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Crystal field effects and electron–phonon interaction in $K_2LiAlF_6:Cr^{3+}$

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ABSTRACT

The crystal field effects and electron–phonon interaction in $K_2LiAlF_6:Cr^{3+}$ elpasolite crystal were studied using the exchange charge model (ECM) of crystal field and harmonic approximation of lattice vibrations. The crystal field parameters (CFP) and energy level scheme for the $[CrF_6]^{3-}$ cluster were calculated. As a further application of the ECM, the crystal field strength $10Dq$ was studied for different "impurity ion–ligand" distances R. By fitting these values to the power law $10Dq \approx R^{-n}$ of coordinate R, the value of n was obtained as 4.56796. Several physical quantities (such as the electron–vibrational interaction constants, Stokes shifts, Huang–Rhys factors and Jahn–Teller stabilization energy) associated with the two normal vibrational modes a_{1g} and e_g of the $[CrF_6]^{3-}$ complex coupled with the Cr^{3+} electronic states, were calculated. The obtained results are compared with experimental data and discussed.

1. Introduction

K_2LiAlF_6 is an A_2BMX_6 elpasolite, with A and B monovalent alkali metals, M a trivalent metal and X a monovalent anion. At low temperature this fluoride has a cubic structure, belonging to the Fm3m space group with the lattice parameter a=7.842 Å and four formula units in a crystal unit cell [1]. Both Li^+ and Al^{3+} ions are octahedrally coordinated by the fluorine ions. From the point of view of ionic radii, the Cr^{3+} ions after doping can in principle replace either Al^{3+} or Li^+ (the ionic radii of Al^{3+}, Li^+ and Cr^{3+} are [2], respectively, 0.53, 0.68 and 0.63 Å). However, since the charge of Cr^{3+} and Li^+ is different, certain charge compensation is needed, which would lead to distortions of the host structure. So, from the point of view of charge mismatch, Cr^{3+} ions will rather substitute Al^{3+} ions being octahedrally surrounded by six fluorine anions. Also, the K_2LiAlF_6 optical measurements [3] indicate that Cr^{3+} ions are octahedrally coordinated and replace the host Al^{3+}, occupying only one kind of crystallographic site. If the Cr^{3+} concentration is rather low, deformations of the host structure due to the Cr^{3+} presence are very small [3]. The chromium-doped elpasolites crystals are promising laser materials and serve as model systems for investigating the crystal field and vibronic effects [3–9].

Experimental spectroscopic studies [3] have shown potential of $K_2LiAlF_6:Cr^{3+}$ crystal for the tunable solid state lasers. The luminescence and absorption spectra from Ref. [3] are used as an experimental support for our calculations.

The main aim of this paper is to extend the optical characterization of the title crystal using the crystal structure data and crystal field theory; calculate the complete energy level scheme of Cr^{3+} ion and compare it with the experimental spectra; perform a microscopic analysis of the crystal field strength $10Dq$ dependence upon the interionic distance R [10] and extract from this dependence the basic parameters of the electron–vibrational interaction.

All calculated results are compared with experimental ones from Ref. [3]; the comparison is discussed.

2. Calculation method

The first step is to find the energy level scheme using the crystal field theory (CFT). The fundamental idea of CFT is that the energy levels of an ion with unfilled electron shell in a crystal field (CF) can be represented as the eigenvalues of the following CF Hamiltonian:

$$H = \sum_p \sum_{k=-p}^{p} B_p^k O_p^k, \tag{1}$$

where B_p^k are the CF parameters (CFP) and O_p^k are the Stevens homogeneous spherical polynomials. If admixture of electronic configurations of opposite party is neglected, the p index takes all

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even values from 0 to $2l$ (with l being the orbital quantum number of electrons in the unfilled electron shell). The first term with $p=0$ produces a uniform shift of all energy levels and can be dropped. In the case of transition metal ions with unfilled d-shell p takes only two values 2 and 4. The values of the crystal field parameters B_p^k can be calculated if the positions of the crystal lattice ions are known. The equations and methods for their calculations vary from one CF model to another. The exchange charge model (ECM) [11] gives an opportunity of direct calculations of the CFP values. In this model the CFP is represented as a sum of two terms, and each of them describes different contributions to the total CF:

$$B_p^k = B_{p,q}^k + B_{p,S}^k \tag{2}$$

The first term $B_{p,q}^k$describes the point charge contribution (the crystal lattice ions are treated at this point as the point charges located at the crystal lattice sites) and is described by the following expression:

$$B_{p,q}^k = -K_p^k \cdot e^2 \cdot \langle r^p \rangle \cdot \sum_i q_i \cdot \frac{V_p^k(\theta_i, \varphi_i)}{R_i^{p+1}} \tag{3}$$

where the sumation is carried out over the lattice ions denoted by i, with electric charges q_i (expressed in units of the electron charge e);R_i, θ_i, φ_i are the spherical coordinates of the ith ligand in the system of reference centered at the impurity center and $\langle r^p \rangle$ is the averaged value of the p-th power of radial coordinate of the impurity ion electrons. The expressions for the V_p^k polynomials and the numerical values of the K_p^k factors are given in Ref. [11].

The second term takes into account all effects of the exchange interaction and covalent bond formation between the ligand's s and p orbitals and the d orbitals of the central ion. The mixture of these orbitals is responsible for the s, σ and π bondings between the impurity ion and ligands (Cr^{3+} and F^-, in our case). The covalence effects are described by the overlap integrals $S(s) = \langle d0|s0 \rangle$, $S(\sigma) = \langle d0|p0 \rangle$, and $S(\pi) = \langle d1|p1 \rangle$,which appear in the following expression of $B_{p,S}^k$:

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i (G_s S(s)_i^2 + G_\sigma S(\sigma)_i^2 + \gamma_p G_\pi S(\pi)_i^2) \frac{V_p^k(\theta_i, \varphi_i)}{R_i} \tag{4}$$

where γ_p are numerical constants given in Ref. [11] and G_s, G_σ and G_π are dimensionless adjustable parameters of the model; they are determined by fitting the calculated energy levels to the lowest observed bands in the experimental absorption spectrum. It is possible to simplify the model by assuming $G_s=G_\sigma=G_\pi$, a reasonable approximation [11], and then only the lowest in energy absorption band is needed for determination of G. Such an approximation invokes only one fitting paramater; nevertheless, agreement between the calculated and observed energy levels is good. The overlap integrals were calculated numerically for a number of different distances between the Cr^{3+} and F^- ions [12] and were approximated as exponential functions of the interionic separation R (R in a.u.):

$$S(s) = 2.7775 \cdot e^{-1.0277 \cdot R}$$

$$S(\sigma) = 1.1674 \cdot e^{-0.7105 \cdot R}$$

$$S(\pi) = 2.093 \cdot e^{-1.0235 \cdot R} \tag{5}$$

where $3\,\text{a.u.} < R < 4\,\text{a.u.}$

The main advantages of the ECM are as follows: (i) a small number of fitting parameters; (ii) possibility to calculate the crystal field parameters and energy levels of impurities in crystals without invoking any assumptions about the impurity center symmetry, but using only crystal structure data; and (iii) possibility to treat the covalent effects quantitatively (by calculating the overlap integrals).

3. Results and discussions

3.1. Crystal field and energy level calculations for K_2LiAlF_6:Cr^{3+}

Using the crystal structure data from Ref. [1], overlap integrals (5) and Eqs. (2)–(5), we calculated the values of the CFP listed in Table 1. To ensure proper convergence of the crystal lattice sums (especially for the second rank CFP, which depend on interionic distance R as $1/R^3$), large clusters consisting of 9358 ions in K_2LiAlF_6 were considered in Eq. (3). These clusters include ions located at distances up to 29.9158 Å from the impurity ion site. As for Eq. (4), only the ligands from the first coordination sphere are taken into account, because the overlap integrals between an impurity ion and ions from further coordination spheres can be safely neglected.

Comparing both contributions to total CFP values, we can see that the ECC contribution is considerably greater than PCC, which emphasizes importance of the covalent effects for this system and confirms validity of application of the ECM in this case.

The next step is to calculate the complete energy level scheme for the Cr^{3+} ion by diagonalizing the Hamiltonian (1). The values of the ECM G parameter along with the Racah parameters, used for the energy level calculation, were obtained by fitting the experimental values of the energy levels from Ref. [3], and they are $G=2.753$, $B=702\,\text{cm}^{-1}$ and $C=3358\,\text{cm}^{-1}$. In Table 2 the obtained results are listed in comparison with the experimental data [3]. The spin–orbit interaction was not considered, since no fine structure of the absorption spectra was reported.

In the second column of Table 2 we have listed the energy values of the split levels, due to the low-symmetry component of CF. It is well known that any surrounding that breaks the spherical symmetry of the free-ion, like CF, can lead to a shift and splitting of the energy levels. These considerations apply to all doped materials such as crystals or even the glasses, for example, where a long-range order does not exist. This is the reason for a small splitting of all Cr^{3+} degenerated energy levels, as presented in Table 2. A small magnitude of this splitting suggests weak distortions around Cr^{3+} ions.

Table 1
Crystal field parameters for K_2LiAlF_6:Cr^{3+}.

CFP	PCC	ECC	Total
	B_{pq}^k	B_{ps}^k	$B_{pq}^k + B_{ps}^k$
B_2^{-2}	5	14	19
B_2^{-1}	0	−5	−5
B_2^0	8	15	23
B_2^1	−15	−38	−53
B_2^2	4	7	11
B_4^{-4}	−36	−136	−172
B_4^{-3}	−455	−1693	−2148
B_4^{-2}	2305	8566	10871
B_4^{-1}	−1374	−5106	−6480
B_4^0	74	274	348
B_4^1	−4301	−15986	−20287
B_4^2	864	3212	4076
B_4^3	−7613	−28289	−35902
B_4^4	−3485	−12949	−16434

PCC and ECC stand for the "point charge contribution", Eq. (3) and "exchange charge contribution", Eq. (4), respectively.