Electron-spin-resonance studies of Cr-ion pairs in LiNbO$_3$:Cr^{3+}

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Electron-spin-resonance studies are carried out on a ferroelectric LiNbO$_3$ single crystal doped with 0.8 wt% chromium. Spectra are obtained at 293 and 77 K. Besides the spectrum of single-Cr-ion transitions, additional characteristics are interpreted as originating from transitions of isolated Cr-ion pairs. The results from our spin-Hamiltonian calculations are in agreement with the experimental results.

Ferroelectric behavior and related properties in crystals of LiNbO$_3$, BaTiO$_3$, and PbTiO$_3$, etc., have been investigated in part by substituting a paramagnetic impurity such as Cr^{3+}, Mn^{2+}, or Fe^{3+} for a small fraction of the positive ions (in the case of LiNbO$_3$, see Refs. 1–12). The impurity ions, such as Cr^{3+}, then serve as a sensitive probe for investigating the crystalline environment and its response to ambient changes (e.g., phase transition).

The structure of LiNbO$_3$ has been investigated by Abrahams, Reddy, and Bernstein.[13] Below the ferroelectric Curie temperature T_C (1190 °C), the crystal is rhombohedral, belonging to the space group $R\,3c$ (C_{3v}^6) at room temperature. In the ferroelectric state the Li and Nb ions of LiNbO$_3$ are surrounded by six oxygen atoms arranged in a distorted octahedron and lie along the c_3 axis of the octahedron but away from its center. Initially it was suggested that the preferential substitution site for Cr^{3+} in LiNbO$_3$ is the Nb site,[14,4] but recent experimental and theoretical studies [ESR, electron nuclear double resonance (ENDOR), and cluster calculations] support Li substitution for various trivalent-cation dopants.[9,15,16]

In the observed ESR spectrum of Cr^{3+} in LiNbO$_3$, forbidden transition intensity such as the $-3/2 \rightarrow 3/2$ transition is anomalously high and not all resonance lines can be attributed to the single Cr^{3+} ion.[4,11] Besides the main spectrum of the single Cr ion at a Nb site, one small additional peak is attributed to Cr^{3+} at the Li site and another, together with a low-field transition at 390 G, is proposed to arise from Fe^{3+} (Ref. 4). The low-field transition, although close to the Fe^{3+} line,[6] behaves differently in field rotation from the Fe line. Besides, Fe lines can be distinguished by the annealing effect in hydrogen atmosphere at about 1000 °C.[9] This work shows that reinterpretation of the low-field transition is possible on the basis of Cr-ion-pair transitions.

In studying the EPR spectrum of a LiNbO$_3$:Cu^{2+} single crystal, it is noticed that the low-field transition intensity increases with Cu^{2+} doping and this leads to a consideration of the interaction of neighboring Cu^{2+} ions by Zhao and Yan.[17] The transition of isolated ion pairs in

the EPR spectrum was proposed in 1952 by Bleaney and Bowers[18,19] to explain the anomalous behavior in the susceptibility and EPR spectrum of copper acetate monohydrate. The influence of ion pairs and, further, that of the interaction between the central metal ion and the next neighbors on the EPR spectra are studied extensively [e.g., in spinel (Refs. 20 and 21) and in emerald and beryl (Refs. 22 and 23)]. It was recently proposed that low-field microwave absorption in high-T_c superconducting copper oxides is spin-resonance absorption due to Cu^{2+}-Cu^{2+} pairs[17,25,26] or, at least, possesses spin-resonance components.[27] The ESR spectrum of nonpiezoelectric single crystals was also studied, showing that the ESR spectra are not interfered by piezoelectric resonances.[28] This study of spin-resonant low-field absorption is based on a comparison between the EPR spectra of high-T_c cuprates and those of LiNbO$_3$:Cu^{2+} or LiNbO$_3$:Cr^{3+}. Hence, it is important to substantiate the corrections of this procedure by a concrete spectrum analysis. This report shows that Cr^{3+}-ion-pair transitions, together with single-Cr^{3+}-ion transitions, provide a satisfactory interpretation of the EPR spectrum of LiNbO$_3$:Cr^{3+}.

In addition to the low-field transition detected in the X-band ESR spectra of Ref. 4, small additional lines in the Q-band ESR of LiNbO$_3$:Cr^{3+} with their symmetry characteristics have been investigated[9] and attributed to a variety of perturbed centers containing single Cr^{3+} ions. Then the ESR measurements in the Q band for Cr^{3+}-ion pairs in LiNbO$_3$ have been briefly reported.[11] Hence, our X-band results for Cr^{3+}-ion pairs in LiNbO$_3$, which are distinguishable from the "fine structure" of the ESR spectra due to other low-symmetry paramagnetic centers, are of interest to ascertain the generality of the ion pairs.

A large single crystal of LiNbO$_3$:Cr^{3+}(0.8 wt. %) is pulled from the melt by use of the Czochralski technique. The crystal axes are checked by x-ray analysis. ESR measurements are carried out on the LiNbO$_3$ crystal by using a Bruker ER-200D spectrometer in the 3-cm wavelength range. Figure 1(a) shows the spectrum at 293 K, in which lines 1–6 are identified as transitions of isolated

Cr^{3+} ions.[4] Some small additional lines due to perturbed paramagnetic centers of Cr^{3+} ions at the vacant sites[9] are also observed (the two small peaks on the right of line 1 and the twist of the rising side of line 3) but a detailed comparison is beyond the scope of this work.

To show that the other resonance lines arise from ion-pair transitions, their angular and temperature dependences are studied. Here we only show a crucial comparison of the theory with the spectra under special conditions. Figure 1(b) shows another spectrum of the specimen at 77 K as the magnetic field is rotated from the c axis by 15°. It can be seen that some lines disappear completely but others appear.

The ESR spectrum of the isolated Cr^{3+} ion is well known.[4] The main spectrum with **H** parallel to the c axis of the crystal is described with the axially symmetric spin Hamiltonian,

$$\mathcal{H}_s = g_z \beta H S_z + \tfrac{1}{3} D O_2^0$$

$$= g_z \beta H S_z + D \left[S_z^2 - \tfrac{1}{3} S(S+1) \right], \tag{1}$$

where O_2^0 is the spin operator of Orbah.[29] After fitting, we obtain $q_z = 1.96$ and $D = 0.39$ cm^{-1} (4267 G), which are in agreement with previous results but D is smaller than the value of 0.45 cm^{-1} reported by Burns *et al.*[2] and the value of 0.41 cm^{-1} reported by Rexford *et al.*[4] All the transitions for the magnetic field **H** along the z axis (c axis) are given as follows:

FIG. 1. (a) ESR spectrum of LiNbO$_3$:Cr^{3+}. Microwave frequency, 9.764 GHz; power, 10 dB, 21 mW; gain, ×10^5; test temperature 293 K; **H**$\|c$. (b) ESR spectrum of LiNbO$_3$:Cr^{3+}. Microwave frequency, 9.549 GHz; power, 10 dB, 21 mW; gain, 5×10^3; test temperature 77 K; the field H is rotated from the c axis by 15°.

Line	1	2	3	4	5	6
Transition (G)	$\left\|-\tfrac{3}{2}\right\rangle \rightarrow \left\|\tfrac{3}{2}\right\rangle$	$\left\|\tfrac{1}{2}\right\rangle \rightarrow \left\|-\tfrac{3}{2}\right\rangle$	$\left\|-\tfrac{1}{2}\right\rangle \rightarrow \left\|\tfrac{1}{2}\right\rangle$	$\left\|-\tfrac{1}{2}\right\rangle \rightarrow \left\|-\tfrac{3}{2}\right\rangle$	$\left\|-\tfrac{3}{2}\right\rangle \rightarrow \left\|\tfrac{1}{2}\right\rangle$	$\left\|-\tfrac{3}{2}\right\rangle \rightarrow \left\|-\tfrac{1}{2}\right\rangle$
H (calculated) (G)	1186	2488	3559	4975	6047	12 094
H (observed) (G)	1200	2405	3520	5070	6045	12 100

The 3520-G peak is the main central transition and it is noted that the allowed transitions ($\Delta m_s = \pm 1$) are much stronger than the forbidden ones ($\Delta m_s = \pm 2$) except for the transition $-\tfrac{3}{2} \rightarrow \tfrac{3}{2}$. One reason for this relatively large amplitude even for smaller Cr^{3+} concentrations is that the energy of this transition with **H**$\|c$ axis is independent of D like that of the $-\tfrac{1}{2} \rightarrow \tfrac{1}{2}$ transition. As the Cr^{3+} concentration increases, the effect of Cr^{3+} pairs may be more noticeable.

The large charge misfit of Cr^{3+} at a Nb or Li site causes lattice distortion, and nonlocal charge compensation is more probable than the local effect. It is likely that another Cr^{3+} ion will replace the nearby Li^{1+} or Nb^{5+} to restore the charge balance. One major competitive mechanism is the charge compensation due to accidental impurities. Even for nominally pure crystals, there are omnipresent Al^{3+} impurities which may come from the vapor of the aluminum oxide powder used in the crystal growth. Another accidental impurity is iron, which can always be detected. Their concentrations are assumed to be smaller by at least one order of magnitude than 0.8 wt. % (=0.46 at. %) (as comparison, Al, 0.01 at. % and Fe 0.001 at. % are determined in Ref. 11 using the same crystal growth technique and similar pure ma-
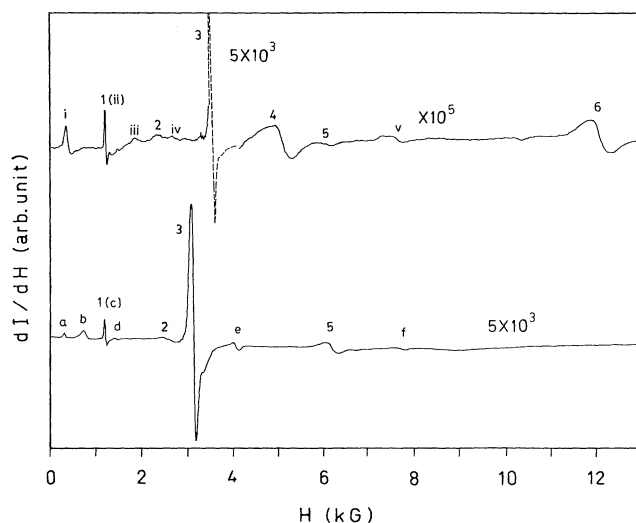
terials). For light doping of Cr^{3+}, Cr^{3+}, (at a Nb or Li site) -Al^{3+} (at a Li or Nb site) pairs are formed and it is difficult to determine which of the Cr^{3+}-Al^{3+} and Cr^{3+}-Cr^{3+} compensation pairs dominates due to the fact that both concentrations are nearly equal. However, for a higher concentration of Cr^{3+} (> 0.02 at. %), incidently present Al or Fe ions are insufficient for full compensation and the close exchange-coupled Cr^{3+}-Cr^{3+} pairs are to play an important role. Certain Q-band ESR lines were suggested to be due to Cr-ion pairs based on their characteristics (sextet). The axial crystal-field parameters in Ref. 11 are 0.392 and 0.164 cm^{-1} for single-ion and pair transitions respectively. It is desirable to compare the X-band ESR results for Cr^{3+} pairs in LiNbO$_3$ with those obtained through measurements in the Q band.[11]

The axially symmetric Hamiltonian of the Cr^{3+}-ion pair is a simple generalization of that of a single isolated Cr^{3+} ion of Eq. (1). It consists in the first instance of the sum of the separate Hamiltonians for two different chromium ions, each in the form of Eq. (1). To this must be added a term representing the superexchange interaction. The perturbation Hamiltonian for Cr^{3+}-ion pairs then takes the form (for simplicity, assuming only one g factor)

$$\mathcal{H}_p = \mathcal{H}_s(1) + \mathcal{H}_s(2) + J\mathbf{s}_1\cdot\mathbf{s}_2$$

$$= g_z\mu_B H[\mathbf{s}_z(1) + \mathbf{s}_z(2)] + D_1\mathbf{s}_z^2(1)$$

$$+ D_2\mathbf{s}_z^2(2) - \tfrac{5}{4}(D_1 + D_2) + J\mathbf{s}_1\cdot\mathbf{s}_2 \qquad (2)$$

where subscripts 1,2 refer to two ions, D_1 and D_2 are different due to the fact that the two ions are at different sites. Since $\mathbf{s}_1\cdot\mathbf{s}_2 = \tfrac{1}{2}[S(S+1) - 15/2]$, where S is the total effective spin of the resulted states of the two ions, the centers of gravity of the four spectroscopic states with $S = 3,2,1,0$ are at energies $(9/4)J$, $(-3/4)J$, $(-11/4)J$,

and $(-15/4)J$ at zero magnetic field, respectively; i.e., the largest term in Eq. (2), the Heisenberg exchange is first diagonalized. The resonance transitions are allowed only between states having the same total spin. The resulting states are $|(\tfrac{3}{2},m_s;\tfrac{3}{2},m_s')S,M_S\rangle$ (the single-ion state symbols will be neglected in the coupled states), for example,

$$|3,0\rangle = \frac{1}{\sqrt{20}}(|\tfrac{3}{2}, -\tfrac{3}{2}\rangle + 3|\tfrac{1}{2}, -\tfrac{1}{2}\rangle + 3|-\tfrac{1}{2}, \tfrac{1}{2}\rangle + |-\tfrac{3}{2}, \tfrac{3}{2}\rangle).$$

The expressions for energy levels are obtained for $\Delta m_s = \pm 1$ as

$$g_z\mu_B H \pm \tfrac{6}{5}(D_1 + D_2) \text{ for } |1,\pm 1\rangle\leftrightarrow|1,0\rangle; \quad g_z\mu_B H \pm (D_1 + D_2) \text{ for } |3,\pm 3\rangle\leftrightarrow|3,\pm 2\rangle;$$

$$g_z\mu_B H + \tfrac{3}{5}(D_1 + D_2) \text{ for } |3,\pm 2\rangle\leftrightarrow|3,\pm 1\rangle; \quad g_z\mu_B H + \tfrac{1}{5}(D_1 + D_2) \text{ for } |3,\pm 1\rangle\leftrightarrow|3,0\rangle;$$

where the transition between $|2m_s\rangle$ does not appear since they do not lead to any difference in transition energy compared with those of the single ion, and for $\Delta m_s = \pm 2$ similar expressions can be readily found. With the aid of these expressions, the transitions labeled i to v are identified. The fitted parameters are $g_z = 1.96$ and $D_1 + D_2 = 0.36$ cm^{-1} (3949 G). The parameter $D_1 + D_2$ is not necessarily associated with the single-ion parameter D, since they have different crystalline environments. The value $\tfrac{1}{2}(D_1 + D_2) = 0.18$ cm^{-1} compares well with the result of 0.164 cm^{-1}.[11] The following transitions are obtained:

Line	i	ii	iii	iv	v
Transitions	$\lvert 3,-2\rangle\to\lvert 3,-3\rangle$	$\lvert 1,1\rangle\to\lvert 1,0\rangle$ $\lvert 3,2\rangle\to\lvert 3,1\rangle$	$\lvert 3,-1\rangle\to\lvert 3,1\rangle$	$\lvert 3,1\rangle\to\lvert 3,0\rangle$	$\lvert 3,-3\rangle\to\lvert 3,-2\rangle$
H (calculated) (I)	392	1182 1188	1779	2769	7511
H (observed) (G)	390	1200	1885	2760	7655

where all H values are in units of gauss. It can be seen that the allowed transitions of the ion pair states $|1,1\rangle\to|1,0\rangle$ and $|3,2\rangle\to|3,1\rangle$ coincide with the forbidden ones of the single-ion states, which further explains the anomalously high intensity of the transition at the low field of 1200 G. It also shows that the transitions in the $S = 3$ multiplet are enough to provide an interpretation to the isolated ion-pair spectrum, which implies that the J value is negative. The exchange path is Cr^{3+}-O^{2-}-O^{2-}-Cr^{3+} and the ab initio calculation based on the Stevens theory[30] is complicated. In the present case, we have not attempted numerical calculations of the exchange interaction. However, it is worthwhile mentioning that pairs of the first order with $J \geq 400$ cm^{-1} are in a nonparamagnetic singlet state at room temperature so that they will not be manifested in the spectra, and only the pairs of the second and third orders with the isotropic-exchange-interaction parameter $J = 1.5$ cm^{-1} are allowed in the calculations of the sextet of lines with $S = 3$ in the EPR spectrum recorded in the 8-mm range[11] and those of $S = 3$ lines in the X band here. This value of J is in the same order of magnitude as that in Ref. 22.

The temperature dependence of line intensities might manifest characteristics of transitions so as to provide an unambiguous line identification, which is based on the depopulation of high-energy states in cooling. However, it is only suitable for comparing transitions within different multiplets. It would not be applicable in our

case since there are essentially only transitions within $S = 3$ multiplet and the 1200-G line is a composite. Hence, we cool the sample to 77 K to make the $S = 3$ transitions more prominent and rotate the field to measure the angular variations.

In a continuous field rotation, lines 4 and 2 of the single-ion-state transition at 5070 G ($|-1/2\rangle \to |-3/2\rangle$) and 2488 G ($|1/2\rangle \to |-3/2\rangle$) shift toward conjugate lines 6 and 5 at 12 100 G ($|-3/2\rangle \to |-1/2\rangle$) and 6047 G ($|-3/2\rangle \to |1/2\rangle$), merge into one, and then successively disappear. Only two lines survive in the 90° rotation. The 1200- and 3520-G lines of the single-ion state transition at 0° shift to 7253 and 1800 G, respectively, at 90°. The rotation pattern was already studied by Rexford et al.[4] Figure 1(b) shows the spectrum at 15° rotation when the first conjugate pair (5070 and 12 100 G) has already disappeared but the second pair (2488 and 6047 G) is still there with only minor displacements. With parameter g_z and D, we use the standard formula for the field rotation of Abrahams and Bleaney[31] and obtain the following transitions (all in units of gauss):

	1	2	3	5
H (calculated) (G)	1200	2550	3150	6300
H (observed) (G)	1215	2600	3153	6200

between quantum states which are now a mixture of the simple states $|\tfrac{3}{2},m\rangle$.

Although the mixture of simple states may increase the intensity of the previously forbidden transition at 1200 cm^{-1}, the intensity variation of the forbidden transitions at 2600 and 6200 G shows that it should still be of low intensity. Hence, the ion-pair-state assumption is essential to interpret the lines left in the spectrum: 325, 791, 1215, 1450, 4080, and 7800 G (a,b,c,d,e,f). Except for the last two transitions, their theoretical values are 390, 720, 1190, and 1438 G, respectively, where the EPR lines b and d at 720 and 1438 G appeared as a result of state mixing in rotation. Line e at 4080 G comes from the line at 4350 G for the $M_s = 1 \rightarrow 0$ transition ($H \| c$), which has been covered by line 4 of the single-ion-state transitions (5070 G) before and appears now. The high-field resonance lines e and f at 4080 and 7800 G deter fitting by the simple spin-Hamiltonian of Eq. (2) [for rotation, an extra term $g_\perp \mu_B (H_x S_x + H_y S_y)$ is added into Eq. (2)]. They show a different character from what is described by this strong-exchange spin-Hamiltonian formalism. The angular variation of the EPR lines associated with the splitting of the $S = 3$ multiplet does not follow that of the $O_2^0(S)$ operator. For example, the conjugate lines at 390 and 7655 G when $H \| c$ axis should approach towards each other in rotation from 0° to 90° or as the energy of the microwave quantum is lowered. However, they behave oppositely—they separate in rotation as shown in Fig. 1(b). It is predominantly that expected for operators of $O_4^0(S)$, $O_4^3(S)$, $O_6^0(S)$, $O_6^3(S)$, and $O_6^6(S)$. In our case, the line at 4080 G can be fitted reasonably well together with the other lines when the operators $O_4^0(S)$, $O_4^3(S)$, and $O_6^3(S)$ are considered. However, the fitting of the 7800-G line has to take other operators into account. This empirical necessity has already been shown in Refs. 22,23 and 32,33 and its origin lies in the second-order corrections to the spin-Hamiltonian formalism for exchange-coupled ion pairs.[23] The increase of parameters may raise doubt about their reasonableness. However, the parameters obtained from the ion-pair spectra at 0° and 90° are used in the whole rotation for dozens of positions, which verifies their appropriateness.

In summary, we assign additional lines in the EPR spectra of $LiNbO_3$:Cr^3 to Cr^{3+}-ion pairs and hence, provide substantial evidence for the existence of Cr^{3+}-ion pairs in samples of $LiNbO_3$ containing 0.8 wt. % Cr^{3+}. It shows that the Cr^{3+}-ion pairs are the usual charge compensation pairs for a high-impurity concentration, as in our case, of about 0.46 at. %. In addition, it confirms the proposition that low-field resonance absorption in $LiNbO_3$:Cr^{3+} originates from Cr^{3+}-ion pairs and provides an interpretation to the anomalously high intensity of the forbidden transition in the single-ion transition. However, it is necessary to further investigate several different concentrations of Cr^{3+} in $LiNbO_3$ besides the argument of angular variation for settling the dispute whether the low-field transition at 390 G originates from the Cr^{3+}-ion pair or from Fe. We defer this to a subsequent study.

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