Studies of EPR Parameters and Local Structure for Cr^{3+} in $NaInS_2$ Crystal

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The EPR parameters (zero-field splitting D and g factors $g_\parallel$, $g_\perp$) of Cr^{3+} in a $NaInS_2$ crystal are calculated from high-order perturbation formulas based on the two spin-orbit coupling parameter model for the EPR parameters of $3d^3$ ions in trigonal octahedral sites. In the calculations, both the contribution to EPR parameters from the spin-orbit coupling parameter of the central $3d^3$ ion and that of ligands are considered. From the calculations it is found that, to explain reasonably the EPR parameters, the local structure (in particular the local trigonal distortion angle θ) in the vicinity of the Cr^{3+} impurity is different from the corresponding structure in the host crystal. The change of the local angle θ with temperature is also obtained from the temperature dependence of zero-field splitting. The results are discussed.

Key words: Electron Paramagnetic Resonance; Defect Structure; Crystal- and Ligand-field Theory; Cr^{3+}; $NaInS_2$.

1. Introduction

When an impurity ion substitutes a host ion in a crystal, the local structure surrounding the impurity may be different from the corresponding structure in the host crystal in the cases of size and/or valence mismatch [1 – 8]. The determination of the local structure of impurity centers is of interest and significance because the properties of solids are closely related to their defect structure. Many studies were made for the local bonding length (i. e., the impurity-ligand distance R) [5 – 8]. However, for the local bonding angle (which is related to the angular distortion of the impurity center), there are relatively fewer studies. If the impurity is a paramagnetic ion, since the EPR parameters of a paramagnetic ion in crystals are sensitive to the local angular distortion of the impurity center, one can obtain useful information on the local structure of an impurity center by analyzing its EPR data [3, 4, 9, 10]. The EPR parameters (zero-field splitting D and g factors $g_\parallel$, $g_\perp$) of Cr^{3+} replacing In^{3+} in the layer structure of a $NaInS_2$ crystal were measured decades ago [11], however theoretical explanation for these EPR parameters has not been made, and the defect structure of the Cr^{3+} impurity center has not been estimated from these EPR parameters, either. The Cr^{3+} ion in $CdInS_2$ crystal has D_{3d} site symmetry [12]. In this paper, we calculate these EPR parameters from high-order perturbation formulas based on the two spin-orbit coupling parameter model for the EPR parameters of $3d^3$ ions in trigonal symmetry. The use of this model is due to the fact that the spin-orbit coupling parameter $\zeta_p^0 (\approx 365\ \mathrm{cm}^{-1}$ [13]) of the ligand ion S^{2-} is larger than that ($\zeta_d^0 \approx 273\ \mathrm{cm}^{-1}$ [14]) of the central Cr^{3+} ion. So, not only the contribution to EPR parameters from the spin-orbit coupling parameters of the central $3d^3$ ion, but also that of ligands should be taken into account. Based on the calculations, the local structure (in particular, the local trigonal distortion angle) of Cr^{3+} impurity centers in a $NaInS_2$ crystal is estimated and a change of the local distortion angle with temperature is suggested from the temperature dependence of zero-field splitting. These results are discussed.

2. Calculation

In the two spin-orbit coupling parameter model [15 – 17], the admixture of the spin-orbit coupling parameters between the d electrons of the central $3d^n$ ion and the p electrons of the ligands via the covalence effects is considered. Thus, the one-electron basis functions should be expressed as a linear combination of atomic orbitals (LCAO), i. e. [15, 16]

$$\psi_r = N_r^{1/2}\left(|d_r\rangle - \lambda_r |P_r\rangle\right), \tag{1}$$

where the subscript $r = t_{2g}$ or e_g denotes the irreducible representation of the O_h group. $|d_r\rangle$ and $|P_r\rangle$ are the d orbitals of the $3d^n$ ion and the p orbitals of ligands, respectively. N_r is the normalization factor and λ_r the orbital mixing coefficient.

From the basis functions and by use of the Macfarlane's perturbation-loop method [18, 19], the high-order perturbation formulas of EPR parameters based on the two spin-orbit coupling parameter models for $3d^3$ ions in trigonal symmetry can be derived as [16, 17]

$$\begin{aligned} D = {} & (2/9)\zeta'^2 v(1/D_1^2 - 1/D_3^2) \\ & - \sqrt{2}\zeta\zeta' v'(2/3D_1D_4 + 1/D_2D_3 + 1/3D_3D_4 \\ & \qquad + 1/D_2D_4 + 4/\sqrt{2}B/D_1D_4D_5) \\ & - \sqrt{2}\zeta'^2 B v'(4/D_3D_4D_5 + 9/2D_2^2D_3), \end{aligned} \tag{2}$$

$$\begin{aligned} g_\parallel = {} & g_s - 8\zeta'k'/3D_1 \\ & - 2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/9D_1^2 \\ & + 4\zeta'^2(k - 2g_s)/9D_3^2 - 2\zeta^2(k + g_s)/3D_2^2 \\ & - 4\zeta\zeta'k'/3D_1D_2 + 4\zeta\zeta'k'/9D_1D_3 \\ & + 4\zeta\zeta'k'/3D_2D_3 + 8\zeta'k'v/9D_1^2 \\ & - 4\sqrt{2}(k'\zeta + k\zeta')v'/3D_1D_4, \\ g_\perp = {} & g_\parallel - 4\zeta'k'v/3D_1^2 + 4\sqrt{2}(2k\zeta' + k'\zeta)v'/3D_1D_4, \end{aligned} \tag{3}$$

where $D_i (i = 1-5)$ are the zero-order energy denominators defined in [18, 19]. v and v' are the trigonal field parameters. B (and C) are the Racah parameters. $g_s (\approx 2.0023)$ is the g factor of a free $3d^n$ ion. The spin-orbit coupling parameters ζ, ζ' and the orbital reduction factors k, k' are written as

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \\ \zeta' &= (N_tN_e)^{1/2}(\zeta_d - \lambda_t\lambda_e\zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_tN_e)^{1/2}(1 - \lambda_t\lambda_e/2), \end{aligned} \tag{4}$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling parameter of d electrons of a free $3d^n$ ion and that of p electrons of a free ligand.

The LCAO coefficients N_r and λ_r in the above formulas can be estimated from the normalization condition [related to (1)]

$$N_r(1 - 2\lambda_r S_{dp}(\gamma) + \lambda_\gamma^2) = 1 \tag{5}$$

and the approximate relationship [15]

$$f_r \approx N_\gamma^2[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_r S_{dp}(\gamma)], \tag{6}$$

where $f_r [= (B/B_0 + C/C_0)/2]$ is the ratio of the Racah parameters for a $3d^n$ ion in a crystal to those for the free ion. $S_{dp}(r)$ are the group overlap integrals. These integrals are related to the impurity-ligand distance R of the studied system. For the $NaInS_2:Cr^{3+}$ system, the host $NaInS_2$ crystal has the α-$NaFeO_2$ structure, the metal-ligand (i.e., In^{3+}–S^{2-}) distance $R_H \approx 2.636$ Å is calculated from the lattice constants $a_0 (\approx 3.803$ Å [12]) $c_0 (\approx 19.89$ Å [12]) and the atom-position parameter $u (\approx 0.26$ [12]). Since the ionic radius $r_i (\approx 0.63$ Å [20]) of the impurity Cr^{3+} is smaller than the radius $r_h (\approx 0.81$ Å [20]) of the replaced host ion In^{3+}, the impurity-ligand (i. e., Cr^{3+}–S^{2-}) distance R in $NaInS_2:Cr^{3+}$ should be unlike the corresponding metal-ligand distance R_H in the host crystal. We therefore estimate reasonably the impurity-ligand distance $R \approx 2.546$ Å in $NaInS_2$: Cr^{3+} by using the approximate formula [21] $R \approx R_H + (r_i - r_h)/2$. According to the distance R and the Slater-type SCF functions [22, 23], we calculate the integrals $S_{dp}(t_{2g}) \approx 0.02772$ and $S_{dp}(e_g) \approx 0.07200$.

The Racah parameters B, C and the cubic field parameter Dq can be obtained from the optical spectra of the crystal under study. Since no optical spectra for $NaInS_2:Cr^{3+}$ crystals were reported, we estimate reasonably the optical spectra parameters B, C and Dq as follows: In view of the fact that the parameters B and C decrease slightly with increasing distance R [24] and the parameter $Dq \sim R^{-5}$ [25, 26], thus, from the optical spectra [27] of the isomorphous $NaCrS_2$ crystal (where the Cr^{3+}–S^{2-} distance R is 2.44 Å [12, 27]), we have for $NaInS_2:Cr^{3+}$

$$\begin{aligned} & B \approx 460\ \text{cm}^{-1}, \quad C \approx 2130\ \text{cm}^{-1}, \\ & Dq \approx 1150\ \text{cm}^{-1}. \end{aligned} \tag{7}$$

The parameters B and C are $B_0 \approx 1030\ \text{cm}^{-1}$ and $C_0 \approx 3850\ \text{cm}^{-1}$ [14] for a free Cr^{3+} ion. Thus we yield $f_r \approx 0.50$. By applying the parameter f_r and the integrals $S_{dp}(r)$ to (5) and (6), we obtain for $NaInS_2:Cr^{3+}$

$$\begin{aligned} & N_t \approx 0.717848, \quad N_e \approx 0.738307, \\ & \lambda_t \approx 0.650368, \quad \lambda_e \approx 0.662547. \end{aligned} \tag{8}$$

Table 1. EPR parameters (zero-field splitting D and g factors) for Cr^{3+} in a $NaInS_2$ crystal.

	D [cm^{-1}]	$g_\parallel$	$g_\perp$
Calculated[a]	-0.627	1.9793	1.9844
Calculated[b]	-0.0393	1.9826	1.9829
Experimental [11]	$-0.0392(30)$	1.983(1)	1.983(1)

[a] Calculated by the trigonal distortion angle θ_H in the host crystal.
[b] Calculated by using the local trigonal distortion angle θ of impurity center.

Substituting these LCAO coefficients and the free-ion values ζ_d^0 and ζ_p^0 (given in Sect. 1) into (4), we have

$$\begin{aligned} &\zeta \approx 251.386\ \mathrm{cm}^{-1}, &&\zeta' \approx 141.496\ \mathrm{cm}^{-1},\\ &k \approx 0.869, &&k' \approx 0.571. \end{aligned} \tag{9}$$

The trigonal field parameters can be calculated from the empirical superposition model [28], i. e.,

$$\begin{aligned} v &= \frac{18}{7}\bar{A}_2(R)(3\cos^2\theta - 1)\\ &+ \frac{40}{21}\bar{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3)\\ &+ \frac{40\sqrt{2}}{3}\bar{A}_4(R)\sin^3\theta\cos\theta,\\ v' &= -\frac{6\sqrt{2}}{7}\bar{A}_2(R)(3\cos^2\theta - 1)\\ &+ \frac{10\sqrt{2}}{21}\bar{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3)\\ &+ \frac{20}{3}\bar{A}_4(R)\sin^3\theta\cos\theta, \end{aligned} \tag{10}$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ stand for the intrinsic parameters. It is found that $\bar{A}_4(R) \approx 3Dq/4$ for $3\mathrm{d}^n$ ions in octahedral sites [17, 28] and $\bar{A}_2(R) \approx (9 \sim 12)\bar{A}_4(R)$ for $3\mathrm{d}^n$ ions in many crystals [17, 29–31]. We take the average value $\bar{A}_2(R) = 10.5\bar{A}_4(R)$ here. The trigonal distortion angle θ denotes the angle between the direction of the distance R and the C_3 axis. From the lattice constants a_0, c_0 and the atom-position parameter u [12] of the host $NaInS_2$ crystal we have

$$\theta_\mathrm{H} \approx 56.40^\circ. \tag{11}$$

Substituting the host angle θ_H and the above parameters into (1) and (2), the EPR parameters D, $g_\parallel$ and $g_\perp$ are calculated. The results (particularly, the zero-field splitting D and the g-anisotropy $\Delta g = g_\parallel - g_\perp$) agree poorly with the observed values (see Table 1). So, as in the case of the local distance R, the local angle θ of the impurity center should differ from the corresponding angle θ_H in the host crystal. The local angle θ is taken as an adjustable parameter, thus, by fitting the calculated EPR parameters to the observed values, we obtain

$$\theta \approx 54.84^\circ. \tag{12}$$

The comparisons between the calculated and experimental EPR parameters are also shown in Table 1.

The temperature dependence of zero-field splitting $\partial D/\partial T \approx -0.8 \times 10^{-4}\ \mathrm{cm}^{-1}/\mathrm{K}$ was also measured for $NaInS_2$:Cr^{3+} crystals [11]. As is known, the temperature dependence of EPR parameters results from both the implicit, or static, contribution due to the change in the local geometry of the paramagnetic center by thermal expansion and the explicit, or vibrational, contribution due to the electron-phonon interaction [32–34]. Müller et al. [11], the researchers of EPR spectra of $NaInS_2$: Cr^{3+}, suggested that the dependence is ascribed to implicit thermal effects. Considering that the zero-field splitting D for the $3\mathrm{d}^n$ ion in trigonal symmetry is much more sensitive to the trigonal distortion angle θ than to the distance R [3, 4, 17] (in fact, if the trigonal distortion vanishes, i.e., $\theta \approx \theta_0 \approx 54.74^\circ$, the angle in the cubic symmetry, the splitting $D = 0$), the contribution to the value $\partial D/\partial T$ from the change of the distance R with temperature can be neglected. Thus, from the suggestion in [11] and the above dependence $\partial D/\partial T$, we obtain for $NaInS_2$:Cr^{3+}, that the change of local angle θ with temperature is $\partial\theta/\partial T \approx 2.2 \times 10^{-4}$ deg/K.

3. Discussion

From Table 1, one can find that by using suitable local structural data, the calculated EPR parameters of $NaInS_2$:Cr^{3+} agree well with the observed values. The calculated g-anisotropy $\Delta g = g_\parallel - g_\perp \approx 0.0003$ is smaller than the experimental error (≈ 0.001 [11]), so the observed isotropic g factors (i.e., $g_\parallel \approx g_\perp \approx g$) can be explained reasonably. However, if the structural data in the host $NaInS_2$ crystal are used, the calculated zero-field splitting D and g-anisotropy $\Delta g (\approx 0.005)$ disagree with the observed values. So, the local structure in $NaInS_2$:Cr^{3+} crystal obtained by studying the EPR parameters can be regarded as reasonable.

The changes of the structural data with temperature in pure $NaInS_2$ crystals were not reported. From the above studies, we suggest that, as in the cases of local structure, the change of local angle θ with temperature may be unlike that of the host angle θ_H with temperature. This point remains to be checked.

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