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Electric-field effect on electron-paramagnetic-resonance spectra for a substitutional Co^{2+} ion in crystalline $SrCl_2$

Zheng Wen-Chen
Chinese Center of Advanced Science and Technology (CCAST) (World Laboratory), P.O. Box 8730, Beijing 100 080, People's Republic of China;
*Department of Material Science, Sichuan University, Chengdu 610 064, People's Republic of China;**
and International Center for Materials Physics, Academia Sinica, Shenyang 110 015, People's Republic of China

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The effect of an electric field applied along the [111] direction on the EPR spectra of $SrCl_2$:Co^{2+} has been investigated theoretically on the basis of a formula of zero-field splitting derived under the weak-field approximation by taking into account only the electric-field-induced displacement of Co^{2+} ions along the [111] direction. It is found that the observed effect of the electric field can be attributed primarily to this displacement. This situation is similar to that in the case of a $SrCl_2$:Mn^{2+} crystal. It appears that the electric-field-induced displacement of the central metal ions is of importance for the understanding of the effect on the EPR spectra due to an applied electric field for smaller-sized impurities in crystals with inversion symmetry. Since the electric-field effect in $SrCl_2$:Co^{2+} is much larger than that in $SrCl_2$:Mn^{2+}, we conclude that there is a stronger dependence of the zero-field splitting on the trigonal distortion for Co^{2+} ions than for Mn^{2+} ions.

I. INTRODUCTION

First-order (linear) electric-field effects on the electron-paramagnetic-resonance (EPR) spectra of transition-metal ions have been extensively investigated for systems lacking inversion symmetry. The applied electric field induces a splitting of each of the EPR lines. This effect can be explained in second-order perturbation theory by assuming that the applied electric field together with the odd internal crystal fields, which are present as a consequence of the lack of inversion symmetry, produces extra splitting similar to those of even internal crystal fields.[1-3] For systems with inversion symmetry, this effect, in principle, cannot be observed. However, for certain cubic systems with inversion symmetry, such as $SrCl_2$:Mn^{2+} and $SrCl_2$:Co^{2+} crystals, a zero-field splitting (ZFS) induced by the electric field has been found.[4,5] For $SrCl_2$:Co^{2+}, Roelfsema and den Hartog[5] found that the change of the resonant magnetic field ΔH depends quadratically on the applied electric-field strength E (i.e., $\Delta H \propto E^2$). For the case $E \| [111]$, they obtained[5]

$$\Delta H = \frac{3D^2}{4g^2\mu_B^2 H_0}[\sin^4\theta' - 8\sin^2\theta'\cos^2\theta'] , \qquad (1)$$

where D denotes the ZFS induced by the electric field and the other symbols are as defined in Ref. 5, and so $|D| \propto E$. For $E = 6$ kV/mm, the value $|D| = 0.0432$ cm^{-1} was obtained. They took the above behavior as a completely different type of electric-field effect and ascribed it at least partly to the electric-field-induced displacements of the central impurity ions. The main reason why this happens is that here the impurity is small compared with the cation of the host lattice. Based on this point of view, Bai and Xu[6] calculated theoretically the induced ZFS's as a function of the relative displacements between the central impurity ion and each of the ligands and found quantitative estimates $\alpha = -4.23 \times 10^{-5}$ Å mm/kV (parallel to the electric field) and $\beta = 8.78 \times 10^{-5}$ Å mm/kV (perpendicular to the electric field) for the displacement coefficients. However, we find three issues concerning this analysis that deserve further scrutiny.

(i) In their calculation,[6] the formula for the ZFS of the $^4A_2$ ground state for $d^{3,7}$ ions in trigonal symmetry given by Macfarlane[7] was used. As is well known, this formula is based on the strong-field approximation and works well only for systems with a strong cubic crystal field (in general, $Dq/B > 2$). However, from the optical spectra of $SrCl_2$:Co^{2+} (Ref. 8), we find $Dq \approx 180$ cm^{-1}, which is much smaller than the Racah parameter B (≈ 750 cm^{-1}). So, Macfarlane's formula is inapplicable here and the values of the displacement coefficients α and β for $SrCl_2$:Co^{2+} obtained in Ref. 6 are therefore questionable. The perturbation formula of ZFS based on the weak-field approximation should be used in $SrCl_2$:Co^{2+} crystal instead.

(ii) In Ref. 6, under the influence of an applied electric field, the displacements perpendicular to this electric field are larger than those parallel to it. This situation is not physically reasonable because $SrCl_2$ is a cubic crystal with inversion symmetry. If the displacements in Ref. 6 are given only relative to the $(CoCl_8)^{6-}$ group, because this group is restricted within the crystal, the large outward displacements of ligands along a direction perpendicular to electric field are still difficult to understand. In fact, a reasonable displacement behavior should be the displacement of Co^{2+} ions (or ligands) only along the direction of the electric field. The ligands' outward displacement perpendicular to the electric field due to electrorestriction is very small and can be ignored.

(iii) In view of the fact that the ionic radius of Co^{2+}

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(=0.72 Å, Ref. 9) is much smaller than that of Sr^{2+} (=1.12 Å, Ref. 9) which it replaces and hence a substantial reduction in the force constant in the vicinity of Co^{2+} ion is in effect, the displacement coefficient α given in Ref. 6 is too small to be regarded as reasonable. In the following we will make a rough estimate of it. Winsum, den Hartog, and Lee[10] calculated theoretically the shape of the potential-energy well of Mn^{2+} as an impurity in $SrCl_2$ by using the polarizable-point-ion model and found that the potential energy curve for displacement in the [111] direction is flat within 0.01 eV over a distance u of 0.5 Å (a similar behavior also occurs—but the potential-energy curve is not so flat—in the other directions). The result is in agreement with experiment. Because Co^{2+} and Mn^{2+} ions have the same ionic charge and nearly equal ionic radius (the ionic radius of Mn^{2+} is 0.80 Å, Ref. 9), we can assume that the form of potential well acting at a Co^{2+}-ion site in $SrCl_2$ crystal is similar to that acting at a Mn^{2+}-ion site. For simplicity, the harmonic approximation, i.e., $U=\frac{1}{2}ku^2$, is used here, from the U and u given above, we have

$$k \approx 1.28 N/m \ . \tag{2}$$

When the electric field E_{ex} is applied along the [111] direction, the new force-balance equation becomes

$$qE_{in}=ks \ , \tag{3}$$

where s denotes the electric-field-induced displacement of a Co^{2+} ion along the [111] direction, and

$$E_{in}=\frac{\epsilon+2}{3}E_{ex} \ , \tag{4}$$

E_{in} and E_{ex} denote the internal and external electric fields, respectively. ϵ (=9.19, Ref. 11) is the dielectric constant of the $SrCl_2$ crystal. Thus, one can obtain the displacement coefficient

$$\alpha=s/E_{ex}\approx 9\times 10^{-3} \text{ Å mm/kV} \ . \tag{5}$$

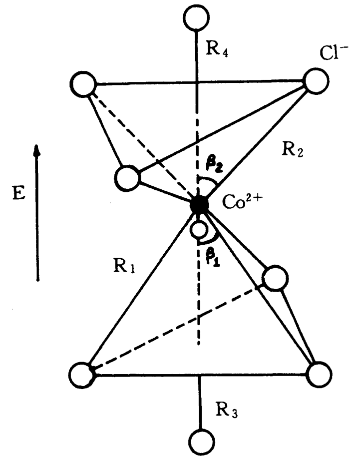

FIG. 1. The local structural parameters for a Co^{2+} ion in $SrCl_2$ crystal. The small open circle denotes a Co^{2+}-ion site without displacement.

Obviously, this result is two orders of magnitude larger than that given in Ref. 6. So, the value of α in Ref. 6 must be considered as unreliable.

From the reasons given above, the theoretical investigation of the electric field effect on the EPR spectra for the $SrCl_2$:Co^{2+} crystal should be done with use of the correct formula of ZFS and the above ionic-displacement model. This is the aim of the present paper.

II. CALCULATION

Under the action of the electric field along the [111] direction, the displacement of Co^{2+} takes place along this direction. This causes the structure of the $(CoCl_8)^{6-}$ group to distort and deviate from its original cubic O_h symmetry to C_{3v} symmetry. The local structural parameters (see Fig. 1) are

$$R_1=(R_0^2+\tfrac{2}{3}R_0 s+s^2)^{1/2}, \quad R_2=(R_0^2-\tfrac{2}{3}R_0 s+s^2)^{1/2}, \quad R_3=R_0+s, \quad R_4=R_0-s, \quad \cos\beta_1=(\tfrac{1}{3}R_0+s)/R_1 \ , \\ \cos\beta_2=(\tfrac{1}{3}R_0-s)/R_2 \ , \tag{6}$$

where R_0 (≈ 3.02 Å) is the anion-cation distance in $SrCl_2$.

The high-order perturbation formula based on the weak-field approximation for the ZFS of the $^4A_2$ ground state of $d^{3,7}$ ions in a trigonal crystal field is[12]

$$\begin{aligned} D=\tfrac{1}{2}\xi^2[&-16X/D_1D_6+40X/3D_2D_3+25X/7D_2D_4+4X/D_2D_6+100X/21D_1D_7-8(\tfrac{10}{3}D_\tau+\tfrac{3}{2}D_\sigma)/9D_3^2 \\ &+5(\tfrac{5}{21}D_\tau+\tfrac{39}{70}D_\sigma)/7D_4^2+2D_\sigma/3D_4D_5-10(\tfrac{3}{14}D_\tau-\tfrac{5}{7}D_\sigma)/3D_4D_6-50(\tfrac{13}{7}D_\tau+\tfrac{2}{7}D_\sigma)/21D_4D_7 \\ &+(\tfrac{5}{9}D_\tau-\tfrac{3}{2}D_\sigma)/9D_5^2+35D_\tau/27D_5D_6-50D_\tau/81D_5D_7+(\tfrac{10}{3}D_\tau+\tfrac{3}{2}D_\sigma)/3D_6^2+10(\tfrac{50}{63}D_\tau-\tfrac{9}{14}D_\sigma)/3D_6D_7 \\ &-25(\tfrac{190}{63}D_\tau-\tfrac{9}{14}D_\sigma)/63D_7^2-5X/3D_2D_5]-\tfrac{160}{3}X\xi^2D_q/D_1D_2D_3 \ , \end{aligned} \tag{7}$$

where ξ is the spin-orbit coupling coefficient. The energy denominators D_i $(i=1-7)$ are given in Ref. 12. From the point-charge-dipole model, we have

$$D_q=-\tfrac{1}{54}eq(1+5p/eR)\langle r^4\rangle[3/R_1^5+3/R_2^5+1/R_3^5+1/R_4^5] \ , \tag{8}$$

$$D_\tau = -eq(1+5p/eR)\langle r^4\rangle \left\{ \tfrac{1}{56}[(35\cos^4\beta_1 - 30\cos^2\beta_1 + 3)/R_1^5 + (35\cos^4\beta_2 - 30\cos^2\beta_2 + 3)/R_2^5 + 8/3R_3^5 + 8/3R_4^5] - \left[\frac{\sqrt{2}}{8}\sin^3\beta_1\cos\beta_1\right]\Big/R_1^5 - \left[\frac{\sqrt{2}}{8}\sin^3\beta_2\cos\beta_2\right]\Big/R_2^5 \right\}, \tag{9}$$

$$D_\sigma = -\tfrac{3}{14}eq(1+3p/eR)\langle r^2\rangle[2/3R_3^3 + 2/3R_4^3 + (3\cos^2\beta_1 - 1)/R_1^3 + (3\cos^2\beta_2 - 1)/R_2^3], \tag{10}$$

$$X = D_\tau/3 - D_\sigma/5, \tag{11}$$

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

From the empirical d orbital of Co^{2+} ion obtained from a great many experimental data of optical spectra for the crystals containing Co^{2+} ion and by using an adjustable parameter N to denote the average covalency reduction effect, we have[13]

$$B = 1063.2N^4\ \text{cm}^{-1},\quad C = 3879.4N^4\ \text{cm}^{-1},\quad \xi = 535N^2\ \text{cm}^{-1},\quad \langle r^2\rangle = 2.357N^2(\text{a.u.})^2, \quad \langle r^4\rangle = 19.4538N^2(\text{a.u.})^4. \tag{12}$$

The parameters p and N can be obtained from the optical spectra of the studied crystal. For $SrCl_2{:}Co^{2+}$, Bai and Xu[6] obtained $N = 0.918$ and $p = 0.193eR$ from the optical spectra.[8] Thus, substituting the parameters N, p, and R_0 into the above formulas, one can find that, in order to fit $|D| = 0.0432\ \text{cm}^{-1}$ caused by the electric field $E = 6$ kV/mm, the displacement of a Co^{2+} ion should be

$$s = 0.024\ \text{Å}. \tag{13}$$

If we assume that the induced displacement s depends linearly on the external electric-field strength, then

$$\alpha = s/E_{\text{ex}} \approx 4\times 10^{-3}\ \text{Å mm/kV}. \tag{14}$$

III. DISCUSSION

From the above calculation, one finds that the displacement coefficient α is close to the approximate theoretical estimate given in Eq. (5). This shows that the observed effect of an electric field on the EPR spectra of $SrCl_2{:}Co^{2+}$ can be explained mainly by the displacement of the central impurity ions along the [111] direction. This situation is similar to that in the case of $SrCl_2{:}Mn^{2+}$.[4] In fact, in order to explain the fact that the observed electric-field effect on the EPR spectra for $SrCl_2{:}Co^{2+}$ at 4.2 K is much larger than that for $SrCl_2{:}Mn^{2+}$ at about 77 K, Roelfsema and den Hartog[5] put forward two possibilities: (i) This, however, does not mean that the shift of the Co^{2+} ion induced by the external electric field is much larger. The shape of a potential well acting at a Co^{2+} impurity site is similar to that acting at a Mn^{2+} impurity site, but the EPR spectra of Co^{2+} ions in crystals may be more sensitive to local structural distortions than those of Mn^{2+} ions. (ii) There is also another possibility for which the central harmonic well is much less significant than for $SrCl_2{:}Mn^{2+}$. This may lead

TABLE I. The spin-lattice coupling coefficient G_{44} and the zero-field splitting for Co^{2+} and Mn^{2+} ions in some crystals.

	$\lvert G_{44}\rvert$ (cm^{-1} per unit strain)	D (cm^{-1})	References
$SrCl_2{:}Co^{2+}$	13.8[a]		16
$SrCl_2{:}Mn^{2+}$	0.37[a]		16
$ZnS{:}Co^{2+}$	81.8		17
$ZnS{:}Mn^{2+}$	0.18		18
$ZnO{:}Co^{2+}$		2.75	19
$ZnO{:}Mn^{2+}$		±0.0236	20
$CdS{:}Co^{2+}$		0.67	21
$CdS{:}Mn^{2+}$		0.000 82	22
$CdSe{:}Co^{2+}$		0.77	23
$CdSe{:}Mn^{2+}$		0.001 56	24

[a] A rough estimate from the zero-field splitting induced by the stress along [111] direction and by using the elastic constants of $SrCl_2$ crystal because the reasonable local elastic constants are difficult to obtain.

to ionic displacements that are larger than those for $SrCl_2$:Mn^{2+} crystal. On the basis of the above calculations, possibility (ii) may, in principle, be ruled out and the large electric-field effect of $SrCl_2$:Co^{2+} can be ascribed mainly to a stronger dependence of the ZFS of Co^{2+} ions on structural distortions. This point is also supported by the following facts.

(i) In our previous papers,[14,15] we pointed out that the spin-lattice coupling coefficient G_{44} for d^n ions in cubic symmetry denotes the dependence of the ZFS D on the trigonal distortion. For d^n ions in four-fold and eight-fold cubic coordination, we have[15]

$$G_{44}=\frac{4}{9}\left[\frac{\partial D}{\partial \ln R_1}\right]_0-\frac{\sqrt{2}}{9}\left[\frac{\partial D}{\partial \beta}\right]_0 . \tag{15}$$

In fact, the value of G_{44} for Co^{2+} is much larger than that for Mn^{2+} in the same crystal (see Table I), suggesting that the above dependence is stronger for Co^{2+} than for Mn^{2+}. This can explain why both the stress-induced[16] and the electric-field-induced ZFS's are much larger for $SrCl_2$:Co^{2+} than for $SrCl_2$:Mn^{2+}.

(ii) The local geometries of Co^{2+} and Mn^{2+} ions located at the same site of a crystal are similar because both ions have the same charge and nearly equal ionic radius. However, the ZFS's of Co^{2+} in the trigonal site of crystals are much larger than those of Mn^{2+} (see Table I). So, the ZFS depends more strongly on the trigonal distortion for Co^{2+} than for Mn^{2+}.

It is noteworthy that on the basis of our calculation, we find that the ZFS does not change linearly with the displacement (and hence with the electric field), but increases faster with growing displacement, particularly, in the case of large ionic displacement. The reasons, in our opinion, may be given as follows: (i) The contribution of anharmonic terms of potential well to the ionic displacement has not been taken into consideration. (ii) Besides the displacement of Co^{2+} ions, other factors caused by the external electric field, such as the change in the dipoles, have not been taken into account either. (iii) Crystal-field theory and the empirical d-orbital description are approximate.

Even so, from what is mentioned above, it can be concluded that the electric-field effect on the EPR spectra of $SrCl_2$:Co^{2+} crystals is mainly due to the displacement of central impurity ions. This situation seems equally applicable to other similar cases of smaller-sized impurities.

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[*] Mailing address.

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