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PARAELECTRIC RESONANCE OF OH$^-$ DIPOLES IN KCl[†]

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The theories of magnetic and electric susceptibilities have many features in common and, in fact, in Van Vleck's[1] classic exposition of the subject, both are treated on an equal footing. With the advent of adiabatic demagnetization, paramagnetic resonances, masers, and other devices, paramagnetism completely overshadowed its electric counterpart. More recently systems comprising electric dipoles embedded in ionic crystals have attracted renewed attention.[2-10] Cooling by adiabatic depolarization of electric dipoles has been demonstrated,[2,5,8] and the energies of the dipoles in an external electric field have been determined indirectly from their optical[3] and thermal properties.[8,10] In the present note we wish to report on the resonance absorption (paraelectric resonance) of OH$^-$ dipoles in KCl in an externally applied dc and microwave electric field.

The possibility of observing the paraelectric-resonance transitions was first mentioned by Kuhn and Lüty.[5] Brief reports on their observation have been given by Dreyfus and Bron[11] and Shepherd and Feher.[12,13] These observations were made at a microwave frequency of ~9 kMc/sec. At this frequency the lines can at best be only partially resolved and not all the transitions can be covered. The present experiments were performed at a frequency of 35 kMc/sec. The improved resolution enabled us to determine the value of the zero-field splitting and the dipole moment (uncorrected for local field effects) and to estimate the dipole-lattice relaxation time at one temperature.

The OH$^-$ ion is introduced as an impurity into the KCl lattice and substitutes for the Cl$^-$ ion.[14] The dipole moments of the OH$^-$ ions orient themselves along the six ⟨100⟩ directions.[3] The application of an external electric field changes the energies of the different dipolar orientations. Resonant transitions between different energy levels can then be induced by a microwave electric field. In order to observe these transitions, the samples[15] were placed into the E field of the microwave cavity or wave guide of a conventional electron-spin-resonance spectrometer. The applied dc field was modulated at 200 cps and its magnitude slowly varied. Under these conditions the signal output is proportional to the derivative of the absorption ($d\chi_e''/dE$).

The experimental traces for an OH$^-$ concentration of 3×10^{16} OH$^-$/cm^3 obtained at 1.3°K and a frequency of 35×10^9 cps are shown in Figs. 1(a) and 1(b) for two orientations of the E field with respect to the crystalline direc-

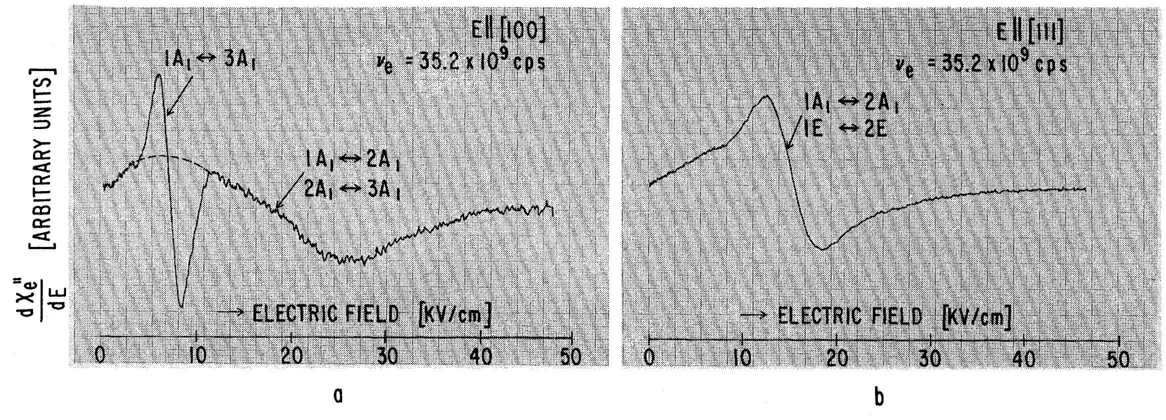

FIG. 1. Paraelectric resonance absorption from OH$^-$ dipoles (3×10^{16} OH$^-$/cm^3) in KCl at $\nu_e = 35.2\times10^9$ cps and $T = 1.3$°K. In (a), E is along the [100] direction. Two resonances are clearly discernible. The relative intensities and linewidths are explained in the text. In (b), E is along the [111] direction. The energy-level diagram giving rise to these transitions is shown in Fig. 2.

tions. For E in the [100] direction, two resonance signals are clearly discernible. The center of the narrow line occurs at an electric field $E = 7.1$ kV/cm and the broad one at $E = 19.4$ kV/cm. The integrated intensity of the narrow line is approximately 30 times smaller than the broader one. As will be shown subsequently, it arises from a "forbidden" transition. For E in the [111] direction [Fig. 1(b)] a single resonance line centered at 15.1 kV/cm is observed. The linewidths were found to be constant in the low-temperature region of 1.3°K $< T < 4.2$°K. At a temperature of 11°K the line of Fig. 1(b) could no longer be resolved. This suggests a dipole-lattice relaxation time at this temperature of the order of 10^{-11} sec.

In order to understand the paraelectric resonance transitions, the energy-level diagram and the transition probabilities for OH^- dipoles in an external electric field are needed. Assuming that the dipoles are completely localized in the six $\langle 100\rangle$ directions, one obtains a sixfold degenerate ground state. An electric field splits this degeneracy in a manner previously described.[3,8] In this simplified picture the transition probabilities between the various energy levels vanish and no resonances can be observed. This difficulty is eliminated when the overlap between the different dipole states is considered. We choose as a basis the six states $|+z\rangle$, $|-z\rangle$, $|+x\rangle$, $|-x\rangle$, $|+y\rangle$, $|-y\rangle$. In a strong crystal field, the basis states will not be exactly orthogonal, i.e., there will be a certain amount of overlap between them. The Hamiltonian for an OH^- ion in the presence of a strong octahedral crystal field can then be written as

$$\mathcal{H}_0 = -\frac{\Delta}{2}\begin{bmatrix} 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \end{bmatrix}. \tag{1}$$

Diagonalization of $\mathcal{H}_0$ produces a ground-state singlet (A_{1g}) with energy -2Δ, a triplet (T_{1u}) at energy 0, and a double (E_g) with an energy $+\Delta$. This result is identical to the one obtained by Devonshire[16] for a dipole in a strong octahedral crystal field.

The Hamiltonian describing the presence of an applied electric field E or a strain S, directed along the $+z$ direction, can be written as

$$\begin{gathered} \mathcal{H}_E = Ep_u\begin{bmatrix} -1 & & & & & \\ & 1 & & & & \\ & & 0 & & & \\ & & & 0 & & \\ & & & & 0 & \\ & & & & & 0 \end{bmatrix}; \\ \mathcal{H}_S = S\begin{bmatrix} 1 & & & & & \\ & 1 & & & & \\ & & -\frac{1}{2} & & & \\ & & & -\frac{1}{2} & & \\ & & & & -\frac{1}{2} & \\ & & & & & -\frac{1}{2} \end{bmatrix}; \end{gathered} \tag{2}$$

where p_u is the dipole moment uncorrected for local fields.[17] The energy level structure for $S = 0$ is obtained by diagonalizing $\mathcal{H}_0 + \mathcal{H}_E$ and is illustrated in Fig. 2(a) for E parallel to the [100] direction and in Fig. 2(b) for E parallel to the [111] direction. The symmetries for the two field directions are C_{4v} and C_{3v}, respectively; the labeling of the levels follows standard group theoretical notation.[18]

The transition probabilities between different levels are obtained in the usual way by calculating the dipole matrix elements connecting the various levels. For the case in which both the dc field E and the rf field E_{rf} point along the [100] direction, the allowed transitions occur between levels $1A_1 \leftrightarrow 2A_1$ and $2A_1 \leftrightarrow 3A_1$ (see Fig. 2). The transition probability between levels $1A_1 \leftrightarrow 3A_1$ is much smaller and depends on the value of the zero-field splitting Δ. Because of the widths of the lines the two allowed transitions in the [100] direction merge into one. With E parallel to the [111] direction, one predicts two allowed transitions (see Fig. 2). These again cannot be resolved and merge into one as observed experimentally in Fig. 1.

We now turn to the origin of the linewidths. Their temperature independence between 1.3°K and 4.2°K suggests that the lines are strain broadened. The effect of a positive strain in the [100] direction is indicated in Fig. 2. Some levels (e.g., $1A_1$ and $3A_1$) move parallel to each other under the application of uniaxial strain. Transitions between two such levels will therefore not be as susceptible to strain broadening as others. These simple considerations explain the observed relative line widths.

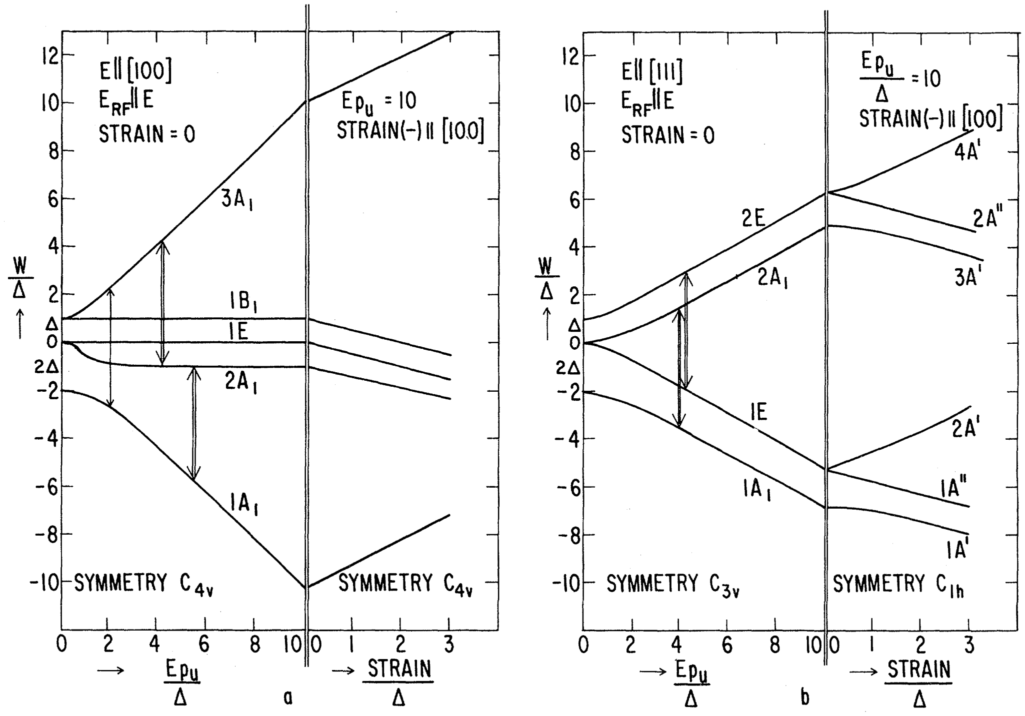

FIG. 2. Energy-level diagram of an OH^- dipole in a crystal field of octahedral symmetry for two orientations of the electric field with respect to the crystalline axis. The double lines indicate allowed transitions, the single line a forbidden transition. The two allowed transitions could not be resolved experimentally because of their widths (see Fig. 1). The effect of positive uniaxial strain in the [100] direction is indicated in the right half of each figure. Strain is responsible for the observed linewidths as explained in the text.

The important quantities characterizing the OH^--KCl system are the zero-field splitting Δ and the dipole moment p_u. From the ratio of the integrated intensities of the allowed and the forbidden transitions and the position of the resonance lines we obtain[19]

$$\Delta = 6200 \pm 600 \text{ Mc/sec (i.e., } 0.30°\text{K)},$$

$$p_u = 4.0 \pm 0.2 \text{ Debye units.}$$

We are at present trying to obtain samples with smaller built-in strains, and investigate further analogies between paraelectric and paramagnetic resonances. It may be noted, for instance, that the saturation of the $1A_1 \leftrightarrow 3A_1$ transition (see Fig. 2) will cause a population inversion between two levels analogous to the Bloembergen type three-level maser.[20] The de-excitation of this system can then proceed either by the emission of electromagnetic energy or by the emission of phonons. A noteworthy difference between the electric-dipole and magnetic-dipole transitions is that the coupling of the former to both the lattice and the electromagnetic field is many orders of magnitude stronger.

We would like to thank R. Isaacson for his assistance in these experiments.

Note added in proof.—After the manuscript was submitted, the 9-kMc/sec work of Bron and Dreyfus appeared [Phys. Rev. Letters 16, 165 (1966), referred to as BD]. There are serious disagreements between our respective results on which we would like to comment.

To start with, concerning the energy-level diagram on which the labeling of the transition is based (compare Fig. 3 of BD with Fig. 2 of the present letter): At $E = 0$, $S = 0$, the energy difference between the A_{1g} and T_{1u} levels is twice the difference between the T_{1u} and E_g. In the diagram of BD these differences are shown equal. Application of an E field splits the E_g state into two (in their figure it becomes a singlet A_1). The E field also splits the T_{1u} state (they show it degenerate together with the B_1 state). Under the application of strain and an E field, it is not clear how the singlet can go over into a four-fold degenerate A_1+E+B_1 state (see extreme right of Fig. 3 of BD).

The most serious discrepancy arises from the position of their resonances and the inferred value for the dipole moment. Their HE_z transition occurs at ~37 kV/cm, whereas our ($1A_1 \rightarrow 2A_1$) transition occurs at ~19 kV/cm. Their calculated dipole moment is therefore an order of magnitude smaller than ours. One possible explanation is that all of their work was done on uniaxially strained samples, even the results labeled $S \sim 0$ [see their Figs. 1(a) and 1(b)]. An alternative possibility is that the curves in Fig. 1(a) of BD are not due to OH$^-$ dipoles. In crystals with a very low OH$^-$ concentration we have seen on occasions resonances due to other chemically unidentified dipoles. None of them, however, had such a small dipole moment.

In order to avoid possible difficulties arising from a comparison of experiments performed at two different frequencies, we show in Fig. 3 results obtained at X band which are similar to the ones referred to in the text.[12,13] Whether to call these curves resonance or not seems to us a matter of opinion or semantics. In the [111] direction [Fig. 3(b)], the absorption simply decreases with E. In the [100] direction [Fig. 3(a)], the increase in absorption at small E can be explained by the fact that the energy separation between $1A_1$ and $2A_1$ initially decreases with increasing E. Thus in spite of the condition that $\hbar\omega < 2\Delta$, an initial increase in absorption due to the transition $1A_1 \rightarrow 2A_1$ can be observed if the wings of the lines overlap.

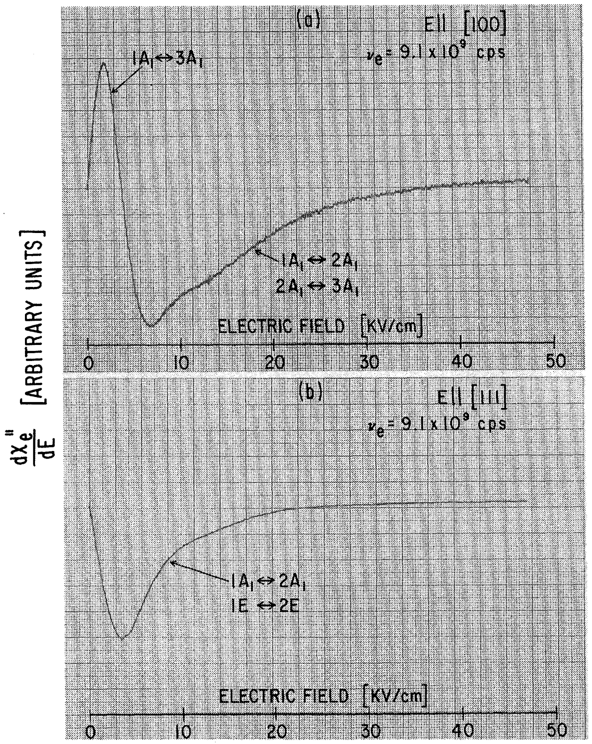

FIG. 3. Power absorption from OH$^-$ dipoles (3×10^{16} OH$^-$/cm^3) in KCl at $\nu_e = 9.1$ kMc/sec and $T = 1.3$°K. Figure 1 shows the resolved resonance lines obtained on the same sample at 35.2 kMc/sec.

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[12] See footnote 12 in Ref. 8.

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[17] It may seem more logical to write for the dipole energy $E_{\mathrm{loc}}p$, where p is the "real" dipole of the OH$^-$ ion. However, since we are not measuring E_{loc} but E applied and, furthermore, the permanent dipole moment of OH$^-$ depends on the applied electric field, we choose to write Ep_u.

[18] See, for example, V. Heine, Group Theory in Quantum Mechanics (Pergamon Press, Inc., New York, 1960), Appendix K.

[19] These values were obtained under the assumption that the strains in the sample are randomly distributed and do not shift the center of the resonance lines. A preferentially oriented strain component could seriously affect these results. We are at present investigating this point in more detail.

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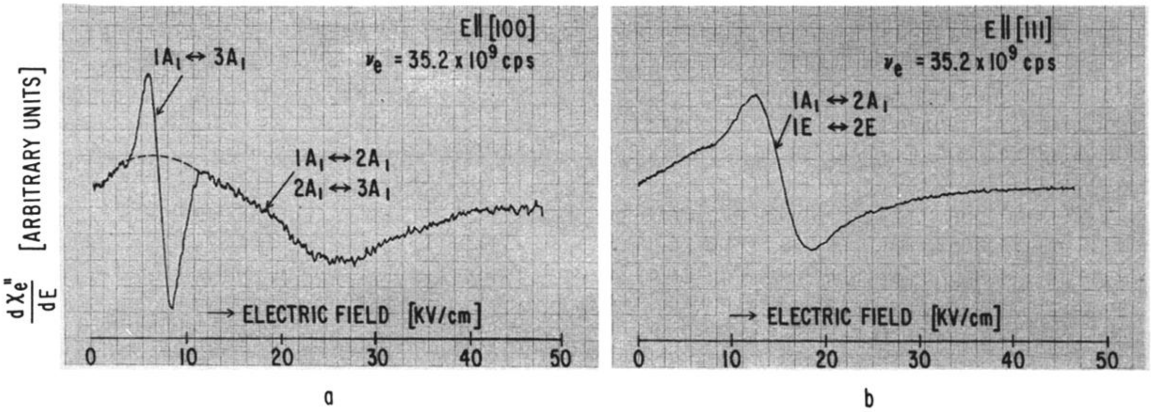

a

b

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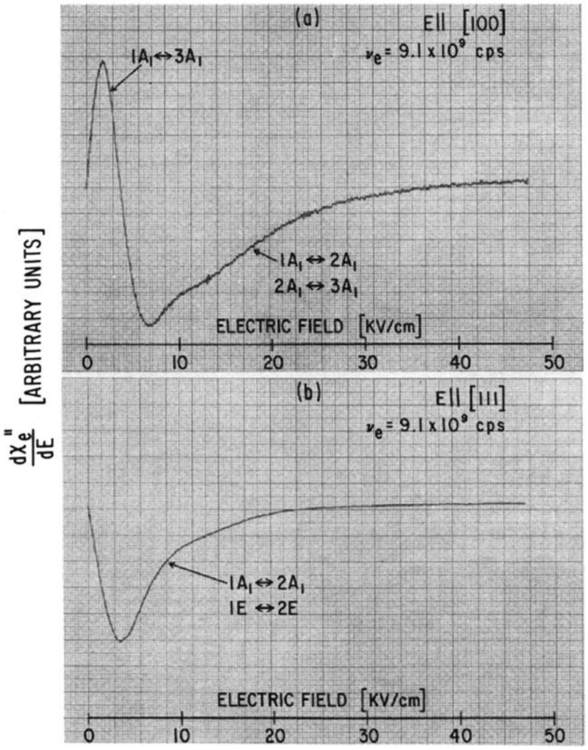

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