

Table I. Summary of experimental results.

Transition	Microwave frequency (Mc/sec)	Magnetic field at center (G)	He <sup>+</sup> <i>n</i> = 4 level separations (exptl.) (Mc/sec)	Estimated uncertainty (Mc/sec)
<i>αf</i>	11 228.2	4798.6	$S = 1770$	$\pm 20$
<i>βe</i>	1783.0	1935.8	$S = 1760$	$\pm 20$
<i>αc</i>	9639.3	4709.1	$\Delta E - S = 20\ 155$	$\pm 20$
<i>βd</i>	11 804.7	5998.5	$\Delta E - S = 20\ 200$	$\pm 20$

are to be compared with the theoretical values<sup>9</sup>  $S = 1769$  Mc/sec and  $\Delta E = 21\ 946$  Mc/sec. We conclude that there is no significant discrepancy between theoretical and experimental values for the  $n = 4$  He<sup>+</sup> level shift and fine structure within the precision of the present experiment. It is hoped to undertake a more precise measurement in which the many corrections not treated in the present work will be fully taken into account.

†Research supported in part by the U. S. Air Force Office of Scientific Research.

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<sup>2</sup>G. Herzberg, Z. Physik 146, 269 (1956).

<sup>3</sup>F. L. Roesler and L. DeNoyer, Phys. Rev. Letters

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<sup>5</sup>E. Lipworth and R. Novick, Phys. Rev. 108, 1434 (1957).

<sup>6</sup>M. Leventhal, K. R. Lea, and W. E. Lamb, Jr., Phys. Rev. Letters 15, 1013 (1965).

<sup>7</sup>G. W. Series and W. N. Fox, J. Phys. Radium 19, 850 (1958).

<sup>8</sup>Ref. 2 gives the following lifetime values in units of  $10^{-8}$  sec: *4S*, 1.4154; *4P*, 0.076 87; *4D*, 0.2258; *4F*, 0.4531.

<sup>9</sup>The theoretical value for  $S$  was obtained using the formulas of G. W. Erickson, Phys. Rev. Letters 15, 338 (1965); the theoretical value for  $\Delta E$  was obtained by scaling the fine-structure splitting of the  $n = 2$  levels of deuterium, as measured by E. S. Dayhoff, S. Triebwasser, and W. E. Lamb, Jr., Phys. Rev. 89, 106 (1953).

## ELECTRIC RESONANCE OF ROTATING DIPOLES IN IONIC CRYSTALS

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(Received 17 November 1965)

Considerable recent interest<sup>1-3</sup> has been shown in the rotational motion of hydroxyl ions when these ions replace halide ions in alkali-halide lattices. Stark-effect measurements have previously been utilized to study the rotational states of diatomic molecules in the gaseous phase.<sup>4</sup> These experiments suggest that similar measurements should be possible in insulating crystals containing rotating, polar ions such as OH<sup>-</sup> or SH<sup>-</sup>, as has indeed been recently pointed out by others.<sup>2,5</sup> This paper reports the first experimental observation of this effect.

In the alkali halides, the rotational motion of OH<sup>-</sup> is hindered by the periodic potential barriers within the octahedral lattice site.<sup>6,7</sup> At low temperatures only states lying below

the potential barriers are occupied. In order to observe transitions between these "tunneling" states in a specific energy range, such as the microwave region, two conditions must be fulfilled. The potential barrier must not be so high as to preclude finite transition probabilities between the states, and yet not so low that the states are split by more than microwave energies.

In the present experiment, samples containing  $10^{-1}$  to  $10^3$  ppm of OH<sup>-</sup> or about 30 ppm of SH<sup>-</sup> were used. These samples were placed in the high microwave electric field of a re-entrant cavity in a 9-kMc/sec system. The experimental technique was an electric analog of the usual epr arrangement. A continuously variable dc electric field,  $E_z$ , was applied par-

allel to the [001] direction of the alkali-halide lattice, which was also the direction of polarization of the microwave field. In addition, a uniaxial strain,  $\epsilon_z$ , could be applied by clamping the crystal in the [001] direction. The microwave-power absorption was obtained by integrating its experimentally obtained derivative with respect to electric field. Hence, the absolute value of the microwave power absorption is uncertain to within a constant of integration. Only measurements made at 1.4°K are reported here.

Figure 1 shows the microwave absorption as a function of  $E_z$ , and various magnitudes of strain,<sup>8</sup> as observed in KCl containing  $\text{OH}^-$ . As seen in Fig. 1(b), the value of the field at which the band at low  $E_z$  (hereafter called the L.  $E_z$  band) appears is essentially independent of  $\epsilon_z$ , whereas the position of the band at high  $E_z$  (hereafter called the H.  $E_z$  band) shifts markedly to higher values of  $E_z$  as  $\epsilon_z$  increases. On the other hand, the intensity of the L.  $E_z$  band decreases markedly with increasing  $\epsilon_z$ , whereas the intensity of the H.  $E_z$  band remains constant to within experimental error. The magnitudes of both bands varies directly with  $\text{OH}^-$  concentration. In samples with greater

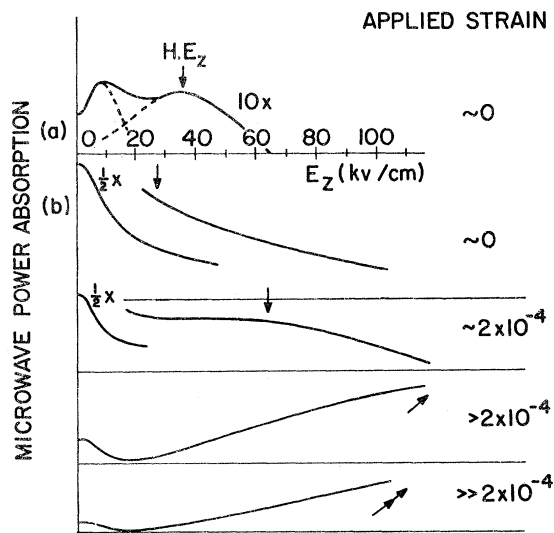


FIG. 1. Microwave absorption at 1.4°K as a function of applied dc electric field,  $E_z$ . (a) Sample of KCl with approximately 0.1 ppm  $\text{OH}^-$ . (b) Sample of KCl with 20 ppm  $\text{OH}^-$  and various values of the applied strain field. (The break in the middle curves refers to the ordinate scale change as is indicated in the figure.) The arrows indicate the observed location of the peak of the H.  $E_z$  band; the peak of the L.  $E_z$  band is evident near  $E_z = 0$ .

than 2 ppm of  $\text{OH}^-$  the widths of the bands increase, and their peak positions change with  $\text{OH}^-$  concentration. These results are evident from a comparison of Fig. 1(a) with 1(b). Similar results to those shown in Fig. 1 were obtained for KBr:KSH; however, in this case the L.  $E_z$  band is somewhat narrower and is shifted to  $23.6 \pm 1$  kV/cm. In contrast, only very weak microwave absorption was observed for LiF:LiOH and KCl:KSH.

To interpret these results, we start with the following model. In KCl:KCN it has been concluded that the  $\text{CN}^-$  rotates such that its center of mass nearly coincides with the center of the halide site.<sup>7</sup> This situation must be modified for the case of  $\text{OH}^-$  in KCl. The ionic radius of  $\text{OH}^-$  is 1.33 Å, and therefore small compared to 1.92 Å for  $\text{CN}^-$  and 1.85 Å for  $\text{Cl}^-$ . Furthermore,  $\text{OH}^-$  is considerably more polar than  $\text{CN}^-$ . A reduction in the electrostatic energy can, therefore, be achieved if the center of mass of the  $\text{OH}^-$  is displaced<sup>9</sup> from the center of the halide site, and the ion is oriented with respect to the nearest-neighbor alkali ions as shown in Fig. 2.

Figure 2 also indicates one of the possible motions the ion can execute in the displaced position. Namely, the ion may move from one potential minimum within the halide site to the next by translating its center of mass, without changing its orientation with respect to the nearest alkali ion.<sup>10</sup> In a second motion (not shown), the center of mass remains stationary, but the ion rotates about axes perpendicular to the axis of the ion and passing through its center of mass.

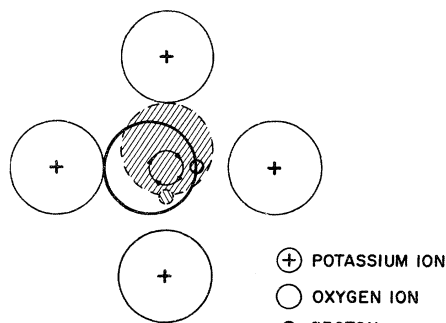


FIG. 2. Displaced position of  $\text{OH}^-$  ion with respect to four of the six nearest-neighbor alkali ions. The translational motion of the center of gravity is shown by the arrows. The alkali ions above and below the halide site, as well as the translational motion out of the plane of the figure, are to be implicitly understood.

An estimate, based on electrostatic fields, indicates that the potential barrier between equivalent rotational sites is 2 to 3 times that between equivalent translational sites. To a first approximation we may, therefore, neglect the rotational motion in discussing the states of the translational motion.

If one makes the further simplifying assumption that the center-of-mass displacement is constant throughout the translational motion, then the Schrödinger equation for the motion is formally the same as that for the rotational states of a rigid diatomic molecule in a cubic potential with minima along  $\langle 100 \rangle$  axes of the lattice. The solutions obtained by Devonshire<sup>6</sup> for this case can therefore be applied here, provided proper account is taken of the displacement of the center of rotation. Accordingly, the ground state consists of three nearly degenerate levels which belong to the  $A_{1g}$ ,  $T_{1u}$ , and  $E_g$  representations of the cubic group. These levels can be split under application of  $E_z$  and  $\epsilon_z$ , as follows immediately from crystal-field theory. The resultant splittings are illustrated in Fig. 3. It can further be readily shown that after the application of these fields, microwaves polarized in the  $z$  direction can cause electric dipole transitions only between  $A_1$  states.

The results for KCl:KOH indicated in Fig. 1, and those for KBr:KSH, follow from a comparison of Figs. 3(a) and 3(c). Since the microwave frequency is fixed, the position of the L.  $E_z$

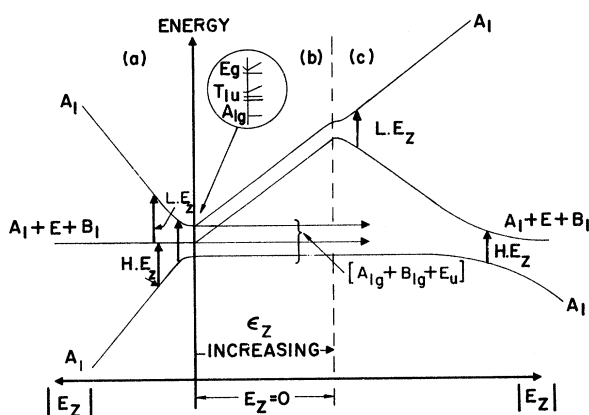


FIG. 3. Energy level scheme for the rotational levels as a function of (a) applied electric field  $E_z$  only, (b) applied strain field  $\epsilon_z$  only, and (c) applied electric field  $E_z$  after application of a fixed magnitude of the strain field. The insert gives the levels and their representations at zero applied field. The observed transitions are indicated as L.  $E_z$  and H.  $E_z$ .

transition is determined primarily by  $E_z$ . In contrast, the electric field value at which the H.  $E_z$  transition occurs increases with increasing  $\epsilon_z$ . The intensity of the H.  $E_z$  transition is independent of  $\epsilon_z$ , since it depends on the population of the ground  $A_1$  state. However, as can be seen from Fig. 3(c), increased  $\epsilon_z$  results in a decrease in the population of the excited  $A_1$  levels and thereby a decrease in the intensity of the L.  $E_z$  transition.

An estimate of the zero-field splitting of the  $E_g$  and  $T_{1u}$  states may be made on the assumption of a strong-field Stark splitting of nearly degenerate levels.<sup>11</sup> However, even the lowest published<sup>1</sup> value for the  $\text{OH}^-$  dipole moment (from crystals with 10 to 100 ppm  $\text{OH}^-$ ) leads to the physically unreasonable result that the  $A_1$  levels cross at  $E_z \sim 3$  kV/cm. It is, however, evident from Fig. 3 that the effective dipole moment depends on the relative energies of the three  $A_1$  states, i.e., on  $E_z$  and  $\epsilon_z$ . Furthermore, the peak position of the L.  $E_z$  band, and thereby the effective dipole moment, depends on the  $\text{OH}^-$  concentration. Consequently, until measurements are made with one other microwave frequency on the present samples, we are limited to the knowledge that the zero-field splitting is considerably less than 9 kMc/sec.

From the width of the L.  $E_z$  band, as observed for samples with  $<2$  ppm  $\text{OH}^-$ , under essentially zero applied stress, we estimate a lifetime in the excited state of about  $3 \times 10^{-9}$  sec.<sup>12</sup> This value is in reasonable agreement with the value of the lifetime obtained by an extrapolation of the results of dielectric measurements at 1.6°K.<sup>13</sup> The extrapolation is based on the assumption of one-phonon emission processes.<sup>14</sup>

Finally, the results on LiF:LiOH and KCl:KSH can be qualitatively understood as follows. In these lattices, the impurity size approaches that of the halide site. The translational motion is accordingly suppressed because the potential barrier for this motion is very high. The classical situation is therefore approached, and microwave induced dipole reorientation becomes negligibly small.

The authors are indebted to Dr. W. Känzig for calling attention to the possibility of the present experiment.

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<sup>7</sup>V. Narayanamurti, *Phys. Rev. Letters* **13**, 693 (1964).

<sup>8</sup>In Fig. 1 the upper two curves present the results for samples which are under just enough stress to insure good electrical contact. We estimate the resultant

strain to be of the order of  $10^{-5}$  to  $10^{-6}$ .

<sup>9</sup>A similar conclusion has been inferred for  $\text{OH}^-$  by Lombardo and Pohl from their electrocaloric measurements of Li-doped alkali halides. G. Lombardo and R. O. Pohl, *Phys. Rev. Letters* **15**, 291 (1965).

<sup>10</sup>Although the center of mass undergoes a simple translation, the ion executes a combined rotational-translational motion. For brevity, we will refer to this motion as "translational."

<sup>11</sup>See Ref. 4, p. 252.

<sup>12</sup>It is clear from Fig. 3(c) that the width, with respect to  $E_z$ , of the  $H. E_z$  band appears broadened by the hyperbolic approach of the lower  $A_1$  states toward each other. The concentration dependence of the band widths and the peak displacement to lower  $E_z$  can be accounted for, to within a factor of 2, in terms of random electric fields produced by nearly  $\text{OH}^-$  ions.

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## POSITRON ANNIHILATION AND THE ELECTRONIC STRUCTURE OF RARE-EARTH METALS\*

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(Received 3 January 1966)

We have measured the angular correlation of the photons from two-quantum positron annihilation in single-crystal disks of the rare-earth metals holmium and erbium, and in yttrium, which has a similar crystal and electronic structure. The coincidence distributions in the three metals are similar and highly anisotropic, and the qualitative features of the  $c$ -axis (0001) results are reproduced by a calculation based on the independent-particle model. In the antiferromagnetic phase, the distribution for the  $c$ -axis holmium crystal is modified, and this change is ascribed to the appearance of magnetic superzone energy gaps.

The experiments were carried out with a conventional parallel-slit geometry,<sup>1</sup> using a magnetically focused  $\text{Co}^{58}$  positron source. The angular resolution of the apparatus was approximately 0.25 mrad. The results for holmium in the paramagnetic phase at room temperature are shown in Fig. 1(a). The  $b$ -axis (10 $\bar{1}$ 0) data do not depart greatly from the parabola corresponding to three free electrons per atom, but the  $c$ -axis curve drops sharply at low angles and has a pronounced hump at about 3 mrad. The large anisotropy in the coincidence curves is in accord with the results

of recent band-structure calculations on hexagonal close-packed rare-earth metals.<sup>2,3</sup> This anisotropy is clearly manifested by the Fermi surface of holmium calculated using the augmented-plane-wave (APW) method. Sections of this surface are shown in the reduced zone in Fig. 2 and a noteworthy feature is the large, approximately flat electron and hole regions normal to the  $c$  axis. These surfaces run parallel to each other over a large region when spin-orbit coupling is taken into account in a relativistic APW calculation,<sup>4</sup> and we propose that their separation primarily determines the  $Q$  vector of the periodic magnetically ordered phases. The mixing of states due to the magnetic periodicity would destroy large areas of these surfaces, thus causing the large observed reduction in electrical conductivity in the ordered state.<sup>5</sup>

The structure in the angular distributions for the  $c$ -axis crystals indicates that these metals can provide a sensitive test of the independent-particle theory of positron annihilation. We have therefore calculated the angular distribution of photons in yttrium, using the independent-particle model,<sup>6</sup> according to which the number of coincidences at an angle  $\theta$  is