{(3)}$	
$F_{2g}(v_5)$	$F_{g}$	$F_{1g} + F_{2g}$	$A_{2g} + E_g + A_{1g} + E_g$	$2A_g + 2E_g$	
$F_{1u}\left(\nu_{3} ight)$	$F_u$	$F_{1u} + F_{2u}$	$A_{2u} + E_u + A_{1u} + E_u$	$2A_u + 2E_u$	
$F_{1u}\left(\nu_{4} ight)$	$F_u$	$F_{1u} + F_{2u}$	$A_{2u} + E_u + A_{1u} + E_u$	$2A_u + 2E_u$	
$F_{2u}\left(\nu_{6} ight)$	$F_u$	$F_{1u} + F_{2u}$	$A_{2u} + E_u + A_{1u} + E_u$	$2A_u + 2E_u$	
$F_{1g}$ (rot)	$F_{g}$	$F_{1g} + F_{2g}$	$A_{2g} + E_g + A_{1g} + E_g$	$2A_g + 2E_g$	
$F_{1u}$ (tr)	$F_u$	$F_{1u} + F_{2u}$	$A_{2u} + E_u + A_{1u} + E_u$	$2A_u + 2E_u$	
Irreducible	represente	ations for the Sc ato	ms		
		$A_{2g}$	$A_{2g}$	$A_g$	
		$E_g$	$E_g$	$E_g$	
		$F_{1g}$	$A_{2g} + E_g$	$A_g + E_g$	
		2 <i>F</i> <sub>1<i>u</i></sub>	$2A_{2u} + 2E_u$	$2A_u + 2E_u$	
		$F_{2g}$	$A_{1g} + E_g$	$A_g + E_g$	
		<i>F</i> <sub>2<i>u</i></sub>	$A_{1u} + E_u$	$A_u + E_u$	
$O_h^3 (Pm\bar{3}n)$ $\Gamma_{\text{Total}} = A_{1g} + 2A_{2g} + 3E_g + 3F_{1g} + 3F_{2g} + 6F_{1u} + 5F_{2u}$					
$D_{3d}^6 (R\bar{3}c)$ $\Gamma_7$		$\Gamma_{\text{Total}} = 4A_{1g} + 5A_{2g} + 9E_g + 5A_{1u} + 6A_{2u}$			
$C_{3i}^2 \equiv S_6^2 \ (H$	₹ <b>3</b> )	$\Gamma_{\text{Total}} = 9A_g + 9E$	$g + 11A_u + 11E_u$		

Table 3.6. (Continued)

degenerated modes split into pairs of one non-degenerated and one double-degenerated mode. This approach predicts that some of the vibrational modes in the real  $Sc_3CrO_6$  structure should be grouped into sets of two or four modes with close frequency (see the last column of Table 3.6). To obtain all vibrational modes in the real  $Sc_3CrO_6$ , the modes originating from Sc atoms, have to be accounted for, too.

In  $Sc_3CrO_6$ , due to the same charge of  $Sc^{3+}$  and  $Cr^{3+}$  ions and relatively close averaged bond length for the two types of  $CrO_6$  and  $ScO_6$  octahedra, we expect that such molecular approach will correctly describe only the modes with highest frequency (internal stretching modes for the  $CrO_6$  octahedra). In Figure 3.8 the calculated by LDC frequencies of all fiftyseven optical  $\Gamma$ -point modes are displayed. It is seen that a group of eight modes are placed in the high frequency region (above 550 cm<sup>-1</sup>). Accounting for their symmetry and their shape (predicted by LDC) we succeed to determine their origin. From the inset of Figure 3.8 it can be concluded that the splitting due to rhombohedrality is smaller than Davydov's splitting. This is expected, because the Davydov's pair of modes actually has different vibrational shape (with very different frequency) for the  $ScO_6$  octahedra.

If we go back to Figure 3.5 we can note that with the increase of the temperature, the crys-

<sup>&</sup>lt;sup>(1)</sup>symmetry of the free  $XY_6$  molecule

<sup>&</sup>lt;sup>(2)</sup>site symmetry of the XY<sub>6</sub> unit in  $O_h^3$  (Pm $\bar{3}n$ )

<sup>&</sup>lt;sup>(3)</sup>crystal symmetry



**Figure 3.6.** The temperature dependence of the normalized relative intensity of the five  $A_a$  lines vanishing at high temperatures.



Figure 3.7. Normal modes of vibration of a free *XY*<sub>6</sub> molecule.

tal stay essentially rhombohedral, because no merge of lines into pairs is observed. However, the decrease of the intensity of five  $A_g$  lines can be expected at hypothetical structural phase transition from  $R\bar{3}$  to  $R\bar{3}c$ , where five  $A_g$  modes in  $R\bar{3}$  become silent  $A_{2g}$  modes in  $R\bar{3}c$  (see Table 3.6). The LDC predicts that the two high frequency  $A_g$  modes experimentally observed at 668 and 698 cm<sup>-1</sup> originate from  $v_1$  Davydov's pair. The mode with higher frequency is the in-phase vibration of the two octahedra, whereas the mode with lower frequency corresponds to the mode with out-of-phase vibration. The molecular approach predicts that the out-of-phase  $A_g$  ( $v_1$ ) vibration has to be transformed into silent  $A_{2g}$  mode in  $R\bar{3}c$ . Indeed, just the  $A_g$  line at 668 cm<sup>-1</sup> is one of the five lines with decreasing intensity.

In summary, single crystals of Sc<sub>3</sub>CrO<sub>6</sub> were grown and studied using x-ray single crys-



**Figure 3.8.** The predicted LDC frequencies of all 57 optical modes in  $Sc_3CrO_6$ .  $A_g$ ,  $E_g$ ,  $A_u$  and  $E_u$  modes are displayed with blue, black, green and red ticks. The splitting of the three stretching  $XY_6$  molecular modes, forming the modes with highest frequency in the  $Sc_3CrO_6$ , is shown.

tal diffractometry, scanning electron microscopy with x-ray microprobe analysis and micro-Raman spectroscopy. The chemical content is non-stoichiometric resulting in two different  $Cr10_6$  and  $(Cr,Sc)20_6$  octahedra, in agreement with the refined  $R\bar{3}$  crystal structure. From appropriately chosen crystal surfaces, polarized Raman spectra in different geometrical configurations were collected at room temperature and the symmetry of all  $9A_g + 9E_g$  Ramanallowed modes was determined. This assignment was confirmed by the results of the performed LDC. A molecular approach for interpretation of the calculated modes was used. It predicts grouping of modes into sets with close frequencies because of two reasons: (a) the presence of two  $Cr0_6$  octahedra in the unit cell, and (b) the rhombohedral structure is very close to a cubic one. Indeed, the origin of the eight high frequency modes (corresponding to the internal stretching  $Cr0_6$  octahedral vibrations), as it was obtained by LDC, justifies this approach. The changes of the Raman spectra, collected at high temperatures, does not support the rhombohedral-cubic phase transition scenario, but rather suggests a possible transition from  $R\bar{3}$  to  $R\bar{3}c$  above the investigated temperature region.

## **4.** Raman spectroscopy and lattice dynamical calculations of rare-earth sesquioxides

The rare-earth sesquioxides  $R_2O_3$  (R – lanthanide, Y and Sc ) have been studied for decades, at the beginning mainly because these oxides form polymorphs. The polymorphs are formed depending upon the cationic radius and also by the influence of external parameters such as temperature and pressure. However, in addition to polymorphism these oxides are promising materials for many technological applications. They are suitable to be used as electroluminescence<sup>[105]</sup> and cathodoluminescence<sup>[106]</sup> sources, oxygen ion conducting electrolyte in solid oxide fuel cells,<sup>[107]</sup> active catalysts for a large number of organic reactions,<sup>[108–110]</sup> high-kgate dielectrics,<sup>[111]</sup> optical parts of high power lasers,<sup>[112]</sup> and materials with strongly hydrophobic surface.<sup>[113]</sup>

#### 4.1. Polymorphism of rare-earth sesquioxides

Depending on the type of the rare-earth, five different crystal structures are known.<sup>[114]</sup> Two of them, the so-called X- and H-phase, are stable only above 2000 K.<sup>[115]</sup> The other three, A-, B-, and C-phase, can be observed at ambient conditions. For the lighter lanthanides, La, Ce, Pr and Nd, the most usual structure is the hexagonal A-type with space group  $P\bar{3}m1$  and one formula unit per cell [see Figure 4.1 (a)]. For R = Sm, Eu and Gd the oxides may exist in both



**Figure 4.1.** (a) The crystal structure of A-type rare-earth sesquioxide, which consists of only seven-fold coordinated cations. (b) In the B-type rare-earth sesquioxide the cations are six- or seven-fold coordinated.

monoclinic B-type or the cubic C-type with space groups C2/m [six formula units per cell, see Figure 4.1 (b)] and  $Ia\bar{3}$  [16 formula units pre cell, see Figure 4.2 (c)], respectively. The rest oxides with R = Tb, Dy, Ho, Er, Tm, Yb, and Lu, exist in C-type structure.

The phase stability of the rare-earth oxides is reviewed in many experimental and theoretical works.<sup>[115–118]</sup> It could be noticed that, due to the fact that the molar volume decrease in the sequence  $C \rightarrow B \rightarrow A$  at room temperature and pressure, it is normal that with applying pressure the B-type structure is favoured over the C-type, and the A-type over the both B and C. The dependencies of the transition pressures on the temperature, as well as, the polymorphic transformations in rare-earth sesquioxides on the temperatures (at ambient pressure) are summarized in Ref. [115].

### 4.2. Single crystals of Sc<sub>2</sub>O<sub>3</sub>

Sharing similar properties,  $Sc_2O_3$  is considered as a C-type rare-earth sesquioxide and can be used as an excellent host material for high power lasers applications.<sup>[107,119-121]</sup> Single crystals of  $Sc_2O_3$  were grown by a high-temperature solution-growth method. They were studied by x-ray single-crystal diffractometry and micro-Raman spectroscopy. In the polarized Raman spectra collected at room temperature all  $4A_g + 4E_g$  and 11 out of  $14F_g$  Raman allowed lines were observed. The vibrational assignment was made by a comparison of the experimentally observed frequencies with calculated ones determined by density functional theory lattice dynamical calculations.

We have made crystallographic characterization of the crystal, which was carried out by xray single-crystal diffractometry as described in Chapter 3. The results are listed in Table 4.1. They are in excellent agreement with the previously published data.<sup>[122]</sup>

Atom	Valence	Wyckoff notation	x	у	Ζ
Sc1	+3	8 <i>b</i>	1/4	1/4	1/4
Sc2	+3	24 <i>d</i>	0.46456	0	1/4
0	-2	48 <i>e</i>	0.39127	0.15470	0.38155

**Table 4.1.** Structural data of  $Sc_2O_3$ . Space group No 206 ( $Ia\bar{3}$ ), Z = 16, a = 9.8300 Å.

The Raman measurements were carried out at room temperature, an objective  $\times 50$  was used both to focus the incident laser beam and to collect the scattered light. To check the presence of resonance effects in the Raman spectra, He-Ne (633 nm) and Ar<sup>+</sup> (515, 488 and 458 nm) lasers were used as excitation sources.

First principles calculations were performed with the CASTEP<sup>[26]</sup> code, using density functional perturbational theory (DFPT) within the local density approximation. Norm-conserving pseudopotentials were generated by the Optimized approach<sup>[123]</sup> with the following atomic valence configurations: O  $(2s^22p^4)$  and Sc  $(3s^23p^63d^14s^2)$ . Brillouin zone summations were carried out with a  $2 \times 2 \times 2$  Monkhorst-Pack *k*-point mesh. The calculated LDA lattice parameters are slightly underestimated, but the agreement with the experimental data is better than 0.3 %.

The C-type crystal structure of  $Sc_2O_3$  can be described as an oxygen-deficient superstructure of the simpler  $CeO_2$  (CaF<sub>2</sub>-type crystal structure) if each fourth oxygen atom from the oxygen chains parallel to all (100) crystal directions is removed <sup>[124,125]</sup> (see Figure 4.2). This reduces the oxygen environment of the Sc atoms from eight (in the CaF<sub>2</sub>-type structure) to six atoms by distributing them onto two different Wyckoff positions (8*b* and 24*d*, see Table 4.1). The Sc atoms at 8*b* positions also have six fold oxygen environment, but this time as a result of the removal of two oxygen atoms, lying on [111] cubic body diagonal. The Sc atoms



**Figure 4.2.** (a) the crystal structure of CeO<sub>2</sub> (CaF<sub>2</sub>-type) –  $2 \times 2 \times 2$  super cell. The eightfold cubic oxygen environment of the two adjacent Ce atoms is given. (b) hypothetical oxygen-deficient superstructure of CeO<sub>2-x</sub> (x = 0.5), the vacancies are represented by the green ellipsoids. (c) the real structure of C-type Sc<sub>2</sub>O<sub>3</sub>.



**Figure 4.3.** Sc atoms occupy two different sets of atomic positions 8*b* and 24*d* corresponding to  $C_{3i}$  and  $C_2$  site symmetry, and the oxygen atoms are on general position 48*e* with  $C_1$  site symmetry.



**Figure 4.4.** The studied  $Sc_2O_3$  single crystal. (x, y) and (x', y') are two pairs of perpendicular directions, parallel to {100} and {110} crystal directions, respectively.

at 24*d* positions have six fold oxygen environment because of the removal of two oxygen atoms, lying on [110] cubic face diagonal (see Figure 4.3). The resulting body-centered  $Ia\bar{3}$  cubic unit cell (with a volume eight times larger than that of the unit cell of the parent CeO<sub>2</sub>) contains 16 formula units. The irreducible representations of the  $\Gamma$ -point phonon modes are  $\Gamma_{\text{Total}} = 4A_g + 5A_u + 4E_g + 5E_u + 14F_g + 17F_u$  (see Table 4.2). The Raman-active modes are

 $\Gamma_{\text{Raman}} = 4A_g + 4E_g + 14F_g$  with the following Raman tensors<sup>[100]</sup>

$$A_{g} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix},$$

$$E_{g}^{(1)} = \begin{bmatrix} b + \sqrt{3}c & 0 & 0 \\ 0 & b - \sqrt{3}c & 0 \\ 0 & 0 & -2b \end{bmatrix}, \quad E_{g}^{(2)} = \begin{bmatrix} c - \sqrt{3}b & 0 & 0 \\ 0 & c + \sqrt{3}b & 0 \\ 0 & 0 & -2c \end{bmatrix},$$

$$F_{g}^{(1)} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{bmatrix}, \quad F_{g}^{(2)} = \begin{bmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{bmatrix}, \quad \text{and} \quad F_{g}^{(3)} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

The symmetry of the lines in the Raman spectra can be easily determined comparing the intensity of the lines in four types of spectra, obtained in different scattering configurations, see Table 4.3. (x, y) and (x', y') are two pairs of perpendicular directions, parallel to {100} and {110} crystal directions, shown in Figure 4.4, where the studied single crystal can be seen, too. Its longest edges are parallel to {100} crystal directions. The polarized Raman spectra,

**Table 4.2.** Wyckoff position of the atoms in the unit cell of  $Sc_2O_3$ . The irreducible representations of the  $\Gamma$ -point phonon modes are  $\Gamma_{Total} = 4A_g + 5A_u + 4E_g + 5E_u + 14F_g + 17F_u$  [Ref. [39,40,100]]

Atom	Wyckoff notation	Irreducible representations
Sc1	8 <i>b</i>	$A_u + E_u + 3F_u$
Sc2	24 <i>d</i>	$A_g + A_u + E_g + E_u + 5F_g + 5F_u$
0	48 <i>e</i>	$3A_g + 3A_u + 3E_g + 3E_u + 9F_g + 9F_u$

collected in the appropriate scattering configurations, mentioned above, are shown in Figure 4.5. The comparison of the spectra, obtained with different excitation wavelength, shows that the relative intensity of the lines in spectra in a given scattering configuration remains nearly the same. This proves their Raman origin and shows that the resonance effects are negligible. The lines, originated by a leakage of the scattered light analyzer (of about 5%) and forbidden for the given geometrical configuration, are marked with filled circles. In the spectra obtained with 633 nm He-Ne line (not shown here), a relatively strong background, rapidly increasing at higher frequencies, was observed. Its origin can be related to the presence of Cr atoms with concentration about  $10^{-4}$  in the Sc<sub>2</sub>O<sub>3</sub> crystal which were added to check the properties of the material for laser applications.

From Figure 4.5 and Table 4.3 the symmetry of the following intense lines can be immediately determined: 221 and 495 cm<sup>-1</sup>–  $A_g$ ; 273, and 430 cm<sup>-1</sup>–  $E_g$ ; 189, 319, 419, and 523 cm<sup>-1</sup>–  $F_g$ . The weak lines at 202, 252, 329, 587, and 669 cm<sup>-1</sup> also have  $F_g$  symmetry. After careful decomposition of the profile of the lines near 359, 391 and 623 – 626 cm<sup>-1</sup> in the different types of spectra, it was found that the line near 359 cm<sup>-1</sup> consists of two lines with  $E_g$  and  $F_g$  symmetry, the line near 391 cm<sup>-1</sup> consists of two lines with  $A_g$  and  $F_g$  symmetry, and the line near 623 – 626 cm<sup>-1</sup> consists of two lines with  $A_g$  (623 cm<sup>-1</sup>) and  $E_g$ 



**Figure 4.5.** Polarized Raman spectra of  $Sc_2O_3$ , collected from (100) surface with  $\lambda_L = 515,488$  and 458 nm excitation at room temperature. The lines, indicated with a wavenumber (in cm<sup>-1</sup>), are allowed for the corresponding geometrical configuration. The lines, marked with filled circles, are forbidden for the given configuration. The geometrical configuration of the spectra as well the symmetry of the lines, allowed for it, are also given.

(626 cm<sup>-1</sup>) symmetry. The frequencies and the symmetry of all lines observed are tabulated in Table 4.4. It can be seen that experimentally observed and calculated frequencies of all  $A_a$ 

**Table 4.3.** Selection rules for Raman-active modes for a crystal structure with  $Ia\bar{3}$  space group in specific scattering configurations. *a*, *b*, *c*, and *d* are non-zero components of the Raman tensors, and  $e^2 \equiv b^2 + c^2$ .

Mode	xx	ух	<i>x'x'</i>	<i>y'x'</i>
$A_{g}$	$a^2$	0	<i>a</i> <sup>2</sup>	0
$E_{g}$	$4e^{2}$	0	$e^2$	3e <sup>2</sup>
$F_{g}$	0	$d^2$	$d^2$	0

and  $E_g$  modes are very close. Moreover, comparing the relative intensity of the experimentally observed lines with the calculated Raman spectrum for  $z(yx)\overline{z}$  (where only modes with  $F_g$  symmetry are allowed), one finds that the relative intensity of the corresponding lines in the two spectra are very close (for better comparison the calculated lines are presented as Lorentzians with linewidth, fixed at  $\Gamma = 3.5 \text{ cm}^{-1}$ , see Figure 4.6). Therefore, we can assign

**Table 4.4.** Comparison between the previously published, experimentally observed  $(\omega_{expt})$  and calculated by CASTEP  $(\omega_{calc})$  frequencies (in cm<sup>-1</sup>) of Raman-active modes of Sc<sub>2</sub>O<sub>3</sub>.

Symmetry	Ref. [126]	Ref. [127]	$\omega_{ m expt}$	$\omega_{ m calc}$	$\Delta \omega$
$A_g$	222	222	221	215	6
	392	391	391	395	-4
	495	495	495	478	17
			623	618	5
$\overline{E_g}$	274	273	273	269	4
	358	358	359	361	-2
		428	430	434	-4
	628		626	620	6
$\overline{F_g}$	190	190	189	180	9
-			202	194	8
			252	249	3
	320	320	319	317	2
			329	325	4
		358	359	361	-2
				366	
	392	391	391	386	5
	419	419	419	426	-7
				444	
				489	
	525	524	523	512	11
			587	584	3
	674		669	663	6

the 11 observed  $F_g$  lines to the  $F_g$  modes with closest calculated frequencies. Based on the LDC it appears that the frequencies of the remaining three  $F_g$  modes should be close to 365, 444 and 489 cm<sup>-1</sup>. From LDC we can also conclude that all modes with frequency below 300 cm<sup>-1</sup> are predominantly vibrations of Sc atoms, whereas those with higher frequency are almost pure oxygen vibrations. This fact can be used for future identification of the corresponding modes in the isostructural C-type phase  $R_2O_3$  compounds.

We have to point out that up to now only non-polarized Raman spectra, obtained from  $Sc_2O_3$  ceramic or powder samples were published.<sup>[126–129]</sup> However, although the frequencies of the lines measured in this work are close to those in Refs. [126–128], there is a systematic frequency difference by 13 cm<sup>-1</sup> with those of Ref. [129]. For this reason in Table 4.4

we give for comparison only the frequencies from the first two papers. It also worth mentioning here that due to the very low signal-to-noise ratio of our Raman spectra we were able to identify lines (e.g. at 202 and 329 cm<sup>-1</sup>) of intensity about three orders weaker than the intensity of the most intense line (at 419 cm<sup>-1</sup>). Therefore, the origin of some additional lines, reported in Ref. [126] or Ref. [129] but not observed in our spectra, is questionable.



**Figure 4.6.** A comparison of the calculated and experimentally measured ( $\lambda_L = 488 \text{ nm}$ )  $z(yx)\bar{z}$  Raman spectrum (where only modes with  $F_q$  symmetry are allowed).

It is worth noting to comment the fact that only one line  $(F_{2g} \text{ at } 419 \text{ cm}^{-1})$  has very large intensity compared to the rest ones. In the parent compound (CeO<sub>2</sub>) due to the smaller unit cell and higher symmetry there is only one Raman-active mode  $F_{2g}$  [464 cm<sup>-1</sup> Refs. [ 130,131]]. The pattern of this mode can be determined only by symmetry considerations – it is triply degenerated out-of-phase anti-stretching oxygen vibration along the {100} crystal directions. Our LDC predict that the shape of  $F_g$  mode at 419 cm<sup>-1</sup> in Sc<sub>2</sub>O<sub>3</sub> is very close to the  $F_{2g}$  one in CeO<sub>2</sub>. So, these two modes can be considered as corresponding ones in these two structures.

In summary, we report a complete analysis of Raman data of  $Sc_2O_3$  single crystals, supported by *ab initio* lattice dynamical calculations. The obtained results can be used as a reference data in studies of other C-type sesquioxides.

#### 4.3. Powders of C-type $R_2O_3$ : a comparative study

Raman spectra of  $R_2O_3$  (R – Sc, Er, Y, Ho, Gd, Eu, and Sm) powders with C-type bixbyite crystal structure are measured. With the help of these data and ones, previously published for other oxides from the same structural family, general dependencies of the frequencies of the Raman lines on the cubic crystal lattice parameter are constructed. Using these dependencies and knowing the symmetry of the lines for one of the oxides – Sc<sub>2</sub>O<sub>3</sub>, shown in Section 4.2, it is possible to determine the symmetry of the lines from the spectra of all compounds. It was

found that the frequency of the six lowest frequency lines scales with the square root of the mass of the rare-earth showing that mainly *R* ions take part in these vibrations. These results agree with performed here lattice dynamical calculations. The anomalous softening of the frequency of some lines in the spectra of  $Eu_2O_3$  is discussed.

Raman spectroscopy, normally combined with other experimental techniques, can be a useful tool for monitoring the phase content at the stages of synthesis of these compounds and the orientation of single crystals and epitaxially grown thin films, for detection of structural phase transitions changing the temperature or the pressure, or for evaluating the chemical content in the case of solid solutions. For all these purposes it is necessary to study some general dependencies of the Raman spectra (the frequency, the relative intensity, and the symmetry of the lines) on the type of the rare-earth.

We have thoroughly browsed the existing literature for Raman studies of C-type  $R_2O_3$  oxides. The most informative papers we found, in order of the increasing ionic radius of the rare-earth, are: for Sc – Refs. [125–129,132,133]; for Lu – Refs. [128,133–137]; for Tm – Refs. [128,133,138–140]; for Er – Refs. [133,141–143]; for Y – Refs. [124,128,129,132,133,136,142–144]; for Ho – Refs. [132,133,140,143,144]; for Dy – Refs. [128,129,133,138,139,141,143, 144]; for Tb – Ref. [140]; for Gd – Refs. [128,133,140,143,145]; for Eu – Refs. [128,129,133, 139,143]; for Sm – Refs. [129,140,143,146,147]; for Nd – Refs. [128,140]; for Pr – Ref. [140]. Although single crystals have been studied in several works, <sup>[124,125,132,136,141,142,147]</sup> only in few of them <sup>[124,125,142]</sup> polarized Raman spectra are shown. In some works, the symmetry of the observed lines in the Raman spectra of Sc<sub>2</sub>O<sub>3</sub> <sup>[125,132]</sup>, Lu<sub>2</sub>O<sub>3</sub> <sup>[136]</sup>, Er<sub>2</sub>O<sub>3</sub> <sup>[132,141,142]</sup>,  $Y_2O_3^{[124,132,142]}$  and Dy<sub>2</sub>O<sub>3</sub> <sup>[141]</sup> has been proposed but, in our opinion, only for Sc<sub>2</sub>O<sub>3</sub> <sup>[125,132]</sup> and to a certain degree for  $Y_2O_3^{[124,132,142]}$  the assignment looks to be full and unambiguous. In Refs. [124,125], the interpretation of the experimental results has been supported by lattice dynamical calculations.

It is natural to expect for such a large family of isostructural compounds that some dependencies of their vibrational properties on their structural characteristics to be found. Given that the Raman spectra are dominated by one very intense line at about 350 cm<sup>-1</sup>, most of the attempts have been made to find the dependence of the frequency of this line on the type of the rare-earth using as a structural parameter the averaged R - 0 distance, <sup>[129]</sup> the number of *f*-electrons of the  $R^{3+}$  ion, <sup>[140,143]</sup> or the mass of the  $R^{3+}$  ion. <sup>[128]</sup> It appears that in this case the unit cell parameter of the cubic crystal lattice is the most suitable parameter since it is known with high accuracy for all members of the family. Ubaldini *et al.* <sup>[128]</sup> have found that the frequency of the most intense line monotonically decreases with the increase of the lattice parameter. Gouteron *et al.* <sup>[132]</sup> gave such kind of frequency dependencies for six lines using data of five rare-earth oxides. Urban *et al.* <sup>[140]</sup>, however, have stressed that there is a deviation from this dependence in the case of the Eu and Yb oxides.

Here we show a well-pronounced dependence of the frequencies of all most-intense lines in the Raman spectra of C-type  $R_2O_3$  on the cubic lattice parameter, based on the data obtained by us for seven oxides as well as on data for other six oxides reported in the literature. Using this dependence and the information concerning the symmetry of the lines, determined by  $Sc_2O_3$  single crystal measurements, <sup>[125]</sup> it is easy to determine the symmetry of the corresponding lines for the rest of the oxides. We also show that in the six modes with lowest
frequency mainly *R* ions take part in the vibrations. The anomalous behavior of the frequency of some lines in the spectra of  $Eu_2O_3$  is also confirmed.

We studied commercially available (SIGMA-ALDRICH and MERCK)  $R_2O_3$  powders (R – Sc, Lu, Er, Y, Ho, Gd, Eu, Sm, and Nd), with purity better than 99.9%, pressed into pellets of diameter 12 mm. The Raman spectra were measured at room temperature in backscattering geometry. An objective ×50 was used both to focus the incident laser beam onto the pellets surface and to collect the scattered light. The He-Ne (633 nm) and Ar<sup>+</sup> (515, 488 and 458 nm) laser lines were used for excitation. No overheating effects were observed at the used laser power of 1.0 mW. Preliminary measurements showed that, due to the transparency of the powder grains (leading to numerous reflections and refractions of the light), the scattered light was completely depolarized, and the Raman spectra in parallel and crossed geometrical configuration of the polarization of the incident and the scattered light were identical. This makes impossible to use the depolarization ratio [the ratio of the intensity of a line in the crossed and parallel polarization see Equation (8) on page 7] of the lines as a criterion for identifying their symmetry.<sup>[146]</sup> Therefore, only a non-polarized spectra were measured. As it was mentioned in previous works, <sup>[129,133,144]</sup> for some laser lines in addition to the peaks, originating by phonon scattering, in the Raman spectra were observed other peaks due to fluorescence and/or electronic Raman scattering, originating by transitions between the electronic states of the  $R^{3+}$  ions or small impurities of other  $R^{3+}$  ions.<sup>[133]</sup> Their presence might confuse the finding of the corresponding phonon Raman lines in the different compounds.

At first, we obtained Raman spectra from all the compounds using the available four laser lines. The Raman spectra for  $Sc_2O_3$  and  $Y_2O_3$ , excited with all laser lines, contain only lines with phononic origin. For  $Er_2O_3$  only spectra obtained with 458 nm excitation were free from additional lines. Though the same holds for Ho<sub>2</sub>O<sub>3</sub>, the optimal excitation is 515 nm. For the Lu<sub>2</sub>O<sub>3</sub> sample, for all excitations, many additional narrow lines were detected. The spectra of Gd<sub>2</sub>O<sub>3</sub> are free from fluorescence lines. There, however, in addition to the Raman lines of the Cphase, additional lines characteristic for the monoclinic B-phase were detected <sup>[145]</sup> showing that the sample is two-phase. In the case of  $Sm_2O_3$  and  $Eu_2O_3$  the lines, characteristic for the monoclinic B-phase<sup>[146,147]</sup> are dominant. Finally, Nd<sub>2</sub>O<sub>3</sub> samples showed Raman spectra of the A-phase.<sup>[148,149]</sup> All these observations are in accordance with the expectations about the phase stability for synthesis at standard conditions of the sesquioxides from this family [the phase diagram as a function of the temperature and the type of the rare-earth can be found in Refs. [115,150]]. For that reason, in order to obtain single C-type phase samples, the  $R_2O_3$ samples (R – Sm, Eu, Gd) were heated at 500 °C in air for three days and after that heated at 300 °C in air for additional three days. After this procedure, the presence of other phases was almost negligible. Later, Eu<sub>2</sub>O<sub>3</sub> was additionally annealed at the same temperatures and time but in oxygen flow (see the discussion below).

In this case we calculated the frequencies of the  $\Gamma$ -point phonons for  $R_2O_3$  (R – Sc, Y and Ho) in the framework of the shell model as implemented in the GULP package.<sup>[19]</sup> The potentials used for the lattice dynamical calculations are listed in Table 4.5. The A parameters for the R ions and the charges were adjusted by a fit to the available crystallographic data, while those for the O – O interaction were taken from Ref. [20].

As it was mentioned before the *R* atoms in the C-type  $R_2O_3$  oxides occupy two types of

**Table 4.5.** Parameters for the short-range interatomic potential. The  $0^{2-}$  ions have a core charge of Y = 1.169 |e|, shell charge of Z = -3.069 |e| and force constant  $k = 72.94 \text{ eV} \times \text{\AA}^{-2}$ . The  $R^{3+}$  ions (Sc, Y, and Ho) were treated as a rigid ones, with core charge of Z = +2.850 |e|.

Atomic pair	<i>A</i> (eV)	ρ (Å)	$C (eV \times Å^6)$
Sc – 0	1213.1	0.3312	0.000
Y – 0	1262.6	0.3491	0.000
Ho – O	1275.2	0.3487	0.000
0 - 0	22764.0	0.1490	27.879

Wyckoff positions, namely 8*b* and 24*d*, whereas all 0 atoms occupy the 48*e* position. It means that theoretically we should have 22 Raman-active modes,  $4A_g + 4E_g + 14F_g$ . However, the number of the experimentally observed lines in the Raman spectra is smaller.<sup>[124,125,132]</sup> The



**Figure 4.7.** Raman spectra of  $R_2O_3$  (R – Sc, Er, Y, Ho, Gd, Eu, and Sm) powders. The laser excitation wavelength is indicated for each spectrum. The peaks marked with star do not originate from scattering by phonons in the C-type crystal structure.

Raman spectra of the studied samples with single (or dominating) C-type phase are displayed in Figure 4.7 where, due to the good signal-to-noise ratio, even the peak with very low intensity can be unambiguously detected. The lines originating from the minor secondary phase of monoclinic  $Gd_2O_3^{[136,145]}$  and  $Sm_2O_3^{[146,147]}$  are marked with stars. The two broad bands in the spectrum of  $Er_2O_3$ , non-originating by phonon scattering, are marked as well.

The frequencies of the lines registered for the studied oxides as well as the frequencies for other isostructural  $R_2O_3$  oxides (taken from the literature) are listed in Table 4.6. The most published data coincide in the frame of the typical experimental accuracy for Raman spectra  $(\pm 1 \text{ cm}^{-1})$ . The dependencies of the most-intense lines with frequencies above 300 cm<sup>-1</sup>, expected to be predominantly oxygen vibrations, on the lattice parameter of the corresponding oxides, starting from Sc<sub>2</sub>O<sub>3</sub> (the compound with smallest lattice parameter) up to Pr<sub>2</sub>O<sub>3</sub> (the compound with largest lattice parameter), are shown in Figure 4.8. The frequency of all corre-



**Figure 4.8.** Dependencies of the frequency of the high-frequency Raman lines on the cubic lattice parameter of the C-type crystal structure. The symmetry of the lines, as determined from  $Sc_2O_3$  single crystal measurements<sup>[125]</sup>, is indicated. The line with an order larger intensity than the others is indicated by a triangle.

sponding Raman lines decreases monotonically with the increase of the cubic lattice parameter. However, all high-frequency Raman lines of Eu<sub>2</sub>O<sub>3</sub>, marked in Figure 4.8 with empty symbols, show anomalous softening. Up to now, it has been reported only for the most-intense line at 339 cm<sup>-1</sup>.<sup>[140]</sup> The symmetry of all corresponding lines also can be easily found, because in the case of Sc<sub>2</sub>O<sub>3</sub> it is unambiguously determined<sup>[125]</sup> (given in Figure 4.8). This assignment is in agreement with those previously done, based on Y<sub>2</sub>O<sub>3</sub> single crystal measurements<sup>[124,132,142]</sup>, except for the  $A_g$  line at 495 cm<sup>-1</sup> in Sc<sub>2</sub>O<sub>3</sub> (431 cm<sup>-1</sup> in Y<sub>2</sub>O<sub>3</sub>). The symmetry of the line at 359 cm<sup>-1</sup> is given as  $E_a + F_a$  not because of an ambiguity but rather

**Table 4.6.** Frequencies of the most-intense lines in the Raman spectra of some C-type  $R_2O_3$ . The symmetry of the lines, as determined by  $Sc_2O_3$  single crystal measurements [Ref. [125]], is listed on the first row. In the bottom of the table are given earlier assignments based on  $Y_2O_3$  single crystal measurements [Refs. [124,132,142]].

R	a (Å)	Reference structure	Fg	Fg	Ag	Fg	$E_g + F_g$	Fg	Eg	Fg	$A_g$	Fg	Fg	Reference Raman
Sc	9.830	[125]	669	523	495	419	359	319	273	252	221	202	189	this work
Lu	10.391	[151]	612	499	454	393	348		146	137	120		98	[135,136]
Tm	10.491	[152]	604	485	438	384	334		144	136	121		97	[138,139]
Er	10.561	[153]	595	478	434	379	334	175	144	135	119		97	this work
Y	10.602	[154]	592	469	431	377	325	235	194	182	162	138	129	this work
Но	10.617	[155]	590	471	430	376	330	176	146	136	120	102	97	this work
Dy	10.668	[153]	589	464	425	371	330		145	136	120		96	[138,139]
Tb	10.729	[156]		450		367					118		95	[140]
Gd	10.817	[157]	569	444	414	361	315	175	145	135	119	110	95	this work
Eu	10.868	[158]	559	425	385	339	289	175	145	134	119	109	94	this work
Sm	10.930	[159]	554	421	393	345	299	179	144	133	118	109	94	this work
Nd	11.072	[160]	539	401		331					116		100	[128,140]
Pr	11.152	[114]		393		322					117		99	[140]
			$F_g + A_g$	$F_g + A_g$	$F_g + E_g$	$F_g + A_g$	$E_g + F_g$	$F_g$	$F_g + E_g$	$F_{g}$	$F_g + A_g$		$F_g$	[124]
			$F_g$	$F_{g}$	$F_{g}$	$F_{g}$	$E_g$		$E_g$	$F_g$	$F_g + A_g$		$F_g$	[132]
			$F_g$	$F_{g}$	$F_g$	$F_g + A_g$	$E_g$				$F_g + A_g$		$F_g$	[142]

due to the presence of two lines with different symmetry and coinciding frequencies. The large uncertainty of the determination of the line symmetry, as shown in Ref. [124], is probably due to the large polarizer leakage seen in the spectra therein.

The comparison of the low-frequency Raman lines is given in Figure 4.9. It is seen that the frequencies of these lines for the lanthanide oxides are almost constant. Assuming that these



**Figure 4.9.** Dependencies of the frequency of the low frequency Raman lines on the cubic lattice parameter of the C-type crystal structure. The frequencies of the lines from the spectra of Sc<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> are normalized to the frequencies of the lines of the other compounds multiplying them by  $\sqrt{m_{Sc}/m_{Ho}}$  and  $\sqrt{m_Y/m_{Ho}}$ , respectively. The symmetry of the lines, as determined by Sc<sub>2</sub>O<sub>3</sub> single crystal measurements<sup>[125]</sup>, is indicated. The full symbols correspond to the lines with higher intensity.

correspond to practically pure lanthanide atoms' vibrations, it appears that the effect of the decrease of the mass of the lanthanide, leading to the increase of the mode frequency, is fully compensated by the effect of the increase of the lattice parameter (or the R – O distance, or the ionic  $R^{3+}$  radius), leading to the decrease of the mode frequency. A similar constant mode frequency was observed for a R-mode in the family  $R_2$ CuO<sub>4</sub> (R – Pr, Nd, Sm, Gd).<sup>[161]</sup>

If we want to check which are the corresponding pure yttrium phonon modes in  $Y_2O_3$ , it is necessary to compare their frequencies with the ones for the lanthanide oxide with the closest unit cell parameter (or closest ionic radius, i.e. Ho) and to correct (normalize) its frequencies, accounting for the very different mass of Y compared to the one of Ho. Therefore, in Figure 4.9, the frequencies of the lines from the spectra of  $Sc_2O_3$  and  $Y_2O_3$  are normalized to the frequencies of the lines of the other compounds, multiplying them by  $\sqrt{m_{Sc}/m_{Ho}}$  and  $\sqrt{m_Y/m_{Ho}}$ , respectively. It is seen that the thus-normalized frequencies for  $Y_2O_3$  are very close to those of  $Ho_2O_3$  (the lanthanide oxide with closest lattice parameter), proving the pure lanthanide origin of these vibrations. Even in the case of  $Sc_2O_3$ , despite the large difference between its lattice parameter and those of the other compounds, the normalized frequencies still have such a value, so the corresponding lines can be identified. Using this cor-



**Figure 4.10.** The softening (in %) of the frequency of the phonon modes in  $Eu_2O_3$  as a function of their expected frequency (if it follows the general dependence).

respondence, the symmetry of the lines, obtained by  $Sc_2O_3$  single crystal measurements, <sup>[125]</sup> can be determined as well.

A comparison between the experimental and calculated Raman-active mode frequencies is shown in Table 4.7. As it is seen, the low-frequency modes obtained from the LDC are in a good agreement with the experiment. The calculations also confirm that in these vibrations mainly R ions take part. This can be seen from Figure 4.11 (a) where are drawn the eigenvectors for the lowest frequency  $F_g$  mode in the case of Sc<sub>2</sub>O<sub>3</sub>, to compare the magnitudes of the atomic deviations Figure 4.11 (b) shows the highest frequency  $A_g$  mode, which is pure oxygen vibration, as expected.

Comparing the data from Figures 4.8 and 4.9, it can be noted that, contrary to the high-frequency modes of  $Eu_2O_3$ , its low-frequency modes do not show any anomalous softening. Their frequencies are practically the same as those of their neighbors by lattice parameter,

Symmetry	Sc <sub>2</sub>	03	Y <sub>2</sub>	03	Нс	0203
	$\omega_{\mathrm{expt}}$	$\omega_{ m calc}$	$\omega_{\mathrm{expt}}$	$\omega_{ m calc}$	$\omega_{\mathrm{expt}}$	$\omega_{ m calc}$
$\overline{F_g}$	189	192	129	132	97	98
-	202	199	138	138	102	103
	252	250	182	181	136	136
	319	306	235	234	176	179
	329	311		244		184
						(Continued)

**Table 4.7.** Experimental [for  $Sc_2O_3$  – this work and Ref. [125]] and calculated frequencies of the Raman-active modes in  $R_2O_3$  (R – Sc, Y and Ho).

Symmetry	Sc <sub>2</sub> O <sub>3</sub>		Y <sub>2</sub>	03	Ho <sub>2</sub> O <sub>3</sub>		
	$\omega_{\mathrm{expt}}$	$\omega_{ m calc}$	$\omega_{ m expt}$	$\omega_{ m calc}$	$\omega_{ m expt}$	$\omega_{ m calc}$	
	359	341	325	288	330	287	
		368		299		291	
	391	386		338		334	
	419	412	377	368	376	364	
		472		416		409	
		491		442		438	
	523	536	469	495	471	494	
	587	605		545		536	
	669	646	592	581	590	574	
Eg	273	273	194	198	146	149	
	359	332	325	290	330	287	
	430	416		366		361	
	626	590		555		555	
$A_g$	221	220	162	162	120	123	
	391	351		306		297	
	495	498	431	460	430	459	
	623	593		553		553	

Table 4.7. (Continued)

Gd<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>. Trying to understand the reason for the anomalous values of the frequencies of the  $Eu_2O_3$  Raman lines, we construct the dependence of the relative softening  $-(\omega_{expt}-\omega_{dep})/\omega_{dep}$  on  $\omega_{dep}$  (here,  $\omega_{expt}$  is the experimentally observed frequency and  $\omega_{dep}$ is the expected one according Figures 4.8 and 4.9). It is given in Figure 4.10. It is seen that the softening is maximal for the modes with frequencies ranging from 300 to 400 cm<sup>-1</sup> (pure oxygen modes). For ionic oxides usually in this frequency region are the oxygen bending (in respect to metal-oxygen bonds) modes. These observations do not favor the previouslyproposed explanation for the origin of the anomalous mode frequency, i.e., the specific Eu<sup>3+</sup> electronic structure.<sup>[140]</sup> Note that just the low-frequency Eu vibrations are not influenced. So, the reason for the anomaly could be in some peculiarities of the oxygen sublattice. Using DFPT lattice dynamical calculations from the previous section, have determined the origin of the most-intensive Raman-active line (in the case of  $Sc_2O_3$  at 419 cm<sup>-1</sup>, corresponding to 339  $\text{cm}^{-1}$  for Eu<sub>2</sub>O<sub>3</sub>) as triply degenerated out-of-phase antistretching oxygen vibration along the (100) crystal directions. Due to the nature of this mode (the directions of the oxygen vibration) its frequency depends most on the oxygen-oxygen interaction. The LDC for  $Y_2O_3$ and Ho<sub>2</sub>O<sub>3</sub> presented here show the same vibrational pattern for the corresponding lines at

377 and 376 cm<sup>-1</sup> (calculated at 368 and 364 cm<sup>-1</sup>), respectively. It can be expected that the



**Figure 4.11.** Eigenvectors for (a) the lowest frequency  $F_g$  mode and (b) the highest frequency  $A_g$  mode in Sc<sub>2</sub>O<sub>3</sub>. As the vectors are taken from the LDC results, the atoms in the primitive cell are shown. The inset in part (b) shows the both full and primitive cells. To get the real deviations the magnitude of the vectors are divided to the square root of the corresponding atom.

other modes in this middle-frequency region have similar oxygen-oxygen stretching (but R – 0 bending) shapes. Our opinion is that only this type of modes is sensitive to a presence of oxygen vacancies in the crystal structure of Eu<sub>2</sub>O<sub>3</sub>. Probably, a small oxygen deficiency is the reason for the anomalous softening of the oxygen modes in Eu<sub>2</sub>O<sub>3</sub>.

For several oxides, it is known that the frequencies of some oxygen vibrations in them are very sensitive to their oxygen content (non-stoichiometry).<sup>[162,163]</sup> Usually, a change of the oxygen content causes noticeable modifications of the structural data. However, examining the structural data for the  $R_2O_3$  oxides, we did not find any anomaly neither for the lattice parameter nor for the partial atomic coordinates of the oxygen ions in the unit cell of Eu<sub>2</sub>O<sub>3</sub>. In order to increase the oxygen content in Eu<sub>2</sub>O<sub>3</sub>, we made an attempt to remove the hypothetical oxygen vacancies by additionally annealing the samples first at 500 °C and after that at 300 °C, both in flowing oxygen for three days. However, the increase of the frequency of the most-intense line was (if any) less than 0.5 cm<sup>-1</sup>. Nevertheless, we believe that the problem concerning the anomalous phonon dynamics of Eu<sub>2</sub>O<sub>3</sub> remains open and needs additional study of structurally well-characterized samples annealed in oxygen at different (high) pressures. This interest is reinforced by some recent publications reporting a detection, via x-ray photoelectron spectroscopy, of oxygen vacancies in  $Eu_2O_3$  samples.<sup>[164,165]</sup>

The most complete so far comparative study of the Raman-active phonon modes in the  $R_2O_3$  (*R* – rare-earth) oxides with C-type bixbyite crystal structure was reported. We studied the optimal conditions (the choice of the laser line and additional temperature annealing of the samples) for measuring the Raman spectra, containing only one-phonon Raman lines, without additional peaks due to photoluminescence, electronic Raman scattering or secondary minor monoclinic B-phase. The results of the measurements of seven oxides as well the previously published results for other six oxides were compared. It appears that due to the large difference between the masses of the oxygen and rare earth ions, the phonons can be separated into two groups – high-frequency pure oxygen vibrations, and low-frequency pure rare-earth vibrations. The high-frequency oxygen modes shows smooth and clear dependence on the type of the oxide, as it monotonously decreases with the increase of the cubic unit cell parameter of the oxide. In opposite, the practically constant frequency of the corresponding low-frequency rare-earth modes in the different lanthanide oxides shows that the effects of the change of the lanthanide mass and the unit cell parameters compensate each other. The LDC show good agreement between the calculated and experimentally observed phonon frequencies, as well confirm the origin of the phonon modes. In the case of  $Eu_2O_3$ , it was observed systematic softening of the frequency for the middle-frequency oxygen vibrations compared to the expected ones from the general dependencies. Analyzing these results, we suggest that the reason for this anomaly is the presence of oxygen vacancies (nonstoichiometry) in its crystal structure. Unfortunately, annealing the samples in flowing oxygen did not change the Raman spectra. The Eu<sub>2</sub>O<sub>3</sub> anomaly needs additional detailed investigation.

## Conclusion

In this thesis we present results of Raman scattering measurements of single crystals YCrO<sub>3</sub>, YMnO<sub>3</sub>, Sc<sub>3</sub>CrO<sub>6</sub> and Sc<sub>2</sub>O<sub>3</sub>, as well powders of  $R_2O_3$  (R – Sc, Lu, Er, Y, Ho, Gd, Eu, Sm and Nd). A systematic study of the quasi-soft modes in  $RBO_3$  perovskites is also discussed.

In the first chapter of this dissertation single crystals of orthorhombic YCrO<sub>3</sub> and finely twinned crystals of YMnO<sub>3</sub> were studied. The symmetry of the lines, observed in the Raman spectra was determined from polarized measurements in different scattering configurations. In comparison to a previously published data for YCrO<sub>3</sub><sup>[31]</sup> two new lines,  $B_{1q}$  and  $B_{2q}$  at 556 and 611 cm<sup>-1</sup>, were registered. The lack of resonance effects was also confirmed by measuring the Raman spectra with four different laser lines. Lattice dynamical calculations were performed in the framework of the shell model in order to facilitate assignment of the observed lines to definite atomic vibrations. As it is expected, the two isostructural compounds have close frequencies for the corresponding modes. However, the difference in the relative peak intensities is significant. According to the structural model proposed by Abrashev et al.<sup>[30]</sup> the intensity of the Raman peaks depends on four basic structural distortions. Thus the large intensity of two of the lines  $[B_{2g}(1) \text{ and } A_g(1)]$  in YMnO<sub>3</sub> is explained by the large Jahn-Teller distortion. However, the relatively low intensity of the rest lines in YMnO<sub>3</sub> in comparison with the corresponding ones in YCrO<sub>3</sub> cannot be explained within this model. The reduced intensity of these peaks is rather due to the fine twinning of the manganite crystals related to the JT ordering.

Further, the idea of the quasi-soft modes in manganites, <sup>[29]</sup> touched on in the first chapter is expanded over several  $RBO_3$  families. From the systematic analysis of the available in the literature structural and Raman data can be concluded that for each family with fixed *B*-atom the frequency of the quasi-soft modes is proportional to the angle of the corresponding octahedra tilts in the orthorhombic *Pnma* structure. The averaged *B* – 0 distance for all members of a particular  $RBO_3$  family, practically does not vary and it is a suitable structural parameter, which can be defined with better accuracy than the widely used ionic radius. The coefficient of proportionality  $\varkappa$ , of the relationship between the tilt angle and the frequency of the quasi-soft mode depend on the averaged  $\langle B-O \rangle$  distance. This dependence can be approximated with equal precision with different functions (power, linear and exponential). All these functions predict with satisfying accuracy the frequency of the soft (quasi-soft) mode(s) in the *RBO*<sub>3</sub> perovskites, which can be used for analysis of structural and Raman spectroscopy data.

The single crystals of Sc<sub>3</sub>CrO<sub>6</sub> were grown by HTS and like the other samples were studied by x-ray single crystal diffractometry, scanning electron microscopy with x-ray microprobe analysis and micro-Raman spectroscopy. The chemical content is confirmed to be non-stoichiometric Sc<sub>6</sub>Cr<sub>1</sub>Cr<sub>1-x</sub>Sc<sub>x</sub>O<sub>12</sub>, x = 0.08, which results in two different Cr1O<sub>6</sub> and (Cr,Sc)2O<sub>6</sub> octahedra. This is in agreement with the refined  $R\bar{3}$  crystal structure. Polarized Raman spectra were collected at room temperature in different geometrical configurations, allowing us to determine the symmetry of all  $9A_g + 9E_g$  Raman-allowed modes. The calculated frequencies by LDC are in a good agreement with the experimentally measured ones, the assignment of modes was also confirmed by the performed calculations. It was used a molecular approach for the interpretation of the calculated modes. It predicts grouping of modes into sets with close frequencies which can be explained by: (a) the presence of two different Cr1O<sub>6</sub> and (Cr,Sc)2O<sub>6</sub> octahedra in the unit cell, and (b) the rhombohedral structure is very close to a cubic one ( $\alpha = 91.97^{\circ}$ ). Indeed, the origin of the eight high frequency modes (internal stretching CrO<sub>6</sub> octahedral vibrations), as it was obtained by LDC, justifies this approach. In addition to the room temperature measurements, non-polarized Raman spectra were collected in the temperature range 20 – 600 °C. With increasing the temperature the intensity of five  $A_g$  lines decreases in comparison to the intensity of the other lines, which suggests a possible transition from  $R\bar{3}$  to  $R\bar{3}c$  above the investigated temperature region.

In the last chapter we report a complete analysis of Raman data and crystallographic characterization of  $Sc_2O_3$  single crystals. The x-ray single-crystal diffractometry, confirmed that the samples are cubic with space group  $Ia\bar{3}$ , which means they are C-type rare-earth sesquioxides. Thus the theoretically predicted Raman-active modes are  $4A_g + 4E_g + 14F_g$ . All  $4A_g$ , and  $4E_g$  as well 11 out of  $14F_g$  modes were observed, as their symmetry was determined by polarized measurements. The experimental results are supported by DFT lattice dynamical calculations. Further, all this was extended to comparative study of the Raman-active phonon modes in C-type  $R_2O_3$  (R – rare-earth) oxides. It was shown that due to the large difference between the masses of the oxygen and rare earth ions, the phonons can be separated into two groups – high-frequency pure oxygen vibrations, and low-frequency pure rare-earth vibrations. The LDC (this time performed in the framework of the shell model) shows good agreement between the calculated and experimentally observed phonon frequencies, as well confirm the origin of the modes. In the case of R = Eu, it was observed systematic softening of the frequency for the middle-frequency oxygen vibrations compared to the expected ones from the general dependencies. Analyzing these results, we suggest that the reason for this anomaly is the presence of oxygen vacancies (non-stoichiometry) in its crystal structure.

## List of publications

- M. Abrashev, N. D. Todorov, J. Geshev, Raman spectra of R<sub>2</sub>O<sub>3</sub> (*R* – rare-earth) sesquioxides with C-type bixbyite crystal structure: A comparative study, J. Appl. Phys. **116**, 103508 (2014).
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