Crystal Field Analysis and Electron-phonon Coupling in Sc$_2$O$_3$:Cr$^{3+}$

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Crystal field analysis of the energy level structure of the Cr$^{3+}$ ion in the Sc$_2$O$_3$ crystal is performed, using the exchange charge model of the crystal field theory. The crystal field parameters acting on the optical electrons of the Cr$^{3+}$ ion at the sites with C$_2$ and C$_{3i}$ symmetry are calculated from the crystal structure data. On the basis of the comparison between experimental absorption and emission spectra and theoretically calculated energy levels of Sc$_2$O$_3$:Cr$^{3+}$, the conclusion is made that the spectroscopic properties of the title host are determined by the Cr$^{3+}$ ion at the positions of C$_2$ local symmetry. The Stokes shift $S = 4.32$ and the energy of the phonons effectively interacting with an impurity center $\hbar \omega = 499$ cm$^{-1}$ are derived from the experimental spectra of absorption and emission.

Key words: Crystal Field Theory; 3$d$-ions; Electron-phonon Coupling.

1. Introduction

Crystals doped with Cr$^{3+}$ have received considerable attention since 1960, when the first laser at all was realized with Al$_2$O$_3$:Cr$^{3+}$ (ruby) [1]. Later on, many other crystals were shown to lase with the Cr$^{3+}$ ion; the number of them is now about 20, and the lasers based on these hosts cover the spectral region between 700 nm and 1100 nm [2]. Such a wide tunability region is entirely due to the vibronic interaction between optical electrons of the Cr$^{3+}$ ion and vibrations of the host lattice ions.

Very often several types of impurity centers co-exist in the same crystal, and not always it becomes possible to unambiguously distinguish between them. Thorough spectroscopic measurements or detailed crystal field calculations are needed in this case to understand the nature of an impurity center. In this paper we use the crystal field theory to analyze the energy level scheme of the octahedrally coordinated Cr$^{3+}$ in a Sc$_2$O$_3$ crystal in which two types of Cr$^{3+}$ positions are available, and deduce the parameters of the electron-phonon coupling from the experimental data found in the literature.

2. Crystal Structure and Spectroscopy of Sc$_2$O$_2$:Cr$^{3+}$

Scandiumoxide (Sc$_2$O$_3$) is a cubic crystal which belongs to the Ia3 space group (space group number 206) [3]. The lattice constant is 9.8459 Å, the unit cell consists of 16 formula units. Among the 32 Sc$^{3+}$ ions in the unit cell, 8 occupy the site with the C$_3i$ symmetry and 24 occupy the site with C$_2$ symmetry. Each Sc$^{3+}$ ion is surrounded by six O$^{2-}$ ions, the Cartesian coordinates of which for both types of the above mentioned positions, obtained using data from [3], are given in Tables 1 and 2.

The experimental spectroscopic data of Cr$^{3+}$-doped Sc$_2$O$_3$ can be found in [4, 5]. The shape of the experimental spectra is typical for octahedrally coordinated Cr$^{3+}$ ions. Analysis of the excitation spectrum performed in [5] led to the following energy level assignment (for the spin-allowed transitions): $^4A_{2g}(4F)$ → $^4T_{2g}(4F)$ at 670 nm (14925 cm$^{-1}$), $^4A_{2g}(4F)$ → $^4T_{1g}(4F)$ at 480 nm (20833 cm$^{-1}$), $^4A_{2g}(4F)$ → $^2T_{1g}(4F)$ at 300 m (33333 cm$^{-1}$). The sharp line around 710 nm (14084 cm$^{-1}$) was assigned to the $^4A_{2g}(4F)$ → $^2E_g(2G)$ spin-forbidden transition. The broad band emission...
3. Crystal Field Calculations for Sc2O3:Cr3+

The energy levels of Cr3+ ion in this work are represented by the eigenvalues of the crystal field Hamiltonian of the form [6]

\[ h = \sum_{p=2.4k=\pm} \sum_{p} B_{p}^{k} O_{p}^{k}, \]  

(1)

where \( O_{p}^{k} \) are the linear combinations of irreducible tensor operators acting on the angular parts of the Cr3+ ion wave functions, and \( B_{p}^{k} \) are the crystal field parameters containing all information about the geometrical structure of an impurity center. As formulated in [6], these parameters can be written as a sum of two terms:

\[ B_{p}^{k} = B_{p,q}^{k} + B_{p,S}^{k}. \]  

(2)

The first contribution is due to the electrostatic interaction between optical electrons of an impurity ion and ions of the crystal lattice (treated as point charges, without taking into account their electron structure), and the second one is proportional to the overlap of the wave functions of an impurity ion and ligands. In other words, this term includes all effects of the covalent bond formation and exchange interaction. Inclusion of these effects significantly improves the agreement between calculated and experimentally observed energy levels. Expressions for calculating both contributions to the crystal field parameters in case of the 3d-ion are as follows [6]:

\[ B_{p,q}^{k} = -K_{p}^{k} e^{2} (r^{p}) \sum_{i} q_{i} V_{i}^{k} \left( \theta(i), \varphi(i) \right) \frac{R(i)^{p+1}}{R(i)}, \]  

(3)

\[ B_{p,S}^{k} \equiv K_{p}^{k} e^{2} \frac{2(2p+1)}{5} \sum_{i} \left( G_{s} S_{i}(i) \right)^{2} + G_{\sigma} S_{\sigma}(i)^{2} + \gamma_{p} G_{\pi} S_{\pi}(i)^{2} \frac{V_{i}^{k} \left( \theta(i), \varphi(i) \right)}{R(i)}. \]  

(4)

The sums are carried out over lattice ions denoted by \( i \) with charges \( q_{i} \); \( R(i) \), \( \theta(i) \), \( \varphi(i) \) are the spherical coordinates of the \( i \)-th ion of the crystal lattice in the reference system centered at the impurity ion. The averaged values \( \langle r^{p} \rangle \) of the \( p \)-th power of the impurity ion electrons coordinate can be found in [7]. The values of the numerical factors \( K_{p}^{k} \) and \( \gamma_{p} \) and expressions for the polynomials \( V_{k}^{j} \) are given in [6]. The overlap integrals between the \( d \)-functions of the central ion and the \( p \)- and \( s \)-functions of the ligands are denoted by \( S_{s}, S_{\sigma}, S_{\pi} \) (they correspond to the integrals \( \langle l|m|\ell' \rangle \) notation) \( S_{s} = \langle d0|s0 \rangle, S_{\sigma} = \langle d0|p0 \rangle, S_{\pi} = \langle d1|p1 \rangle \). \( G_{\sigma}, G_{\pi}, G_{\epsilon} \) are dimensionless adjustable parameters of the model, which are determined by the positions of the first three absorption bands. Very often they can be assumed to be equal to each other; \( G_{\sigma} = G_{\pi} = G_{\epsilon} = G \). In this paper we use this simplified model. The advantage of the exchange charge model is that, if the \( G \) parameter is determined to fit the first absorption band, the other energy levels, located higher in energy, will also fit the experimental spectra fairly well.

Initially the exchange charge model has been formulated and developed for rare earth ions [6], but later on it has also been successfully applied to the transition metal ions in different hosts [8–12].

Since the second rank point charge parameters \( B_{p,q}^{k} \) decrease not so fast as the fourth rank parameters \( B_{4,q}^{k} \) (as \( 1/R^{3} \) and \( 1/R^{5} \), respectively), the contribution of the ligands from the second and further coordination spheres can be quite significant. To increase the accuracy in calculating the point charge contribution to the crystal field parameters, we considered a large cluster,
Table 4. Positions of energy levels (in cm$^{-1}$) of octahedral Cr$^{3+}$ in Sc$_2$O$_3$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C$_3$ site</th>
<th>C$_2$ site</th>
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<td>$B_{2}^{3}$</td>
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<td>$B_{2}^{2}$</td>
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<th>$B_{2}^{4}$</th>
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consisting of 596 ions, namely 1 Cr$^{3+}$, 235 Sc$^{3+}$, and 360 O$^{2-}$. This cluster enables to take into account the contribution of ions located at distances up to 14.44 Å in the case of the C$_2$ impurity center and 16.15 Å in the case of the C$_3$ impurity center. For the exchange charge parameters in (4) only the nearest ligands were taken into account, since the overlap between an impurity ion and ligands from other than the first coordination sphere can be safely neglected.

Using (1)–(4), the ligand positions from Tables 1 and 2, and the gaussian radial wave functions for the Cr$^{3+}$ and O$^{2-}$ ions from [13], we obtained the values of the crystal field parameters given in Table 3. The crystal field Hamiltonian was diagonalized in the space of 10 wave functions of the lowest $4P$ and $4F$ terms of the Cr$^{3+}$ ion. The Racah parameter $B$, which defines the energy gap between the two above terms, was chosen to be 590 cm$^{-1}$ [5]. A significant reduction of this parameter in comparison to that of a free ion, $\beta = B_{\text{complex ion}}/B_{\text{free ion}} = 0.64$ (for the free Cr$^{3+}$ ion we use the value $B = 918$ cm$^{-1}$ [14]), known as the nephelauxetic effect, is caused by the covalency. The strong nephelauxetic effect for the Cr$^{3+}$ ion in Sc$_2$O$_3$ indicates a high degree of covalency and serves as a firm justification of exchange charge model for the considered case. The adjustable parameter $G$ was defined by fitting the calculated splittings to the experimental ones, and turned out to be 35.485 for the Cr$^{3+}$ in the C$_2$ position and 35.120 for the Cr$^{3+}$ ion in the C$_3$ position. The obtained energy levels are listed in Table 4, in comparison with experimental ones.

Since the absorption bands of Cr$^{3+}$ in Sc$_2$O$_3$ are very broad and were not decomposed in [5] into individual bands, we found the averaged values of the energies for the group of states arising from the orbital triplets after they are split by the low-symmetry component of the crystal field. On the other hand, we assume that the barycenter of the group of levels arising from the same triplet in C$_2$ or C$_3$ symmetry corresponds to the energetical position of the same triplet in O$_h$ symmetry. One can see from Table 4 that the energy level scheme calculated for the C$_2$ center agrees a bit better with experimental results than the energy level scheme for the C$_3$ center. Also the splitting of the orbital triplet states, which defines the width of the absorption and emission bands, must be analyzed. The full width at half maximum (FWHM) of the $4T_{2g}$$-4A_{2g}$ emission band at 300 K is about 2658 cm$^{-1}$ [5], and the splitting of the $4T_{1g}$ state in the C$_2$ symmetry is closer to that value than in the C$_3$ symmetry (3030 cm$^{-1}$ and 1558 cm$^{-1}$, respectively). The FWHM of the $4A_{2g}$$-4T_{1g}$ ($4P$) absorption band at 300 K is about 4500 cm$^{-1}$ [5], and, again, it is better reproduced by the C$_2$ symmetry (6577 cm$^{-1}$) than by the C$_3$ symmetry (1762 cm$^{-1}$). Since no experimental data on the FWHM of the $4A_{2g}$$-4T_{1g}$ ($4P$) absorption band were found in [5], we can not compare the results of our calculations directly with experimental measurements, but such a large splitting (7881 cm$^{-1}$) of the $4T_{1g}$ ($4P$) state in case of the C$_3$ symmetry seems significantly overestimated in comparison with the same result for the C$_2$ symmetry (4221 cm$^{-1}$) and splittings of other two orbital triplets, $4T_{2g}$ ($4F$) and $4T_{1g}$ ($4F$). This consideration leads to the conclusion that the Cr$^{3+}$ ion preferably substitutes the Sc$^{3+}$ ion at the positions of the C$_2$ symmetry.
4. Evaluation of the Parameters of Electron-phonon Interaction

To study the electron-phonon coupling of the Cr\(^{3+}\) ions with the lattice vibrations in Sc\(_2\)O\(_3\) we used the single-coordinate configurational model in harmonic approximation [15]. This model is based on the assumption that the nearest environment of the impurity ion oscillates harmonically about its equilibrium position. This displacement is described by the \(Q\) coordinate. A typical diagram of the potential energies of electronic states as a function of the vibrational coordinate \(Q\) for the case of a strong crystal field (when the orbital doublet \(2E_g\) is located below the orbital triplet \(4T_{2g}\)) is sketched in Figure 1.

The two main parameters which describe the electron-phonon coupling are the Huang-Rhys parameter \(S\) and the effective phonon energy \(\hbar\omega\). The former is defined as the number of phonons of the energy \(\hbar\omega\) excited in the absorption transition [15]:

\[
S = \frac{E_{\text{dis}}}{\hbar\omega}
\]  
(5)

(where \(E_{\text{dis}}\) is defined in Fig. 1). \(S\) and \(\hbar\omega\) are related to the difference \(\Delta E\) between the first absorption and corresponding emission band peaks [15, 16]:

\[
\Delta E = (2S - 1)\hbar\omega.
\]  
(6)

The second equation which is required to calculate \(S\) and \(\hbar\omega\) is [15]

\[
\Gamma(T) = 2.35\hbar\omega\sqrt{S\coth\left(\frac{\hbar\omega}{2kT}\right)}.
\]  
(7)

where \(\Gamma(T)\) is the FWHM at the absolute temperature \(T\). In order to solve the equations (6) and (7) we used spectroscopic data from [5]. According to these data, the energetic Stokes shift \(\Delta E\) is about 3814 cm\(^{-1}\), and \(\Gamma(T)\) of the \(4T_{2g} - 4A_{2g}\) emission band at 300 K is about 2658 cm\(^{-1}\). Solving (6) and (7) yields \(S = 4.32, \hbar\omega = 499\) cm\(^{-1}\). It is interesting to compare the obtained value of the effective phonon energy \(\hbar\omega\) with the results for fluoride crystals (\(\hbar\omega = 260\) cm\(^{-1}\) for Cs\(_2\)NaAlF\(_6\):Cr\(^{3+}\) [16]). The energy of the effective phonon in Sc\(_2\)O\(_3\) is 1.9 times larger than in the fluoride. Therefore, a smaller number of phonons would be required to bridge the \(4T_{2g} - 4A_{2g}\) energy gap, and non-radiative quenching of the \(4T_{2g}\) state in Sc\(_2\)O\(_3\) would be more probable than in fluorides. This conclusion is supported by measurements of the \(4T_{2g} - 4A_{2g}\) emission lifetime reported in [5] for Sc\(_2\)O\(_3\):Cr\(^{3+}\) (it is about 70 \(\mu\)s at 300 K) and in [17] for Cs\(_2\)NaAlF\(_6\):Cr\(^{3+}\) (it is significantly greater, about 180 \(\mu\)s at 300 K, indicating the less important role of the non-radiative processes in quenching of the excitation energy in the last case).

5. Conclusions

Calculations of the crystal field parameters and energy level structure of the octahedrally coordinated Cr\(^{3+}\) ion in Sc\(_2\)O\(_3\) were performed in the framework of the exchange charge model of crystal field, which has only the adjustable parameter \(G\), describing the overlap between the wave functions of the central ion and its ligands. Two possible sites – with C\(_2\) and C\(_{3i}\) local symmetry – for the Cr\(^{3+}\) ion were considered. The positions of the energy levels and orbital triplet splittings obtained for the Cr\(^{3+}\) ion at the position with C\(_2\) symmetry agree better with experimental spectra than those ones for the C\(_{3i}\) position. Therefore, the spectroscopic properties of the Sc\(_2\)O\(_3\):Cr\(^{3+}\) crystal are mainly determined by the Cr\(^{3+}\) ion at the positions of C\(_2\) symmetry. The exchange charge model with its
possibility of explicit inclusion of the overlap integrals into the expression for calculating the crystal field parameters provides an adequate description of the energy level scheme of Cr$^{3+}$ in the studied crystal. The Stokes shift $S = 4.32$ and the effective phonon energy $\hbar \omega = 499 \text{ cm}^{-1}$ have been deduced from the experimental spectra of emission and absorption.

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