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Theoretical studies of the electron paramagnetic resonance and optical spectra of Cr^{3+} ions in the rhombohedral phase of a LaAlO_3 crystal

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Abstract. In this paper, by introducing a factor f to denote the contraction effect of perovskite crystals along the trigonal axis in the cubic-to-trigonal phase transition, the expressions for calculating the zero-field splitting D , the first excited-state splitting $\Delta(^2E)$ and the anisotropy of the EPR g -factor (characterized by $\Delta g = g_{\parallel} - g_{\perp}$) for $3d^3$ ions in the trigonal phase of this perovskite structure from the rotation angle α have been put forward. On the basis of these expressions, the zero-field splitting D , the splitting $\Delta(^2E)$ and the anisotropy of the g -factor for Cr^{3+} in the trigonal phase of a LaAlO_3 crystal are calculated by using two parameters obtained from the optical spectra of a similar crystal. The results show reasonable agreement with the experimental values.

1. Introduction

The lanthanum aluminate (LaAlO_3) crystal has recently attracted interest because it is one of the most common substrates for the epitaxial growth of superconducting thin films [1, 2]. The crystal has a perovskite structure which undergoes a structural phase transition from cubic to trigonal at about 800 K owing to the condensation of the R_{25} zone-boundary phonon mode [3]. For paramagnetic ions in the crystal, the phase transition can cause splittings of some energy levels and change in the EPR g -factor from isotropy to anisotropy. For instance, for Cr^{3+} ions in a LaAlO_3 crystal, the zero-field splitting D , the first excited-state splitting (or the R-line splitting) $\Delta(^2E)(= E(\bar{E}) - E(2\bar{A}))$ and the anisotropy of the g -factor (characterized by $\Delta g = g_{\parallel} - g_{\perp}$) were observed in the trigonal phase from the EPR and optical measurements several decades ago [4, 5]; however, until now no theoretical explanations for these splittings and the anisotropy have been given. The reasons may be due to the lack of the expressions that relate these splittings and the anisotropy to the order parameter for this type of phase transition. In this paper, we first of all establish the expressions for calculating these splittings and the anisotropy for $3d^3$ ions in the trigonal phase of the perovskite structure by introducing a contraction factor f . From these expressions, as an example, the zero-field splitting D , the R-line splitting $\Delta(^2E)$ and the anisotropy of the g -factor for Cr^{3+} ions in the trigonal phase of a LaAlO_3 crystal are reasonably explained.

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2. Calculation methods

The trigonal phase of the LaAlO_3 crystal is the result of a rotation of alternate AlO_6 octahedra around pseudo-cubic body diagonals (i.e. the C_3 axis) by the angle α which is the order parameter of this type of phase transition [3]. Figure 1 shows the rotation of an AlO_6 octahedron. Obviously,

$$b_{\perp} = \frac{b}{\cos \alpha} = \frac{a}{2\sqrt{3} \cos \alpha} \simeq \frac{a}{2\sqrt{3}} \left(1 + \frac{\alpha^2}{2}\right) \quad (1)$$

$$b_{\parallel} = \left(\frac{1}{3} - u\right)c = \left(\frac{1}{3} - \frac{1}{4}\right)c = \frac{1}{12}c \quad (2)$$

where a and c are the lattice constants and $u (= 0.25[6])$ is the oxygen parameter in the trigonal phase. Different from the case of the cubic-to-tetragonal phase transition (such as in SrTiO_3) where the rotation around the tetragonal axis at the transition leads to an expansion along the C axis (i.e. the C_4 axis) of the crystal and so the lattice constant $c > a$ [7, 8], the present rotation results in a contraction along the C axis (i.e. the C_3 axis) of the crystal and so the lattice constant c is smaller than $\sqrt{6}a$, the value in the cubic phase [9]. We can define a factor f to denote the contraction effect, i.e.

$$c = \sqrt{6}a(1 - f\alpha^2) \quad (3)$$

and then

$$f = \left(\sqrt{6}\frac{a}{c} - 1\right) / \alpha^2. \quad (4)$$

The factor f can be obtained from the x-ray and neutron diffraction data, i.e. the lattice constants a and c and the oxygen parameter x which is related to the rotation angle α by the formula [3]

$$x = \frac{1}{2} \left(1 \pm \frac{1}{\sqrt{3}} \tan \alpha\right). \quad (5)$$

For a LaAlO_3 crystal, from the values of a , c and x obtained by the x-ray and neutron diffraction measurements [6, 10], we have $f \simeq 0.28$.

The trigonal distortion of the AlO_6 octahedron can be represented by the value of $\beta - \beta_0$, where β is the angle between the bonding direction and the C_3 axis (see figure 1) and $\beta_0 (\simeq 54.74^\circ)$ is the same angle in the regular octahedron. Obviously,

$$\tan \beta = \frac{b_{\perp}}{b_{\parallel}} = \frac{6}{\sqrt{3}} \frac{a}{c} \left(1 + \frac{1}{2}\alpha^2\right) \simeq \sqrt{2} \left[1 + \left(f + \frac{1}{2}\right)\alpha^2\right]. \quad (6)$$

In the case of a small trigonal distortion, $\beta - \beta_0$ is very small, and we have

$$\beta - \beta_0 \simeq \tan(\beta - \beta_0) = \frac{(\tan \beta - \tan \beta_0)}{(1 + \tan \beta \tan \beta_0)} \simeq \frac{\sqrt{2}}{3} \left(f + \frac{1}{2}\right)\alpha^2. \quad (7)$$

The zero-field splitting D for $3d^n$ ions in crystals with a small trigonal distortion can be written as

$$D \simeq (\beta - \beta_0)(\partial D / \partial \beta)_0 \quad (8)$$

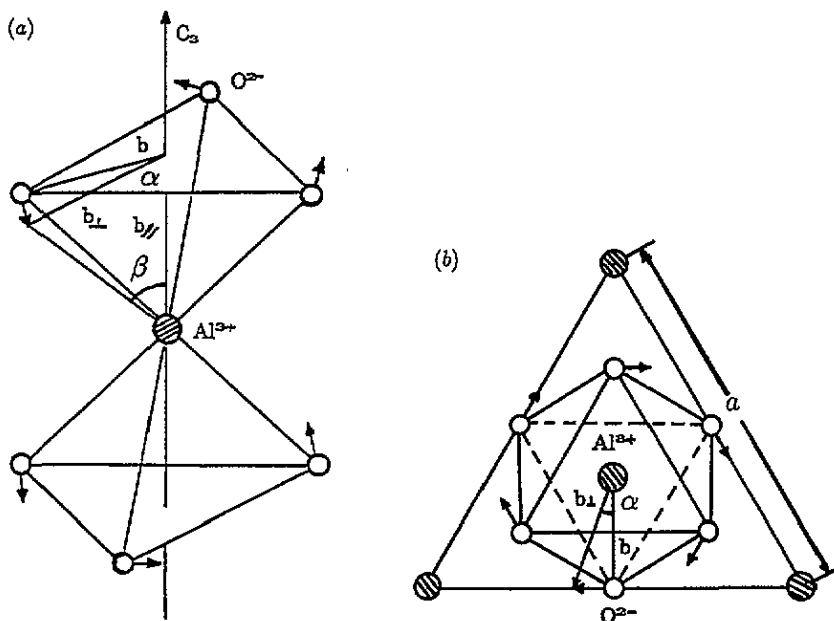


Figure 1. Rotation of an AlO_6 octahedron at cubic-to-trigonal phase transition for the $LaAlO_3$ crystal: (a) schematic drawing of the rotation around the Z (i.e. C_3) axis; (b) schematic drawing of the Z projection of the rotation.

where the subscript 0 denotes that the differentiation is done for the case of cubic symmetry. $(\partial D/\partial\beta)_0$ is related to the spin-lattice coupling coefficient G_{44} in cubic phase, i.e. [11]

$$G_{44} = -\frac{\sqrt{2}}{6} \left(\frac{\partial D}{\partial\beta} \right)_0. \quad (9)$$

So, from equations (7)–(9), we have

$$D = -2\left(f + \frac{1}{2}\right)G_{44}\alpha^2. \quad (10)$$

Thus, a simple and uniform relation between the zero-field splitting D for a paramagnetic ion in the trigonal phase and the spin-lattice coupling coefficient G_{44} in the cubic phase is established. The expression is similar to that in the cubic-to-tetragonal phase transition where $D = \frac{3}{2}(k - \frac{1}{2})G_{11}\phi^2$ [12]. Obviously, the zero-field splitting D is directly proportional to the square of the order parameter α . This point is understandable because the local point symmetry at the paramagnetic ion has a centre of inversion [13].

Similarly, we have

$$\Delta g = (\beta - \beta_0)[\partial(\Delta g)/\partial\beta]_0 = -2\left(f + \frac{1}{2}\right)F_{44}\alpha^2 \quad (11)$$

where F_{44} is the spin-lattice coupling coefficient in the cubic phase related to the g -factor [14]; for $3d^3$ ions,

$$\Delta(^2E) \simeq (\beta - \beta_0) \left(\frac{\partial \Delta(^2E)}{\partial\beta} \right)_0 = \frac{\sqrt{2}}{3} \left(f + \frac{1}{2} \right) \left(\frac{\partial \Delta(^2E)}{\partial\beta} \right)_0 \alpha^2. \quad (12)$$

Obviously, equations (10) and (11) are suitable for all paramagnetic ions.

For $3d^3$ ions, the expressions for G_{44} , F_{44} and $[\partial\Delta(^2E)/\partial\beta]_0$ can be obtained from the high-order perturbation formulae for D , Δg and $\Delta(^2E)$ based on the strong-field scheme [11, 14–16]. These formulae [15, 16] and expressions [11, 14] have been successfully used to explain the parameters D , Δg , $\Delta(^2E)$ and the spin–lattice coupling coefficient G_{44} and F_{44} for $3d^3$ ions in many crystals and can be regarded as reasonable. According to these formulae and expressions, we have

$$G_{44} = \frac{\sqrt{2}}{27}\xi^2 \left(\frac{1}{D_3^2} - \frac{1}{D_1^2} \right) \left(\frac{\partial v}{\partial \beta} \right)_0 + \xi^2 \left(\frac{2}{9D_1D_4} + \frac{1}{3D_2D_3} + \frac{1}{9D_3D_4} + \frac{1}{3D_2D_4} \right. \\ \left. + \frac{4\sqrt{2}B}{3D_1D_4D_5} + \frac{4B}{3D_3D_4D_5} + \frac{3B}{2D_2^2D_3} \right) \left(\frac{\partial v'}{\partial \beta} \right)_0 \quad (13)$$

$$F_{44} = \frac{4}{3} \frac{\xi K}{D_1D_4} \left(\frac{\partial v'}{\partial \beta} \right)_0 - \frac{2\sqrt{2}\xi K}{9} \frac{1}{D_1^2} \left(\frac{\partial v}{\partial \beta} \right)_0 \quad (14)$$

$$\left[\frac{\partial \Delta(^2E)}{\partial \beta} \right]_0 = 4\xi \left(-\frac{1}{3D_7} + \frac{4B}{D_7D_{12}} + \frac{B}{D_7D_{13}} - \frac{4B}{D_{10}D_{12}} + \frac{B}{D_{10}D_{13}} \right) \left(\frac{\partial v}{\partial \beta} \right)_0 \\ + 2\sqrt{2}\xi B \left[\frac{4\sqrt{3}}{D_7D_{12}} - \frac{\sqrt{3}}{D_7D_{13}} - \frac{4}{D_8D_{12}} - \frac{1}{D_8D_{13}} \right] \left(\frac{\partial v'}{\partial \beta} \right)_0 \quad (15)$$

where the zero-order energy denominators D_i are defined in the original literature [15]†, and from the point-charge-dipole model [11]

$$\left(\frac{\partial v}{\partial \beta} \right)_0 = \frac{18\sqrt{2}}{7} eq \left(1 + \frac{3p}{eR_0} \right) \frac{\langle r^2 \rangle}{R_0^3} + \frac{60\sqrt{2}}{7} Dq \quad (16)$$

$$\left(\frac{\partial v'}{\partial \beta} \right)_0 = -\frac{12}{7} eq \left(1 + \frac{3p}{eR_0} \right) \frac{\langle r^2 \rangle}{R_0^3} + \frac{30}{7} Dq \quad (17)$$

with

$$Dq = -eq \left(1 + \frac{5p}{eR_0} \right) \frac{\langle r^4 \rangle}{6R_0^5} \quad (18)$$

where q is the charge of ligands and p is the dipole, an adjustable parameter.

3. Calculation for $\text{LaAlO}_3:\text{Cr}^{3+}$

Now we use the above expressions to study the parameters D , Δg and $\Delta(^2E)$ for the $\text{LaAlO}_3:\text{Cr}^{3+}$ crystal. Utilizing the empirical d orbital of the Cr^{3+} ion and introducing a parameter N to denote the average covalency reduction effect, we have [17]

$$B = 920.48N^4 \text{ cm}^{-1} \quad C = 3330.71N^4 \text{ cm}^{-1} \quad \xi = 240N^2 \text{ cm}^{-1} \\ \langle r^2 \rangle = 2.4843N^2 \text{ au} \quad \langle r^4 \rangle = 16.4276N^2 \text{ au.} \quad (19)$$

† There is a misprint in [15]: according to the definition, $D_7 = \Delta + 6B$ should be replaced by $D_7 = 2C + 6B$.

The parameter N , Dq (and hence the parameter p from equation (18)) can be derived by fitting the observed optical spectra of the studied crystal. By using the method, good agreement between the calculated and observed spectral band positions were obtained for Cr^{3+} ions in many oxides, such as Al_2O_3 [17], MgO [11], spinels [18] and garnets [19, 20]. For the $\text{LaAlO}_3:\text{Cr}^{3+}$ crystal, insufficient optical spectroscopy data have been reported; however, we can reasonably estimate the parameters N and p by using the data for Cr^{3+} ions in other similar cases. Considering that the octahedral sites of $\text{YAG}:\text{Cr}^{3+}$ and $\text{LaAlO}_3:\text{Cr}^{3+}$ have the same $(\text{CrO}_6)^{9-}$ group and a similar cation–ligand distance R_0 (note that, for YAG , $R_0 = 1.937 \text{ \AA}$ [21] and, for LaAlO_3 in the cubic phase, $R_0 = 1.904 \text{ \AA}$ [9]), the parameters N ($\simeq 0.93$) and p ($\simeq 0.014eR_0$) for $\text{YAG}:\text{Cr}^{3+}$ [20] can be applied to the case of $\text{LaAlO}_3:\text{Cr}^{3+}$. This point is supported by the following fact: according to the strong-field approximation [15], the ${}^4\text{A}_1\text{--}a{}^2\text{E}$ separation $\Delta E = E(a{}^2\text{E}) - E({}^4\text{A}_1) \simeq 9B + 3C$. From the above parameter N , we obtain $\Delta E \simeq 13\,671 \text{ cm}^{-1}$, which is very close to the observed value (about $13\,630 \text{ cm}^{-1}$ [5]) at low temperatures. Thus, applying the parameters N ($K \simeq N^2$), p and the value of R_0 for LaAlO_3 to the above formulae, we obtain

$$G_{44} \simeq 4.3 \text{ cm}^{-1} \quad F_{44} \simeq 0.032 \quad [\partial\Delta(^2\text{E})/\partial\beta]_0 \simeq 1324 \text{ cm}^{-1}. \quad (20)$$

Significantly, the calculated values of G_{44} and F_{44} are close to the observed values for Cr^{3+} ion in similar oxides, such as in MgO where $G_{44} \simeq 4.2 \text{ cm}^{-1}$ [22] and $F_{44} \simeq 0.029(6)$ [23].

The rotation angle α is temperature dependent. For the LaAlO_3 crystal at room temperature, from the x-ray and neutron diffraction experiments [6, 10], we obtain the oxygen parameter $x \simeq 0.474(1)$ and hence the rotation angle $\alpha \simeq 5.16 \pm 0.20^\circ$. The latter is close to that (about $5.8 \pm 0.2^\circ$) obtained from the EPR measurement for the $\text{LaAlO}_3:\text{Fe}^{3+}$ crystal [3] and the theoretical calculation [24]. If we assume that the local contraction factor f and rotation angle α in the vicinity of the Cr^{3+} ion are the same as those in the host crystal, from equations (10), (11) and (20), we obtain for $\text{LaAlO}_3:\text{Cr}^{3+}$ at room temperature

$$D \simeq -(543 \pm 50) \times 10^{-4} \text{ cm}^{-1} \quad \Delta g \simeq -(0.0004 \pm 0.000\,04). \quad (21)$$

They are compared with the observed values in table 1.

No observed value of the R-line splitting $\Delta(^2\text{E})$ at room temperature has been reported; we therefore calculated the splitting at 77 K. From [3, 4], the rotation angle $\alpha \simeq 6.2 \pm 0.2^\circ$ at 77 K. Thus, substituting the values of α and $[\partial\Delta(^2\text{E})/\partial\beta]_0$ into equation (12), we obtain, at 77 K,

$$\Delta(^2\text{E}) \simeq 5.7 \pm 0.3 \text{ cm}^{-1}. \quad (22)$$

The result is also compared with the observed value in table 1.

Table 1. EPR and optical spectra for the Cr^{3+} ion in the trigonal phase of a LaAlO_3 crystal.

	D at 291(1) K (10^{-4} cm^{-1})	Δg		$\Delta(^2\text{E})$ at 77 K (cm^{-1})
		At 291(1) K	At 14 K	
Calculation	-543(50)	-0.000 40(4)	-0.000 59(4)	5.7(3)
Experiment	-421(1) [2] ^a	-0.0025(15) [2]	-0.0023(15) [29]	5.4 [3]

^a The sign should be negative as shown in [29].

4. Discussion

From table 1, it can be seen that, for D and $\Delta(^2E)$, the calculated results in sign and magnitude are in good agreement with the observed values and, for Δg at 291 K, there is good agreement in sign but poor agreement in magnitude. The sources of error may be, in our opinion, as follows.

(i) The perturbation formulae, the point-charge-dipole model and the empirical d orbital are approximate; in particular, in the perturbation formulae of g -factors [16], the contribution arising from ligand spin-orbit coupling is discarded. Such a contribution has been shown [25–27] to play a significant role for some complexes involving d^3 and other d ions. However, as pointed out in [26,27], because the spin-orbit coupling constant (about 150 cm^{-1}) of the O^{2-} ion is smaller than that (about 240 cm^{-1}) of the Cr^{3+} ion, the contribution to the g -factors from the spin-orbit interaction of oxygen ligands is small for the Cr^{3+} ion in oxides. Even so, for the present calculations neglecting this contribution may be one source of error.

(ii) The calculated value of Δg is based on the assumption that the local geometry (local rotation angle and contraction factor) in the vicinity of the Cr^{3+} ion is the same as that of the host ion. However, the assumption, sometimes, is not suitable. For example, Moreno *et al* [28] pointed out that the local structural parameters in the vicinity of impurity ions differ from those in the host crystal for Mn^{2+} ions in the cubic and tetragonal phases of fluoroperovskites and Zheng [12] found that the local rotation angle ϕ for the Cr^{3+} ion in a $SrTiO_3$ crystal at the cubic-to-tetragonal phase transition is unlike that in the bulk.

(iii) There may be marked errors existing in the observed Δg -value at 291 K because it was measured more than 30 years ago [4]. This point seems to be supported by the following fact: the latter measurement showed that $\Delta g \simeq 0.0023(15)$ at 14 K [29]. From the rotation angle $\alpha \simeq 6.25 \pm 0.20^\circ$ at 14 K [3,24], we obtain $\Delta g \simeq 0.00059(4)$. The result is close to the lower limit of the observed value ($\Delta g \simeq 0.0008$). So the EPR and optical spectra (including the R-line site and splitting) for the Cr^{3+} ion in the trigonal phase of $LaAlO_3$ can be reasonably explained by using the two parameters obtained from the optical spectra of a similar crystal.

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