Local Lattice Distortion near Co^{2+} in $SrLaAlO_4$ Crystal

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The local tetragonal distortion in the vicinity of substitutional Co^{2+} impurities in $SrLaAlO_4$ crystal is studied by fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ to the observed values. The result shows that the local distortion is mainly due to the elongation of metal-ligand distance $R_\perp$ perpendicular to the C_4 axis. This point is consistent with the expectation based on the consideration of ionic radius sum. This smaller tetragonal distortion of the oxygen octahedron surrounding the Co^{2+} impurity than that in the host crystal is supported by the result obtained in Cr^{3+}-doped $SrLaAlO_4$ crystal. – Pacs: 61.70Rj; 76.30Fc; 71.70Ch

Key words: Defect structure; Electronic Paramagnetic Resonance (EPR); Crystal Field Theory; $SrLaAlO_4$ Crystal; Co^{2+} Ion.

1. Introduction

The local lattice distortions in the vicinity of substitutional impurities in doped materials have generated a strong interest because the properties of solid materials are closely related to their defect structures. Some methods, such as EXAFS, magnetic resonances (EPR and ENDOR), Rutherford backscattering (RBS) channeling techniques and optical spectra, have been used to study the defect structures. When the impurity ion is a paramagnetic ion, the EPR method is an effective one for the studies of defect structures because the EPR spectra of a paramagnetic ion are very sensitive to its immediate environment. As an example, in this paper, we study the local lattice distortion of a Co^{2+} impurity center in $SrLaAlO_4$ crystal by calculating its EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$.

The $SrLaAlO_4$ crystal has a tetragonal structure similar to that of K_2NiF_4. It is a very suitable substrate material for epitaxial growth of high-T_C superconductors thin films [1] because it is chemically stable, has a low dielectric constant, and its lattice matches very well with that of high-T_C superconductors. The impurity can result in local lattice distortions and may influence the lattice match, so the above study is of interest. The study is based on the perturbation formulas of the EPR parameters for a $3d^7$ ion in a tetragonal octahedral field obtained from a cluster approach [2]. In these formulas, the contributions from the configuration interaction (CI) and covalency (CO) effect are considered, and the parameters related to both effects can be estimated from the optical spectra and the structural data of the studied system. From the study, the local lattice distortion in the vicinity of a Co^{2+} ion in $SrLaAlO_4$ is obtained, and the result is discussed by comparing with that for a Cr^{3+} ion in the same $SrLaAlO_4$ crystal.

2. Calculation

The Co^{2+} impurity replaces Al^{3+} in $SrLaAlO_4$ crystal. The Al^{3+} ion occupies the center of a tetragonally elongated oxygen octahedron with $R_\perp \approx 1.885$ Å and $R_\parallel \approx 2.121$ Å [3] (where $R_\perp$ and $R_\parallel$ denote the metal-ligand distances perpendicular to and parallel with the C_4 axis). The EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for $SrLaAlO_4$:Co^{2+} were reported [3]. In order to calculate these EPR parameters, the perturbation formulas based on the cluster approach for the $3d^7$ ion in tetragonal symmetry are used. They are [2]

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$$g_{\parallel} = 2 + \frac{4(k\alpha+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + 2\left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right]\nu_1 - 2\frac{\alpha}{\alpha'}\left[\frac{3}{x} - \frac{4}{x+2}\right]\nu_3}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}},$$

$$g_{\perp} = \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{2k\alpha}{x+2} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2\nu_4 + \frac{8}{(x+2)^2}\nu_5 + \frac{12}{x(x+2)}\nu_6 - \frac{\alpha}{\alpha'}\frac{4}{x+2}\nu_7}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}}, \tag{1}$$

$$A_{\parallel} = P\left\{-\frac{\kappa}{2}\left[2 + \frac{8\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right]}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}}\right] + \frac{4k\alpha\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right]}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}}\right\}$$

$$+ P'\frac{2\left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right]W_X + \left(\frac{\alpha}{\alpha'}\right)^2 W_Z - 4\left(\frac{\alpha}{\alpha'}\right)^2\left[\frac{3}{x} - \frac{4}{x+2}\right]W_{XZ}}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}},$$

$$A_{\perp} = P\frac{-2\kappa\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{12}{x(x+2)}\right] + \frac{8k\alpha}{x+2}}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}} + P'\frac{-\frac{12}{x(x+2)}W_X - \left(\frac{\alpha}{\alpha'}\right)^2 W_Z - \frac{32}{(x+2)^2}W_{XY} + \frac{\alpha}{\alpha'}\frac{4}{x+2}W_{XZ}}{\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}}, \tag{2}$$

with

$$\nu_1 = \frac{k'\zeta'}{3}\left[\frac{15f_1^2}{2E_{1X}} + \frac{2q_1^2}{E_{2X}}\right],\ \nu_3 = \frac{k'\zeta'}{3}\left[\frac{15f_1f_2}{2E_{1X}} - \frac{2q_1q_2}{E_{2X}}\right],\ \nu_4 = \frac{k'\zeta'}{3}\left[\frac{15f_2^2}{E_{1X}} + \frac{4q_2^2}{E_{2X}}\right],\ \nu_5 = \frac{4k'\zeta'q_3^2}{3E_{2Z}}, \tag{3}$$

$$\nu_6 = \frac{k'\zeta'}{3}\left[\frac{15f_3^2}{2E_{1Z}} + \frac{2q_3^2}{E_{2Z}} + \frac{8\rho^2}{2E_3}\right],\ \nu_7 = \nu_3/2,$$

where ζ and ζ' are the spin-orbit coupling coefficients. k and k' are the orbital reduction factors. P and P' are the dipolar hyperfine parameters. κ is the core polarization constant. x is determined from the energy splitting Δ [$= E(^4A_2) - E(^4E)$] of the ground orbital state $^4T_1$ in the tetragonal field by using the expression

$$\Delta = \frac{\zeta\alpha'^2}{3\alpha}\left[\frac{3}{x} + \frac{4}{x+2}\right] - \frac{\zeta\alpha}{6}(x+3). \tag{4}$$

The splitting Δ and the energy denominators E_{1X}, E_{1Z}, E_{2X}, E_{2Z} and E_3 can be calculated from the d-d transition energy matrices for the $3d^7$ ion in tetragonal symmetry.

The parameters α, α', f_i, q_i and W_{ij} in the above formulas are related to the configuration interaction due to the admixture among the ground and excited states, and their expressions are given in [2] (to save space, these expressions are not written here). It should be pointed out that the tetragonal field parameters D_s and D_t (which are related to the local structural data) occur in these expressions and the d-d transition energy matrices. From the superposition model [4] which has shown to be successful in explaining the crystal field parameters of $4f^n$ and $3d^n$ ions [4 - 7], the tetragonal field parameters can be written as

$$D_s = \frac{4}{7}\overline{A}_2(R_0)\left[\left(\frac{R_0}{R_\perp}\right)^{t_2} - \left(\frac{R_0}{R_\parallel}\right)^{t_2}\right],$$

$$D_t = \frac{16}{21}\overline{A}_4(R_0)\left[\left(\frac{R_0}{R_\perp}\right)^{t_4} - \left(\frac{R_0}{R_\parallel}\right)^{t_4}\right], \tag{5}$$

where $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [4, 5]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters with the reference R_0 ($= \overline{R}$). For $3d^n$ ions in octahedra, $\overline{A}_4(R_0) \approx (3/4)D_q$ [4, 5]. Many studies [5 - 7] have indicated that $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 9\sim12$, and we take $\overline{A}_2(R_0) \approx 12\overline{A}_4(R_0)$ here.

From the cluster approach, the parameters ζ, ζ', k, k', P and P' can be expressed as [2]

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),\ \zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),$$

$$k = N_t(1 + \lambda_t/2),\ k' = (N_tN_e)^{1/2}(1 - \lambda_t\lambda_e/2),$$

$$P = N_tP_0,\ P' = (N_tN_e)^{1/2}P_0, \tag{6}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficient of d electrons of a free $3d^7$ ion and that of p electrons of a free ligand ion. P_0 is the dipolar hyperfine parameter of a free $3d^7$ ion. N_γ and λ_γ ($\gamma = e_g$ or t_{2g}) are the normalization factor and the orbital mixing coefficient. They can be obtained from a semiempirical LCAO method [2, 8]. According to the method, we have the approximate relationship

$$f_\gamma = N_\gamma^2\left[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)\right] \tag{7}$$

and normalization condition

$$N_\gamma\left(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2\right) = 1, \tag{8}$$

where $S_{dp}(\gamma)$ is the group overlap integrals which can be calculated from Slater-type SCF functions [9, 10] and the average metal-ligand distance $\overline{R}$ [$= (2R_\perp + R_\parallel)/3$]. f [$\approx (B/B_0 + C/C_0)/2$] is the ratio of Racah parameters for a $3d^n$ ion in a crystal to those of free ion. For a $SrLaAlO_4$:Co^{2+} crystal, from optical spectra [3] we have

$$D_q \approx -1030\,\mathrm{cm}^{-1},$$
$$B \approx 810\,\mathrm{cm}^{-1},\ C \approx 2880\,\mathrm{cm}^{-1}. \tag{9}$$

For a free Co^{2+} ion, $B_0 \approx 1115$ cm^{-1}, $C_0 \approx 4366$ cm^{-1}, $\zeta_d^0 \approx 533$ cm^{-1} [11], $P_0 \approx 254 \times 10^{-4}$ cm^{-1} [12] and for a free O^{2-} ion, $\zeta_p^0 \approx 136\,\mathrm{cm}^{-1}$ [13]. Thus we have $f_\gamma \approx 0.693$. If we apply the structural data $R_\perp$ and $R_\parallel$ of the host $SrLaAlO_4$ crystal [3], the average distance $\overline{R}_\parallel$ (≈ 1.96 Å) is obtained. Then the integrals $S_{dp}(\gamma)$ and hence N_γ and λ_γ can be calculated. Thus we obtain $\zeta \approx 459$ cm^{-1}, $\zeta' \approx 439$ cm^{-1}, $k \approx 0.926$, $k' \approx 0.756$, $P \approx 213 \times 10^{-4}$ cm^{-1}, $P' \approx 215 \times 10^{-4}$ cm^{-1}. Substituting these parameters, the distances $R_\perp$ and $R_\parallel$ of host crystal and $\kappa \approx 0.325$ [14] into the above formulas, we can calculate the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$. The results are compared with the observed values in Table 1. It can be seen that some of the calculated values (e. g., $g_\perp$ and $A_\perp$) are in poor agreement with the observed values. So, the local lattice distortion in the vicinity of the Co^{2+} impurity should be taken into account. Since the sum of ionic radius of Co^{2+} and O^{2-} (i. e., $R \approx r_{Co^{2+}} + r_{O^{2-}} \approx 2.04$ Å [15]) is much greater than the distance $R_\perp$ (≈ 1.885 Å) but smaller than the distance $R_\parallel$ (≈ 2.121 Å) in the host $SrLaAlO_4$, we expect that the local distortion is mainly caused by the elongation of

Table 1. EPR g-factors and hyperfine structure constants for Co^{2+} in $SrLaAlO_4$ crystal.

	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^{-4}cm^{-1})	$A_\perp$ (10^{-4}cm^{-1})
Calculation[a]	1.980	4.790	−102	76
Calculation[b]	1.981	4.875	−102	96
Experiment [3]	1.975 (1)	4.870 (5)	104 (1)	101 (3)

[a] Calculated by using the structural data of the host crystal.
[b] Calculated by considering the local lattice distortion.

$R_\perp$ by an amount ΔR and assume that the distance $R_\parallel$ remains unchanged for simplicity. Thus, we obtain

$$\Delta R \approx 0.04\ \text{Å and } R_\perp \approx 1.925\ \text{Å} \tag{10}$$

by fitting the calculated EPR parameters to the observed values (so $R_\perp$ is closer to the sum of the ionic radius of Co^{2+} and O^{2-}). The comparisons between the calculated and observed EPR parameters are shown in Table 1. It should be pointed that in the calculation $S_{dp}(\gamma)$ and hence N_γ and λ_γ are slightly changed because of the small change of $\overline{R}$. Thus, the parameters used in the above calculation become $\zeta \approx 459$ cm^{-1}, $\zeta' \approx 438$ cm^{-1}, $k \approx 0.925$, $k' \approx 0.755$, $P \approx 213 \times 10^{-4}$ cm^{-1}, $P' \approx 214 \times 10^{-4}$ cm^{-1}.

3. Discussions

From the above study one can find that $\Delta R > 0$. The elongation of $R_\perp$ is consistent with the expectation based on the consideration of the sum of the ionic radii and can be regarded as reasonable. Thus, the tetragonal distortion [characterized by the value of $(R_\parallel - R_\perp)$] of the oxygen octahedron surrounding the Co^{2+} impurity is smaller than that in the host crystal. This point can be supported by the following fact obtained for the Cr^{3+} impurity in the same $SrLaAlO_4$ crystal. The EPR measurement [16] showed that the zero-field splitting D of Cr^{3+} in $SrLaAlO_4$ was small but the value of D was not given in [16]). For the Cr^{3+} ($3d^3$) ion in tetragonal symmetry, we have [17]

$$D = \frac{35}{9}\left[\zeta'^2(1/E_1^2 - 1/E_3^2) - 9B\zeta\zeta'/E_2E_3^2\right]D_t. \tag{11}$$

So, the small splitting D points to the small tetragonal field parameters D_t and hence to the small tetragonal distortion $(R_\parallel - R_\perp)$ of the $(CrO_6)^{9-}$ octahedron from (5). It appears that the tetragonal distortion of the oxygen octahedron surrounding the impurity ion

may become smaller than that of the $(AlO_6)^{9-}$ octahedron in the host $SrLaAlO_4$ crystal when the impurity ions have greater ionic radii than the replaced Al^{3+} ion (note: $r_{Co^{2+}} \approx 0.72$ Å, $r_{Cr^{3+}} \approx 0.63$ Å and $r_{Al^{3+}} \approx 0.51$ Å [15]). This point may be useful for studies of the lattice match of $SrLaAlO_4$ with epitaxial thin films.

The hyperfine structure constant given in [3] is nearly isotropic, i.e., $A_{\parallel} \approx A_{\perp}$. This point is very difficult to be understood because the $(CoO_6)^{10-}$ octahedron is tetragonally distorted and the g-tensor is very anisotropic. In our calculation, the values of $A_{\parallel}$ and $A_{\perp}$ are indeed close to each other (i.e., $|A_{\parallel}| \approx |A_{\perp}|$), however, the sign of $A_{\parallel}$ is opposite to that given in [3], so the A-tensor is also anisotropic. Because of the poorly resolved structure of the hyperfine lines in the experiment [3], the sign of $A_{\parallel}$ should be further studied.

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