

# Resonance vibrations of F<sup>-</sup> and F<sup>+</sup> - centers in $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals

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**Abstract.** A recursive method is used to simulate the lattice dynamics of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals with F<sup>-</sup> and F<sup>+</sup>-centers in terms of the shell model. The local density of vibrations of atoms in the 1<sup>st</sup> and 2<sup>nd</sup> coordination spheres of a cluster comprising 1000 ions is calculated. Frequencies of defect-induced symmetrized vibrations are determined. The calculation results are compared with the data of the optical absorption in oxygen-deficient Al<sub>2</sub>O<sub>3</sub> crystals.

## 1. Introduction

Anion-deficient crystals of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are widely used in many fields of engineering because of their unique physical properties. Some of these properties are due to intrinsic defects of the oxygen sublattice, including anion vacancies capturing one electron (F<sup>+</sup>-centers) or two electrons (F-centers). Specifically, some most significant optical and luminescence characteristics of corundum crystals are explained by dynamic processes involving the said electron centers. In this connection, it is necessary to study the effect of F<sup>+</sup>- and F-centers on vibration spectra of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals.

Some papers are known today [1-7] dedicated to the experimental and theoretical research into lattice dynamics in ideal corundum crystals. Results of model and first-principle calculations of the formation energy and the specific features of the electronic structure of anion vacancies in different charge states in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are reported in [8-14]. Also, model calculations of the lattice dynamics in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> containing the aforementioned defects are given in [15, 16]. However, frequencies of localized vibrations are determined only for independent directions in the cited papers. This approach to the determination of the frequencies can, in some cases, lead to an ambiguity when they are compared with the relevant experimental data.

The present study is concerned with the computer simulation of the lattice dynamics in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals containing F<sup>+</sup>- and F-centers with account for the symmetry classification of localized vibrations.

## 2. Model and computing method

Pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals belong to the trigonal system with the space symmetry group  $R\bar{3}c$  ( $D_{3d}^6$ ). Their rhombohedral primitive cell includes two formula units (10 atoms). The lattice parameters  $a = 5.128$  Å and  $\alpha = 55.287^\circ$ , as well as the structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are given in [2]. Each oxygen ion O<sup>2-</sup> is surrounded by a slightly distorted tetrahedron of four nearest Al<sup>3+</sup> ions. In this tetrahedron, the Al–O bond for two aluminum ions is 1.86 Å long (we shall label these aluminum ions Al(1) and assume them to be ions of the first coordination sphere), while the other two aluminum ions (labeled

Al(2)) are spaced 1.97 Å from the oxygen ion, see Figure 1. The nearest octahedral neighborhood of an Al<sup>3+</sup> ion comprises oxygen ions O<sup>2-</sup>, three of which are spaced 1.86 Å from Al<sup>3+</sup>, while the other three are 1.97 Å distant.

In this study we use the well-known shell model [17] for simulation of the lattice dynamics in the crystals. In this model, the lattice energy is written as

$$E_{lat} = \frac{1}{2} \sum_{\substack{i,j \\ j \neq i}} \varphi(r_{ij}) + \frac{1}{2} \sum_i k_i \mu_i^2 = \frac{1}{2} \sum_{\substack{i,j \\ j \neq i}} [V^c(r_{ij}) + V^b(r_{ij})] + \frac{1}{2} \sum_i k_i \mu_i^2 \quad (1)$$

where  $\varphi(r_{ij})$  is the potential of the pair short-range interaction between the  $i$ -th and  $j$ -th ions,  $k_i$  is the constant of elasticity between the core and the electron shell of the  $i$ -th ion, and  $\mu_i$  is the displacement of the shell relative to its core. The interaction between the ion cores is assumed to be a long-range purely Coulomb interaction. The interaction between the electron shells has two components: the long-range purely Coulomb interaction and the short-range interaction described by the Buckingham potential [9]. Thus, we have

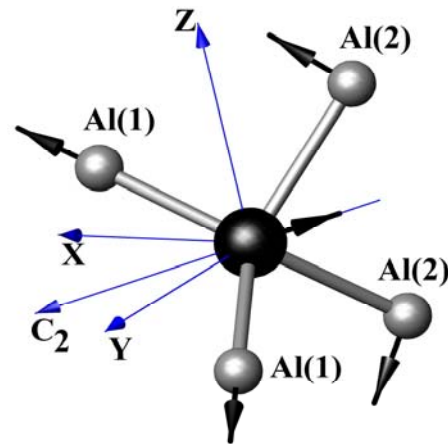
$$V^c(r_{ij}) = \frac{X_i X_j}{r_{ij}^c} + \frac{X_i Y_j}{|\bar{r}_j^s - \bar{r}_i^c|} + \frac{Y_i X_j}{|\bar{r}_j^c - \bar{r}_i^s|} + \frac{Y_i Y_j}{|\bar{r}_j^s - \bar{r}_i^s|} \quad (2)$$

$$V^b(r_{ij}) = A_{ij} \exp(-|\bar{r}_j^s - \bar{r}_i^s|/\rho_{ij}) - \frac{C_{ij}}{|\bar{r}_j^s - \bar{r}_i^s|^6} \quad (3)$$

where  $X_i$  and  $Y_i$  are the charges of the core and the electron shell of the  $i$ -th ion;  $A_{ij}$ ,  $\rho_{ij}$ , and  $C_{ij}$  are constants depending on the ion type. Values of the ion-ion potential in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals are adopted from [16]. They were obtained by theoretical fits to the measured elastic and dielectric constants, the lattice constants, the lattice energy and the phonon dispersion curves in three high-symmetry directions.

The effect of F<sup>+</sup>- and F-centers, which are charged relative to the lattice, on the vibration spectrum of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals was analyzed by computation of symmetrized local densities of vibrational states (SLDVS). The local densities were calculated for ideal and defective crystals, which were simulated by clusters containing 1000 ions. SLDVS were calculated by the recursive method [18]. The region containing about 4000 ions was considered for calculation of the Coulomb component of the diagonal elements in the force constant matrices of the ion-ion interaction by the Ewald method.

We calculated SLDVS projected onto the region containing the first two coordination spheres around an O<sup>2-</sup> ion or F<sup>+</sup>- and F-centers in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals. Notice that oxygen ions occupy positions of the point symmetry group C<sub>2</sub>. An oxygen ion O<sup>2-</sup>, two ions Al(1) and two ions Al(2) are related with the 15-dimensional displacement space, which is divided into irreducible one-dimensional representations A and B of the point group C<sub>2</sub>:  $\Pi(15 \times 15) = 7A + 8B$ . If rotation and translation are excluded from the consideration, nine vibrations 5A + 4B are present in the said region. In this case, an oxygen ion can complete one fully symmetric vibration A and two



**Figure 1.** Picture of a possible A-symmetry vibration of the region OAl<sub>4</sub> containing five ions. The C<sub>2</sub> axis is the axis of rotation through 180°.

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vibrations whose symmetry is determined by the representation B. Ions Al(2) complete the same type of motion. By way of example, Figure 1 shows directions of the ion motion during A-type vibrations.

Models of  $F^+$ - and F-centers (coordinates of atoms in the defective region and the effective charge) can be found in [10,11]. According to these papers, the localization of the electron density at the center of a vacancy is about 90% and 80% for  $F^+$ - and F-centers in the ground state respectively. The rest of the charge is smeared over the nearest neighbors.

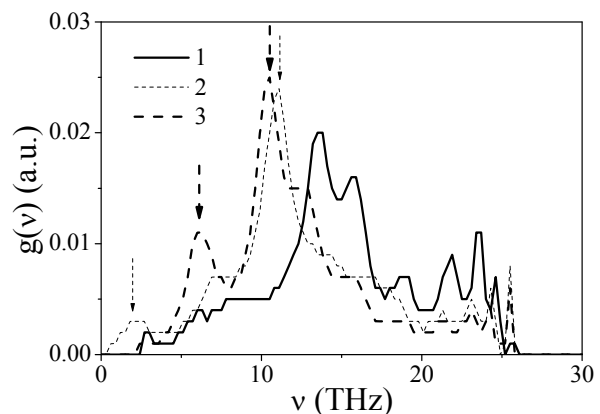
### 3. Results and discussion

SLDVS in ideal and defective  $\alpha$ - $Al_2O_3$  crystals were calculated in terms of the aforementioned approaches with using of original program package [19]. The maxima of SLDVS in the defective crystal, which differed from those in the ideal crystal, were identified as resonance vibrations induced by defects. Figure 2 presents SLDVS for Al(2) ions completing one of A-vibrations in the ideal corundum and for the same ions, but located near  $F^+$ - and F-centers in the defective corundum. It is seen that the local densities are redistributed to the low-frequency region when  $F^+$ - and F-centers are formed. If an  $F^+$ -center is formed, the maximum peaks are observed at the frequencies of 1.5 THz and 11.1 THz; if an F-center appears, they occur at 6.1 THz and 10.5 THz.

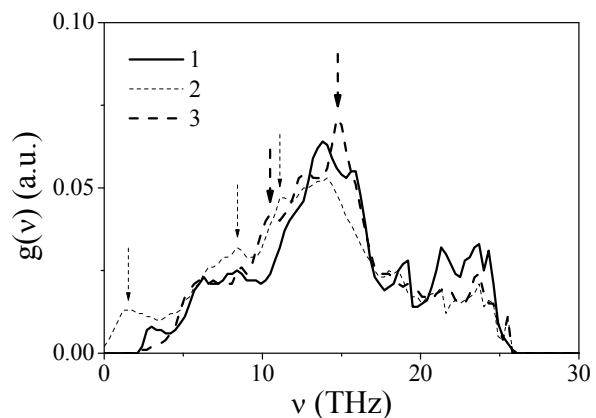
Figure 3 depicts total SLDVS of the A type of all the aluminum ions in the first and second coordination spheres surrounding an oxygen ion in ideal  $\alpha$ - $Al_2O_3$  or  $F^+$ - and F-centers in defective  $\alpha$ - $Al_2O_3$ . Accordingly to our calculations  $F^+$ -centers are responsible for resonance vibrations 1.5 THz, 8.4 THz and 11.1 THz., which are related with displacements of Al(1) and Al(2) ions. At the same time F-centers are responsible for resonance frequencies 10.5 THz and 14.7 THz.

The SLDVS of Al ions were summed for the B-symmetry too. The table gives calculated frequencies of the resonance vibrations induced by oxygen vacancies in different charge states in the nearest Al ions in  $\alpha$ - $Al_2O_3$  crystals. The number and the quantitative values of the frequencies of the induced resonance vibrations differ. It is seen that vibrations with the B-symmetry have a higher frequency in the case of  $F^+$ - and F-centers.

Unfortunately, we are not aware of papers dealing with the Raman scattering or the IR absorption by  $F^+$ - and F-centers in oxygen-deficient crystals of the aluminum oxide, which would allow performing a detailed comparative analysis of our calculated values and the relevant experimental data. At the same time, the table contains experimental estimates of the frequency of the effective phonons governing the temperature



**Figure 2.** SLDVS projected onto displacements of one of the possible A-symmetries of Al(2) ions around an oxygen ion in the ideal crystal (curve 1), near an  $F^+$ -center (curve 2), and near an F-center (curve 3) in the defective crystal.



**Figure 3.** Total SLDVS projected onto A-symmetry displacements of Al ions located in a spherical region of 2.0 Å radius around an oxygen in the ideal crystal (curve 1), near an  $F^+$ -center (curve 2), and near an F-center (curve 3) in the defective crystal.

behavior of the optical absorption and luminescence bands of the centers under study in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The measurements [12,20] provide just rough estimates of the averaged frequency of vibrations in the context of the single-phonon approximation. Nevertheless, the calculated and experimental estimates are in satisfactory mutual agreement, see Table 1. The discussed comparison is well justified considering a dominant contribution of localized vibrations to the dynamics of the processes involving defects of the imperfect lattice. From this and the performed calculations it may be concluded that the effective vibrations revealed in [12,20] are due to the induced localized vibrations of the A-symmetry on aluminum atoms in the 1<sup>st</sup> and 2<sup>nd</sup> coordination spheres nearest to F<sup>+</sup>- and F-centers. Directions of the displacements of Al(1) and Al(2) ions are just shown in Figure 1.

**Table 1.** Frequencies of resonance vibrations induced on Al ions by defects.

Symmetry type	Frequency (THz)	
	F-center	F <sup>+</sup> -center
Calculation		
A	10.5	1.5
	14.7	8.4 11.1
B	14.3	20.8
	21.3	23.2
	23.5	
Experiment		
	9.8 [20]	12.0 [12] 12.7 [20] 10.2 [21]

#### 4. Conclusion

The lattice dynamics in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals containing F<sup>+</sup>- and F-centers has been reported as simulated by the shell method. Frequencies of symmetrized resonance vibrations induced on nearest Al ions by defects have been evaluated. They have been compared with effective phonon frequencies determined in independent experimental studies. This study was supported by RFBR (grant No. 07-02-12015).

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