

Effects of Applied Electric Fields on Paramagnetic Resonance in Chrome Alums

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The paramagnetic resonance spectra of single crystals of potassium chrome alum and ammonium chrome alum have been investigated in the presence of applied electric fields at 9.3 kMc/sec in the temperature range 4–300°K. The measurements were made in an effort to detect the possible existence of a term of the form $\xi\mu_0\sigma\cdot E$ in the interaction Hamiltonian for an electron in an electromagnetic field. Such a term corresponds to the existence of an electron electric dipole moment and would result in a lifting of Kramers' degeneracy for a magnetic ion in a crystalline field. No such term was observed, and the upper limit on ξ obtained was $\xi < 0.007$. A dependence of the dielectric loss on electric field was observed in both alums at microwave frequencies.

I. INTRODUCTION

POSSIBLE implications of parity nonconservation and time-reversal noninvariance in electromagnetic interactions have been investigated theoretically by Sachs and Schwebel.^{1,2} They have generalized the electromagnetic four-potential in order to include a pseudovector part as well as a vector part. This pseudovector potential modifies the interaction Lagrangian, resulting in a Hamiltonian for spin one-half particles which is symmetrized with respect to the electric and magnetic field variables at the expense of sacrificing parity conservation and time-reversal invariance. Restrictions are imposed so that Lorentz and gauge invariance are retained. Such a theory has particular significance to the problem of the energy levels of a magnetic ion in a paramagnetic crystal. For magnetic ions which have an odd number of unpaired electrons, Kramers' theorem states that the crystalline electric field can never remove the last twofold degeneracy of the energy levels. Wigner³ has shown that such an assumption is equivalent to invariance of the Hamiltonian under time reversal. Thus, any violation of Kramers' theorem would support the theory of Sachs and Schwebel.

If P (parity) and T (time-reversal invariance) are not conserved, Sachs¹ has shown that the interaction Hamiltonian for a single $3d$ electron in a dilute para-

magnetic crystal can be expressed as follows:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \quad (1)$$

where

$$\mathcal{H}_0 = -(\hbar^2/2m)\nabla^2 + \varphi_0 - ik\sigma\cdot\nabla\varphi_0\times\nabla, \quad (2)$$

and

$$\mathcal{H}_1 = \varphi_c + \varphi_e - ik\sigma\cdot[\nabla(\varphi_c + \varphi_e)\times\nabla] - (\xi\mu_0/e)\sigma\cdot\nabla(\varphi_0 + \varphi_c + \varphi_e). \quad (3)$$

The total potential energy φ consists of three contributions: φ_0 of the free atom, φ_c due to the crystalline field, and φ_e due to an externally applied field. Here σ is the electron spin operator, μ_0 is the Bohr magneton, and ξ is a small mixing parameter. For simplicity we have assumed no nuclear spin. The last term in \mathcal{H}_0 corresponds to the spin-orbit energy, where $k = (\hbar/2mc)^2$. We shall see that the crystal structures of interest are those that lack an inversion center, in which case the spin-orbit term in \mathcal{H}_1 will give no contribution.

We may obtain the energy eigenvalues by perturbation theory, expressing $\langle\mathcal{H}_0\rangle$ in terms of the free atom eigenfunctions $|n\rangle$.

$$\mathcal{H}_0|n\rangle = W_n^{(0)}|n\rangle. \quad (4)$$

By expressing \mathcal{H}_1 in terms of commutator brackets (see Sachs and Schwebel²), one can obtain $\langle\mathcal{H}_1\rangle$ by a second-order perturbation calculation. The leading term which is linear in ξ is

$$\langle\mathcal{H}_1\rangle_n^{(1)} = \frac{k\xi\mu_0}{e} \sum_{n' \neq n} \frac{\langle n|\sigma\cdot\nabla\times(\nabla\varphi_0\times\nabla)|n'\rangle\langle n'|\varphi_c - e\mathbf{E}_0\cdot\mathbf{r}|n\rangle + tr}{W_n^{(0)} - W_{n'}^{(0)}}. \quad (5)$$

We have considered here the case where φ_e is equal to $-e\mathbf{E}_0\cdot\mathbf{r}$, the energy associated with a uniform external field \mathbf{E}_0 . Since the operator $\sigma\cdot\nabla\times(\nabla\varphi_0\times\nabla)$ will couple only the states n and n' which have different parities, the potential $\varphi_c - e\mathbf{E}_0\cdot\mathbf{r}$ must contain odd terms if it is to couple the same states $|n\rangle$ and $|n'\rangle$. In the absence of an applied electric field, this means that the space group which describes φ_c must lack an inversion center if

$\langle\mathcal{H}_1\rangle_n^{(1)}$ is not to vanish. It should be emphasized that the existence of a nonzero term $\sigma\cdot\mathbf{E}$ is dependent upon the presence of spin-orbit coupling. If the spin-orbit coupling were not present, it can be shown that the electron would experience no anomalous force. The magnitude of $\langle\mathcal{H}_1\rangle_n^{(1)}$ is of the order of $\eta\xi\mu_0|-\nabla\varphi_c/e + \mathbf{E}_0|$. Here η is a reduction factor, approximately equal to the spin-orbit interaction energy divided by the energy separation between lowest energy states of opposite parity.

If an interaction of the form $\sigma\cdot\mathbf{E}$ does exist, it should

¹ M. Sachs, Ann. Phys. **6**, 244 (1959).

² M. Sachs and S. Schwebel, Ann. Phys. **8**, 475 (1959).

³ E. Wigner, Z. Physik **43**, 624 (1927).

be possible to detect its existence by means of a paramagnetic resonance experiment.

II. EXPERIMENTAL RESULTS

The paramagnetic resonance spectra of potassium chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and ammonium $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystals were studied in the presence of applied electric fields. The choice of these crystals was motivated by the observed anomalies in the zero-field energy level splittings reported by Bleaney,⁴ and by the specific heat measurements of de Klerk, Steenland, and Gorter.⁵ Bleaney has observed two splittings in potassium chrome alum below 160°K of 0.26 cm^{-1} and 0.15 cm^{-1} . In ammonium chrome alum, splittings of 0.314 cm^{-1} and 0.242 cm^{-1} were observed below a transition point of 81°K. The experiments of de Klerk *et al.* were performed at temperatures low enough so that only the lowest energy doublet of the Cr^{3+} ion was populated, yet high enough so that dipole-dipole interactions were negligible. For a twofold degenerate level, they expected an entropy of order $R \ln 2$, but observed a value less than this. These two experiments have never been satisfactorily explained. Both experiments suggest an apparent lifting of some of the Kramers' degeneracy.

In these crystals, the paramagnetic ion Cr^{3+} has three unpaired $3d$ electrons, resulting in a fourfold degenerate ground state. The $^4F_{3/2}$ ground state is split by the cubically symmetric field into two triplets and a singlet. The triplets lie much higher than the singlet level and give rise to absorption lines in the visible. The crystalline field is not purely cubic, however, because of the electric dipole moments of the octahedron of six water molecules surrounding the Cr^{3+} ion (nearest neighbors). Distortion of this octahedron gives rise to a trigonal component which splits the quadruply degenerate singlet into two doublets of spin $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$. In such crystals, the orbital angular momentum is "quenched" and does not contribute to first-order magnetic properties. If a term of the form $\xi \eta \mu_0 \sigma \cdot E$ is present in the Hamiltonian, the conventional Zeeman splitting magnetic resonance condition will be modified accordingly. Thus, the ordinary Zeeman term will be replaced by

$$g\mu_0(\sigma \cdot H + \eta\xi\sigma \cdot E), \quad (6)$$

where H and E are applied magnetic and electric fields. In a conventional field-modulated magnetic resonance experiment the dc magnetic field H_0 is modulated at an audio frequency while sweeping through the resonance at a constant frequency ω . This enables one to utilize a narrow band detection scheme and results in a signal which is the derivative of the absorption. Since E and H appear symmetrically in Eq. (6), application of an audio-frequency electric field

should also modulate the absorption, with the effect reduced by the factor $\eta\xi$.

Single crystals of pure $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and dilute crystals of the isomorphous aluminum alum doped with chromium ($\text{Al}:\text{Cr}=30:1$) were grown from water solution. The crystals were cut and polished in the form of slabs approximately $1 \times 5 \times 5$ mm, with edges parallel to the cubic $[100]$ axes. Thin gold electrodes (0.001 in. thick) were attached to the broad faces with a thin layer of polystyrene cement. The sample was mounted in a TE_{102} resonant cavity with the electrodes parallel to the ends of the cavity. In such an arrangement, the rf magnetic field is not appreciably reduced, as was verified by checking the intensity of the resonance with electrodes in place, but only the conventional magnetic field modulation applied. Leads of No. 40 enameled copper wire were brought out through the narrow side of the cavity.

The spectrometer used was a modified Varian V-4500 X-band instrument operated at approximately 9.3 kMc/sec. The apparatus was calibrated by observing the signal obtained with the minimum magnetic field modulation which would maintain a signal-to-noise ratio of greater than 3:1.

The same audio-frequency oscillator (usually operated at 200 cps) was then used to apply an electric field of approximately 1000 v rms to the sample. Measurements were made in the temperature range 4°–300°K, with most of the data obtained at 77°K, which is below the transition temperatures reported by Bleaney.

The results of the experiment may be summarized as follows: No evidence of a term in the Hamiltonian of the form $\sigma \cdot E$ was observed. In the dilute crystals the sensitivity was such that $\eta\xi < 5 \times 10^{-5}$.

For ammonium chrome alum, the spin-orbit interaction energy is of the order of 100 cm^{-1} ,⁶ and the denominators of Eq. (5) are of the order 15 000 cm^{-1} ,⁷ thus η is approximately 7×10^{-3} . Consequently, we obtain $\xi \leq 0.007$. For the concentrated alums, an upper limit on ξ was more difficult to obtain because of an unexpected nonresonant signal, apparently due to a modulation of the dielectric properties of the crystal by the electric field. As a result the limiting value of ξ obtained was $\xi \leq 0.015$. Any modulation linear in the applied electric field will yield an audio signal at the modulation frequency and results in differentiating the absorption curve. If by some mechanism an applied electric field modulates the dielectric properties of the crystal in a nonresonant manner, the reflection coefficient of the resonant cavity will be modulated at twice the applied field frequency. A variation of either the real or imaginary parts of the dielectric constant can have

⁴ B. Bleaney, Proc. Roy. Soc. (London) **A204**, 203 (1951).

⁵ D. de Klerk, M. J. Steenland, and C. J. Gorter, Physica **15**, 649 (1949).

⁶ C. F. Davis and M. W. P. Strandberg, Phys. Rev. **105**, 447 (1957).

⁷ F. J. Spedding and G. C. Nutting, J. Chem. Phys. **3**, 369 (1935).

TABLE I. Electron electric dipole moment (EDM) (expressed in units of $e\hbar/2mc$).

EDM	Experiment	Reference
<0.01	Absence of $K \rightarrow L_1$ x-ray transitions in heavy atoms	8
<0.04	Hyperfine splitting of positronium ground state	8
<0.06	Metastable 2s state in hydrogen	8
<0.008	Lamb shift	8, 9
<0.007	This work	
<0.0002	Electron beam	10

such an effect. When electric modulation is applied, a second harmonic audio signal was obtained independent of the dc magnetic field. This signal is proportional to the microwave carrier power level. Sweeping the magnetic field through resonance causes a large change in reflected power for a concentrated crystal of the size used. Hence, this variation in power level, which effectively multiplies the constant audio signal, is superimposed on any effects linear in E but is almost completely filtered out in the detection circuit. For the dilute crystals the change in power level is much less; consequently, a lower limit on ξ could be obtained.

The exact mechanism of the dielectric effect has not been established. That the effect is not an instrumental one was established by applying a dc bias to the crystal in addition to the ac dielectric modulation. Application of a bias of 270 v dc increased the nonresonant audio signal by a factor of approximately 30, and the signal amplitude varied linearly with bias field. An attempt was made to observe a hysteresis loop at 77°, but no effect of this nature was detected.

III. DISCUSSION

A term of the form $\xi\mu_0\sigma\cdot E$ in the Hamiltonian is equivalent to the existence of an electron electric dipole moment of order $\xi\mu_0$. Values of ξ obtained from various experiments are given in Table I. It should be emphasized that the theoretical interpretation made by Salpeter *et al.*⁸ differs from the theory of Sachs discussed here, so the values⁸⁻¹⁰ quoted in Table I can only be

⁸ E. E. Salpeter, Phys. Rev. **112**, 1642 (1958).

⁹ G. Feinberg, Phys. Rev. **112**, 1637 (1958).

¹⁰ D. F. Nelson, A. A. Schupp, R. W. Pidd, and H. R. Crane, Phys. Rev. Letters **2**, 492 (1959).

compared as experimental data. The smallest value to date was obtained in the electron beam experiments of Nelson *et al.*¹⁰ Investigation by means of paramagnetic resonance in solids is complicated by the complex environment of the paramagnetic ion in the crystal. Because the spin-orbit coupling and term splittings enter into the expressions for experimentally observed quantities, the measurement is not as clean-cut as is a free-electron or isolated-atom experiment. It is not possible to use applied fields much stronger than 10 kv/cm with chrome alum crystals without causing the crystal to break down.

Since no evidence for a lifting of Kramers' degeneracy in chromic alums was found, the zero-field splitting anomalies must be attributed to another mechanism. The possibility of several different chromium sites giving rise to different splittings is plausible. For the ammonium alums such an explanation is satisfactory, but for potassium chrome alum this model is not consistent with the specific heat data. The presence of a hyperfine splitting could be used to explain the specific heat, but Bleaney has pointed out that there is insufficient natural abundance of Cr⁵³, the only odd isotope, to cause an appreciable effect.

The dielectric behavior of the alums is not presently well understood. Various investigators¹¹ have reported unusual dielectric behavior of the alums as a function of temperature. The apparent electric field dependence of the dielectric loss observed in this experiment can be described phenomenologically by an expression of the form $\epsilon'' = \epsilon_0''(1 + \alpha E^2)$. Behavior of this type has been observed above the Curie point in barium-strontium titanate by Roberts.¹² He found the dielectric constant was reduced to half its zero-field value by application of an electric field of 7 kv/cm. Any such effect in the alums is much weaker and was not determined quantitatively.

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¹¹ J. H. E. Griffiths and D. Powell, Proc. Phys. Soc. (London) **A65**, 289 (1952).

¹² S. Roberts, Phys. Rev. **70**, 890 (1947).