

of the  $V_k$  center. Such a process requires no electron acceleration by the field. However, this situation should result in an emission intensity in phase with the reference signal at twice the field frequency, in contrast to that observed.

The application of a dc field of the same peak-to-peak value as the corresponding ac field failed to give any emission intensity on the same scale as the rms signal obtained with the ac field. This is attributed to the fact that the crystal is given the opportunity to polarize and build up sufficient space charge to effectively quench the electron acceleration in the crystal.

A study of other alkali halides is being undertaken to determine the dependence of the existence or magnitude of electroluminescence on the characteristic breakdown fields of these materials. It is also hoped that frequency-dependent measurements will yield some useful information on the transport of charge carriers

in alkali-halide crystals.

\*Research supported in part by U. S. Air Force Office of Scientific Research.

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## EFFECT OF APPLIED ELECTRIC FIELD ON THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF DOPED FERROELECTRIC ROCHELLE SALT

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(Received 5 September 1967)

A linear shift of the epr lines of  $\text{Cu}^{2+}$ -doped Rochelle salt by an applied electric field has been observed in the high-temperature paraelectric phase. The shifts become asymmetric with respect to the polarity of the applied field in the ferroelectric phase and disappear at low temperatures in the antiferroelectric phase, demonstrating that it is only the instability of the crystal lattice connected with the ferroelectric transitions which makes the electric-field effect easily observable.

Bloembergen<sup>1</sup> was the first to point out that linear effects of the applied electric field on the epr spectra of ions occupying sites which lack inversion symmetry could be observed. The shifts should be particularly interesting and pronounced in ferroelectrics and in this Letter we report the first observation of this ferroelectric epr Stark effect.

Recent epr and optical studies<sup>2-4</sup> of  $\text{Cu}^{2+}$ -doped Rochelle salt<sup>5</sup> did not show significant changes in the spectra on going through the two Curie points but demonstrated that the  $\text{Cu}^{2+}$  ions are located on the sites of the Na atoms and that the 3d copper orbitals and the 2s and 2p orbitals of the four oxygen ligands (1, 7, 5, 10) form molecular orbitals with  $C_{2v}$  (and nearly

$D_{2h}$ ) symmetry. Since the  $\text{Cu}^{2+}$  sites thus lack inversion symmetry, linear effects of the applied electric field on the epr spectra<sup>1</sup> should be observable.

The measurements were made on a  $\text{CuCl}_2$ -doped Rochelle-salt crystal, containing 0.05 wt.% of  $\text{Cu}^{2+}$  ions with the electric field applied along the ferroelectric  $a$  axis. Spontaneous polarization was observed between +16 and -11°C. The hysteresis loops were found to be displaced from the center in the  $x$  and  $y$  directions, indicating the presence of an internal bias of about 950 V/cm and the stabilization of a particular direction of the spontaneous polarization due to the  $\text{Cu}^{2+}$  impurities. In the absence of the applied electric field the epr spectra

could be described by the following spin Hamiltonian:

$$\mathcal{H} = \beta \vec{H} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A} \cdot \vec{I},$$

where  $S = \frac{1}{2}$ ,  $I(\text{Cu}^{63}) = \frac{3}{2}$ , and the principal values of the  $g$  and  $A$  tensors are equal<sup>4</sup> to the following:  $g_1 = 2.046$ ,  $g_2 = 2.055$ ,  $g_3 = 2.325$  and  $A_1 = 16 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_2 = 35 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_3 = 153 \times 10^{-4} \text{ cm}^{-1}$ . There are four physically nonequivalent  $\text{Cu}^{2+}$  sites ( $A_1$ ,  $B_2$ ,  $B_3$ , and  $A_4$  in the notation of Blinc, Petkovšek, and Zupančič<sup>6</sup>) in the unit cell, which are, at least in the high-temperature paraelectric phase, all chemically equivalent and which are related by the symmetry operations of the  $P2_12_12$  space group.<sup>7</sup> Since a previous  $\text{Na}^{23}$  magnetic resonance study showed<sup>6,8</sup> that the  $A$ - and  $B$ -site electric-field-gradient tensors behave differently at the two Curie points, an orientation was selected where the existence of a small splitting between the  $A$ - and  $B$ -site epr lines allowed us to study the effects of the applied electric field on the  $A$ - and  $B$ -site  $\text{Cu}^{2+}$  ions separately.

The temperature dependence of the effect of the applied electric field on the splitting between the  $A_1$  and  $B_2$  (and  $A_4$  and  $B_3$ , respectively)  $\text{Cu}^{2+}$  resonance lines  $\Delta H = (\delta H_{A,B})_{E \neq 0} - (\delta H_{A,B})_{E=0}$  is shown in Fig. 1(a) for  $\vec{E} \perp \vec{H}$ . Since the effects are practically identical on all four  $\text{Cu}^{63}$  hyperfine lines, only the shifts for the  $m_I = \frac{1}{2}$  lines are presented. Below  $-50^\circ\text{C}$  no measurable shifts could be observed. At  $-40^\circ\text{C}$  the shifts are still small, but nevertheless very definite: When the field is applied in one (say  $+a$ ) direction, the separation between the  $A$  and  $B$  lines increases, whereas it decreases when the polarity of the field is reversed ( $-a$ ). The  $A$  and  $B$  lines thus shift in opposite directions indicating that the matrix elements  $p$  of the Hamiltonian  $\mathcal{H}_E = eEx$ , describing the interaction of the electric field in the  $a$  direction with the  $A_1$ - and  $B_2$ -site charge distributions, have opposite signs. Since in the low-temperature antiferroelectric phase (as well as in the high-temperature paraelectric phase) the  $A_1$  and  $B_2$  as well as the  $A_4$  and  $B_3$  sites are related by twofold screw axes parallel to the  $b$  direction which map  $p_a$  into  $-p_a$ , this is exactly what is expected. In the ferroelectric phase, this symmetry element disappears and the electric field effects depend on the direction of the field with respect to the natural polarity of the sample. If the field is applied

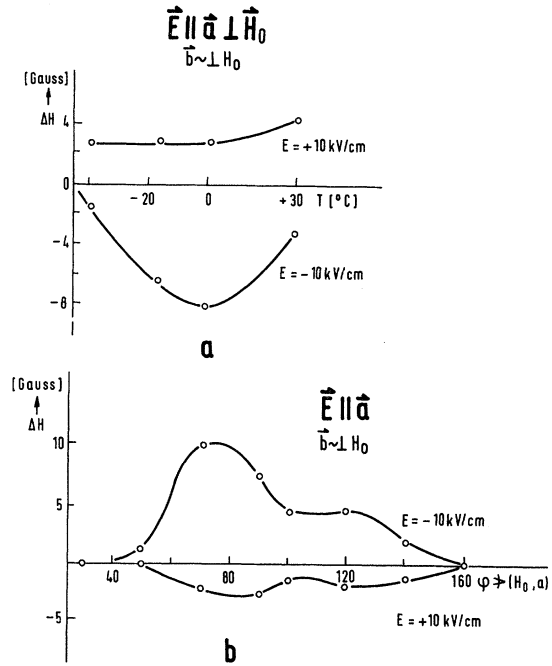


FIG. 1. (a) Temperature dependence of the effect of the applied electric field on the separation between  $A$ - and  $B$ -site  $\text{Cu}^{2+}$  lines in Rochelle salt. (b) Dependence of the electric field effect in the ferroelectric phase on the angle between  $\vec{E}$  and  $\vec{H}$ .

in the  $-a$  direction, the reduction of the splitting between the  $A$  and  $B$  lines is a factor 4 larger than in the antiferroelectric phase, whereas a field in the  $+a$  direction produces only a small enhancement of the splitting which is not much larger than the one produced by the same field strength at  $-40^\circ\text{C}$ . What is even more interesting is that it is only the  $A$ -site spectrum which seems to be anomalously shifted when the field is applied in the  $-a$  direction. The field in the  $+a$  direction produces no anomalies.

On going to the high-temperature paraelectric phase, the  $+E$  shifts increase and the  $-E$  shifts decrease, so that the electric field effects are again linear and symmetric with respect to the polarity of the applied field.

The dependence of the shifts in the ferroelectric phase on the angle  $\varphi$  between  $\vec{E}$  and  $\vec{H}$  is presented in Fig. 1(b). The shifts are largest for  $\varphi = 75^\circ$  and no effect was found for  $\vec{E} \parallel \vec{H}$ . The asymmetry of the effect with respect to the polarity of the applied field is again very pronounced.

It seems that in the two nonferroelectric phases the effects of the applied electric field on

the energy levels of the  $\text{Cu}^{2+}$  ions can be well understood by the theory developed by Ham<sup>9</sup> and Druzhinin<sup>10</sup> which shows that

$$g_{ij}(E_k) = g_{ij}^{(0)} + \sum_k T_{ijk} E_k + \dots,$$

$$A_{ij}(E_k) = A_{ij}^{(0)} + \sum_k Q_{ijk} E_k + \dots,$$

where  $T_{ijk}$  and  $Q_{ijk}$  represent third-rank tensors describing the first-order change in the  $g$  and  $A$  tensors in the external field. The theory for the ferroelectric case still has to be developed and would apparently have to take into account the asymmetric shifts of the ions in the internal electric field and the change in the effective lattice force constants with temperature.

The "Stark" effect epr method thus seems to be particularly well suited for the study of lattice instabilities in displacive ferroelectrics. For Rochelle salt the present results demonstrate that it is the surrounding of the  $A$  sites which becomes unstable or disordered at the lower Curie point and that  $B$  sites are primarily affected at the higher Curie point.<sup>8</sup> The decrease of the anomalous polarizability of the  $A$  sites for a particular direction of the applied field at the higher Curie point is probably a

consequence of the disappearance of the spontaneous polarization field. The disappearance of the effect at low temperatures further shows that it is only the instability of the system connected with the ferroelectric transitions which makes the electric field shifts easily observable.

The authors are indebted to Mr. A. Levstik for the spontaneous polarization measurements.

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## MAGNETIC MOMENT OF $\text{ZrZn}_2$ UP TO 150 kG: IS "PURE" $\text{ZrZn}_2$ FERROMAGNETIC?

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(Received 1 September 1967)

We present magnetic-moment measurements in polycrystalline and single-crystal  $\text{ZrZn}_2$  for fields to 150 kG. The high-field susceptibility is identical for all materials whereas the low-field moment varies over a wide range. The data indicate that the low-field moment is correlated with trace impurities (such as Fe and Ti) and details of preparation. We suggest a localized-moment model for ferromagnetism in impure  $\text{ZrZn}_2$  which is consistent with our results; but it is not yet clear whether or not "pure"  $\text{ZrZn}_2$  is ferromagnetic.

An interesting feature of  $\text{ZrZn}_2$  is that both Zr and Zn are nonmagnetic metals which are individually superconducting, yet the compound appears to be ferromagnetic. During the last decade numerous studies<sup>1</sup> in  $\text{ZrZn}_2$  have been pursued particularly for evidence of itinerant electron ferromagnetism. In this Letter we

present high-field magnetic-moment measurements which force us to re-examine the source of the ferromagnetism in the usual  $\text{ZrZn}_2$  compounds and to inquire whether or not "pure"  $\text{ZrZn}_2$  is ferromagnetic at all. The results are of direct interest to currently active studies of the theories of band magnetism, dilute