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Abstract. By introducing a release factor k, the expressions for calculating the splittings of the $^4A_2$ and ^2E states for $3d^3$ ions in the tetragonal phase of the perovskite structure have been established. According to these expressions, the splittings of the $^4A_2$ and ^2E states are studied for Cr^{3+} in a tetragonal $SrTiO_3$ crystal by applying the parameters obtained from optical spectra and from the EPR g-factor. It is found that, to reach a good fit between theory and experiment, the local rotation angle ϕ in the vicinity of the Cr^{3+} ion is required to be 1.8 that of the host ion.

The structure phase transition from cubic to tetragonal is known to occur in some crystals of perovskite structure at the transition temperature T_c. For $3d^n$ ions in these crystals, the phase transition can cause splittings of some energy levels. For example, the splittings of $^4A_2$ and ^2E states for the Cr^{3+}-doped $SrTiO_3$ crystal were observed from the EPR spectrum [1] and the optical spectrum [2] several decades ago. However, no satisfactory theoretical investigations have been made for these splittings. In this paper, we first of all establish the simple expressions for calculating these splittings for $3d^3$ ions in the perovskite structure by introducing a release factor k. Based on this, by assuming that the local rotation angle ϕ in the vicinity of the Cr^{3+} ions is 1.8 that of the host ion, the splittings of $^4A_2$ and ^2E for Cr^{3+} in tetragonal $SrTiO_3$ can be reasonably explained from the parameters which were obtained from the optical spectrum and the EPR g-factor and applied satisfactorily to the explanations of spin–lattice coupling coefficients G_{ij} and F_{ij} for cubic $SrTiO_3$: Cr^{3+}.

The tetragonal phase of the above perovskite structure is the result of the rotation of MX_6 octahedra around one of their tetragonal c-axes by the angle ϕ [3,4]. The rotation of the MX_6 octahedron leads to release of the MX bond along the tetragonal axis due to the acoustic–optic phonon coupling [5]. The more relaxed the above MX bond, the greater is the difference between the lengths $R_\parallel$ and $R_\perp$ (where $R_\parallel$ and $R_\perp$ are the bonding lengths parallel and perpendicular, respectively, to the tetragonal axis). Because $R_\parallel$ and $R_\perp$ are related to the lattice constants a and c, i.e.

$$R_\parallel = c/2 \qquad R_\perp = a/2\cos\phi \simeq a(1 + \tfrac{1}{2}\phi^2) \tag{1}$$

we can define a factor $k = (c/a - 1)/\phi^2$ to denote the release effect. Obviously, the more relaxed the MX bond, the larger is the factor k. Two assumptions are often used in the literature.

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(i) In the rotation, the MX_6 octahedra remain in the exact octahedral form (i.e. no release) [4, 6, 7].

(ii) The volume of the initial cubic cell and of the derived pseudo-cubic cell due to the MX_6 octahedral rotation are the same [3, 8, ,9].

For assumption (i), $k = \frac{1}{2}$ because $c/a = 1/\cos\phi \simeq 1 + \frac{1}{2}\phi^2$ and, for assumption (ii), $k = \frac{3}{2}$ because $c/a - 1 \simeq \frac{3}{2}\phi^2$ [3]. It is noteworthy that for some crystals, the two assumptions are not suitable. Usually, the factor k can be obtained from c/a and ϕ, which can be measured independently by many experimental methods, such as x-ray diffraction [10], large-angle double-crystal x-ray diffractometry [7], neutron diffraction [11] and the EPR spectrum [4] (by assuming that the local geometry of the paramagnetic probe is the same as that of host crystal). For example, for $SrTiO_3$, from the x-ray diffraction (by analysing the integrated intensity) [10], large-angle double-crystal x-ray diffractometry [7] and neutron diffraction [11] measurements, we obtain $k \simeq 0.7$.

The tetragonal distortion of the MX_6 octahedron can be represented by the bonding angle α which is defined as [12]

$$\tan\alpha = R_\perp/R_\parallel = (a/c)(1 + \tfrac{1}{2}\phi^2) \simeq (1 + \tfrac{1}{2}\phi^2)/(1 + k\phi^2). \tag{2}$$

Let us introduce $\theta = \alpha_0 - \alpha$ (where $\alpha_0 = \frac{\pi}{4}$ rad denotes the angle in cubic symmetry); in the case of small tetragonal distortions, θ is very small, and we have

$$\tan\alpha = (\tan\alpha_0 - \tan\theta)/(1 + \tan\alpha_0 \tan\theta) \simeq (1 - \theta)/(1 + \theta). \tag{3}$$

Thus, from equations (2) and (3), we obtain

$$\theta = \tfrac{1}{2}(k - \tfrac{1}{2})\phi^2. \tag{4}$$

The splitting of the $^4A_2$ state is twice the zero-field splitting D for $3d^3$ ions in an octahedron [13]. For the crystals with a small tetragonal distortion, the zero-field splitting can be expanded as

$$D \simeq D(R_0, \alpha_0) + (R - R_0)(\partial D/\partial R)_0 + (\alpha - \alpha_0)(\partial D/\partial \alpha)_0 \simeq (\alpha - \alpha_0)(\partial D/\partial \alpha)_0 \tag{5}$$

where the subscript o denotes the value in the regular octahedron. $(\partial D/\partial \alpha)_0$ is related to the spin–lattice coupling coefficient G_{11} in cubic symmetry [12], i.e.

$$G_{11} = -\tfrac{1}{3}(\partial D/\partial \alpha)_0. \tag{6}$$

Thus we have

$$D = -\theta(\partial D/\partial \alpha)_0 = \tfrac{3}{2}(k - \tfrac{1}{2})G_{11}\phi^2. \tag{7}$$

Obviously, the order parameter is the rotation angle ϕ because $D = C_2\phi^2$ [14] and equation (7) is suitable for $3d^n$ ions.

Now let us study the splitting D of Cr^{3+} in tetragonal $SrTiO_3$ from the expression. The spin–lattice coupling coefficient $G_{11} = 0.68$ cm^{-1} for $SrTiO_3:Cr^{3+}$ [15] was calculated from the theoretical formula based on Macfarlane's high-order perturbation formula. The result is consistent with the experimental value if we assume that the local elastic constants s_{ij} are about twice the host elastic constants. The assumption is reasonably physically [15. 16] and is supported by studies of the pressure dependence of the g-factor [17] (or studies of the

spin–lattice coupling coefficients F_{ij} [16]). A host rotation angle $\phi^h \simeq 1.4° \simeq 0.024$ rad at 80 K for a $SrTiO_3$ crystal was obtained in [7, 10. 11]. Substituting the values of k, G_{11} and ϕ^h into equation (7), we find that $2D \simeq 2.4 \times 10^{-4}$ cm^{-1}, which is too small when compared with the observed value (table 1). To reach a good fit between theory and experiment, we should assume that the local rotation angle ϕ^l in the vicinity of the Cr^{3+} ion is 1.8 that of host ion, i.e. $\phi^l \simeq 1.8\phi^h \simeq 0.043$ rad at 80 K. If we consider that for different local structures the local properties, including the local rotation angle, may be different, the assumption can be understood. For example, in a $SrTiO_3$: Fe^{3+} crystal, the octahedral rotation angle $\bar{\phi}$ related to the Fe^{3+}–V_0 centre is smaller than that of the FeO_6 octahedron, i.e. $\bar{\phi}$ (Fe^{3+}–V_0) $= \phi/(1.59 \pm 0.05)$ [8]. It is noteworthy that the assumption is also supported by the optical measurement for the splitting of the ^2E state. Similar to the splitting of the $^4A_2$ state, for the splitting $\Delta(^2E)$ in the tetragonal phase, we have

$$\Delta(^2E) \simeq |(\alpha - \alpha_0)\{\partial[\Delta(^2E)]/\partial\alpha\}_0| = |-\tfrac{1}{2}(k - \tfrac{1}{2})\{\partial[\Delta(^2E)]/\partial\alpha\}_0\phi^2|. \quad (8)$$

The expression shows that the splitting of the ^2E state is, as the splitting of the $^4A_2$ state, proportional to ϕ^2.

Table 1. Splittings of $^4A_2$ and ^2E states for a $SrTiO_3$:Cr^{3+} crystal at 80 K.

	Calculation		
	I[a]	II[b]	Experiment
$2D$ (cm^{-1})	2.4×10^{-4}	7.6×10^{-4}	$(8.0 \pm 0.6) \times 10^{-4}$ [1]
$\Delta(^2E)$ (cm^{-1})	0.5	1.7	1.5 ± 0.2 [2]

[a] Calculation using the host rotation angle ϕ^h.
[b] Calculation using the local rotation angle ϕ^l.

From Macfarlane's [13] high-order perturbation formula based on the strong-field scheme, we obtain

$$\{\partial[\Delta(^2E)]/\partial\alpha\}_0 = -(72B^2/D_{12}^2 + 2\xi^2/3D_{14}^2)(\partial\mu/\partial\alpha)_0$$
$$+ (96B^2/D_{12}D_{13} - 8\xi^2/9D_{14}^2)(\partial\delta/\partial\alpha)_0 \quad (9)$$

with

$$D_{12} = \Delta + 14B + 3C \qquad D_{13} = \Delta + 5B \qquad D_{14} = \Delta - 9B - 3C. \quad (10)$$

By using the point-charge dipole model, we have [15]

$$(\partial\mu/\partial\alpha)_0 = \tfrac{48}{7}eq(1 + 3p/eR.)\langle r^2\rangle/R_0^3 - \tfrac{200}{7}D_q \quad (11)$$

$$(\partial\delta/\partial\alpha)_0 = -\tfrac{36}{7}eq(1 + 3p/eR_0)\langle r^2\rangle/R_0^3 - \tfrac{200}{7}D_q \quad (12)$$

where q is the charge on the ligand and p is the dipole. The parameters used in the above formula are the same as those used in the calculations of spin–lattice coupling coefficients G_{ij} and F_{ij}[15, 16], i.e. $B = 920.48N^4$ cm^{-1}, $C = 3330.71N^4$ cm^{-1}, $\xi = 240N^2$ cm^{-1}, $\langle r^2\rangle = 2.4843N^2$ au and $\langle r^4\rangle = 16.4276N^2$ au obtained from the empirical d orbital of the Cr^{3+} ion by introducing a parameter N to denote the average covalency reduction effect;

$N = 0.938$ and $p = 0.048eR_0$ obtained from the optical spectrum and the EPR g-factor; $R_0 = 1.95$ Å obtained from x-ray diffraction data. Thus, we find that

$$\{\partial[\Delta(^2E)]/\partial\alpha\}_0 = 9300 \text{ cm}^{-1}. \tag{13}$$

Substituting this value, the factor k and the local rotation angle ϕ^l into equation (8), we obtain $\Delta(^2E) \simeq 1.7$ cm^{-1}, which is consistent with the observed value. However, if the host rotation angle ϕ^h is used, the result is rather different from the observed value (see table 1). It appears that, from EPR and optical spectra, some useful information about the local rotation angle in the structure phase transition can be obtained.

In summary, by assuming suitable local parameters, the spin–lattice coupling coefficients G_{ij} and F_{ij} in the cubic phase [15, 16], and the splittings of $^4A_2$ and ^2E states in the tetragonal phase for a SrTiO$_3$:Cr^{3+} crystal can be reasonably explained by using two adjustable parameters N and p obtained from the optical spectrum and the EPR g-factor.

Acknowledgments

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