der of magnitude too small quantitatively to explain the present observations. Van Kranendonk and Sears[15] have ascribed such a difference to an alteration of the ratio c/a. This is ruled unlikely since $\Delta(c/a)$ would have to increase greatly as pressure was applied to quantitatively match the data. Hydrogen supports little shear and it is not physically apparent why the crystal would tend to become less than close packed as the material is squeezed.

It has been pointed out by Ebner and Sung[16] that, although terms such as the V_{20} sum to zero over close-packed nearest neighbors in a rigid lattice, this is not in general true when zero-point motion is appreciable. If this is the case here, then the anomalous splitting should reflect both the detailed nature of the correlations in zero-point motion and the significant non-EQQ interactions. Detailed quantum crystal calculations are needed in order to test this hypothesis, and are currently in progress, as are experiments at higher pressures. Furthermore, since a quantitative interpretation of the splittings depends on the equation of state, a redetermination of it is needed, and is being pursued.

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Optical Detection of Paramagnetic Resonance of the Self-Trapped Exciton in KBr

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Paramagnetic resonance of the self-trapped exciton has been studied in KBr. The general features of the spectra confirm the validity of Kabler's model of a V_K center having trapped an electron. We describe special aspects of the optical technique used to detect the resonance.

Intrinsic luminescence in alkali halides is known to occur through radiative decay of the self-trapped exciton.[1,2] The hole is highly localized on two adjacent, covalently bonded, halide ions, so that the self-trapped exciton may be regarded as an X_2^{--} molecular ion in an excited level or as a V_K center (self-trapped hole) having trapped an electron.[3,4] In most of the alkali halides, two emission bands are observed. On the basis of lifetime measurements[3] and studies of linear polarization and of circular polarization[5] in a magnetic field, the high- and low-energy bands have been assigned to transitions originating from a spin singlet and a spin triplet, respectively. The existence of a long-lived emission band, showing temperature-dependent circular polarization in a magnetic field,[5] suggests the possibility of optical detection of the paramagnetic resonance of the triplet state. Using simple techniques described by Geschwind,[6] we have detected the resonance of the self-trapped exciton in NaCl, RbBr, and KBr. The last mentioned

crystal was studied in detail and the results will be presented here. A similar resonance has been observed recently in CsBr by Marrone, Patten, and Kabler.[7]

The apparatus is very similar to the one previously used[8] for the detection of EPR in the excited level of F centers in CaO. Luminescence was excited by an x-ray tube operated at 50 kV, 20 mA, which was magnetically shielded and placed between the coils of a 12-in. Varian magnet. The anode was approximately 20 cm from the sample. The sample was located in a slotted TE_{011} microwave cavity and could be rotated around a vertical axis. Different cavities were used to cover X, K_u, and K bands; they were immersed in the helium bath of a metal cryostat. The microwaves were chopped at an audio frequency. When the magnetic field was swept slowly through resonance, this frequency component appeared in the light signal and was detected with standard lockin detection techniques. The emitted light could be detected along two directions (parallel or perpendicular to the magnetic field) so that the effect of microwaves could be monitored on light which was circularly polarized (σ_+ or σ_-) or linearly polarized (π) along the field direction or linearly polarized (σ_V and σ_H) along the vertical and horizontal perpendicular directions. Spectra obtained for the [110] orientation of the magnetic field are shown in Fig. 1. Their appearance depends very much on the polarization of the monitored light: Certain lines appear in σ_+ polarization and not in σ_- and vice versa. When several lines overlap, for example, in the region around 4000 G, the possibility of observing one or the other by changing the polarization of the monitored light allows a great enhancement of the resolution. Moreover, such effects are very useful for the identification of the transitions giving rise to the observed lines.

The emission is assumed to originate from the ${}^3B_{1u} \rightarrow {}^1A_g$ transitions[5] of the self-trapped exciton (the local symmetry is D_{2h}). Inside the $S=1$ excited level the Zeeman effect may be accounted for by an effective spin Hamiltonian,

$$\mathcal{H}_s = \mu_B \vec{\mathbf{H}} \cdot g\vec{\mathbf{S}} + D(S_z^2 - \tfrac{2}{3}) + E(S_x^2 - S_y^2),$$

where the effect of hyperfine coupling has been neglected; O_z is chosen along the main axis [110] of the defect and O_x and O_y along the [001] and [1$\bar{1}$0] axes, respectively.[9] The spin states may be expressed in terms of the real functions $|M_x\rangle$, $|M_y\rangle$, $|M_z\rangle$. The true states are products of one of these by the orbital state $|B_{1u}\rangle$; they transform as $|b_{2u}\rangle$, $|b_{3u}\rangle$, and $|a_u\rangle$, respectively. Since the x,y,z components of the electric dipole operator transform as b_{3u}, b_{2u}, b_{1u} and since the ground state is $|a_g\rangle$, transitions are allowed from the $|b_{2u}\rangle$ and $|b_{3u}\rangle$ levels and they are y and x polarized, respectively. It should be noted that the light emitted by a given center is always polarized in a plane perpendicular to the axis of this center; the same rule has been observed previously in another case of a triplet-singlet transition made allowed by spin-orbit interaction.[8] The energy levels and the selection rules for the [110] and [1$\bar{1}$0] sites, whose axes are, respectively, parallel to and perpendicular to the magnetic field, are shown in Fig. 1 where we have assumed D is positive.

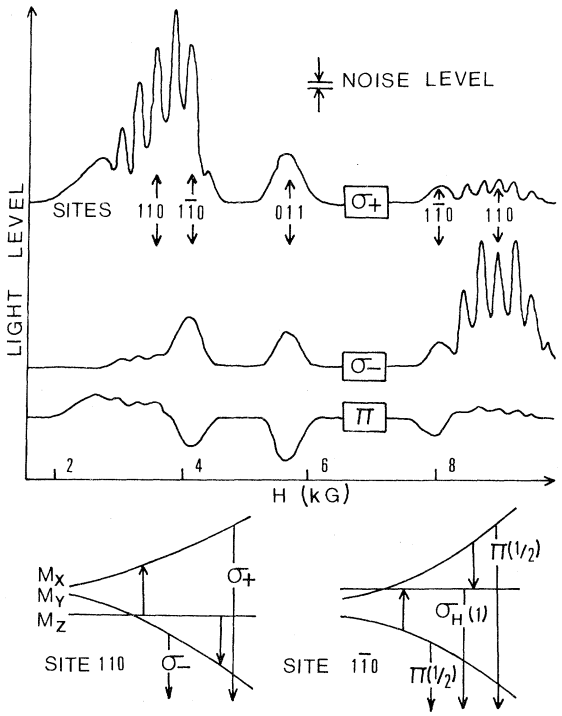

FIG. 1. EPR spectra of the self-trapped exciton in KBr for σ_+, σ_-, and π polarizations of the monitored light. The magnetic field was along a [110] direction of the crystal. The microwave frequency was 17 GHz and the temperature 1.6°K. Optical selection rules shown in the lower part of the figure allowed the assignment of the various lines to the six sites as indicated on the σ_+ and σ_- spectra.

The lines with a seven-component structure at 3500 and 8900 G are seen in σ_+ and σ_- polarizations, respectively, and not in π polarization; they must be assigned to the $\Delta M = \pm 1$ transitions of the [110] site. The polarization of these lines shows that D is *positive*. The two lines at 4100

and 8000 G, which are observed both in σ_+ and σ_- polarizations, and with the reverse sign in π polarized light, may be assigned to the $\Delta M = \pm 1$ transitions of the $[1\bar{1}0]$ site. This assignment is confirmed by additional spectra which show that these transitions are observed in σ_H light but not in σ_V as expected from the fact that for this orientation of the crystal the [110] site emits σ_H but not σ_V light (see Fig. 1).

The lines at 5700 and 2500 G were assigned to transitions of the four remaining sites (which are magnetically equivalent), and to $\Delta M = 2$ transitions, respectively. These assignments were not in contradiction with the variation of the line positions with field orientation. However, the lines were too broad to be followed when the field was rotated in the (110) plane. Their identification would thus have been impossible without the help of the optical selection rules. The positions of the lines of the [110] and $[1\bar{1}0]$ sites give D, E, g_z, and g_y; additional spectra had to be taken with H parallel to the [001] direction in order to determine the value of g_x. The validity of the form of the spin Hamiltonian used and of the line assignments was checked by measurements at 10 and 24 GHz. Twelve line positions, measured for various orientations of the field and microwave frequencies, were used to determine the five parameters of the spin Hamiltonian by a least-squares fitting procedure. The values obtained are $D/2\beta = 2610 \pm 10$ G, $E/2\beta = 400 \pm 10$ G, $g_x = 2.019$, $g_y = 2.032$, and $g_z = 1.983$ (± 0.005).

The seven-component pattern observed on the two $\Delta M = 1$ transitions of the [110] site is obviously due to hyperfine interaction with the nuclear spin ($I = \frac{3}{2}$) of the two bromine ions forming the molecular ion. The nuclear moments of the two isotopes ^{79}Br and ^{81}Br differ by only 10%, so that they do not give rise to distinct spectra. Unfortunately, this hyperfine pattern was unresolved for most magnetic field orientations, and it was possible to determine only one component of the tensor describing the hyperfine coupling, $A_z = 260$ G.

These results can be compared with the predictions of the simple model describing the self-trapped exciton as a V_K center having trapped an electron in a relatively diffuse "$1s\sigma_g$" orbital.[4] The hyperfine splitting A_z would be due mainly to interaction of the spin $\frac{1}{2}$ of the hole with the two central bromine ions, and the linewidth of each of the seven components would be due to interaction of the spin $\frac{1}{2}$ of the electron with the neighboring ions. When electron and hole are coupled in an $S = 1$ state, the effect of each of these hyperfine interactions is divided by 2. The value of 250 G found for A_z is indeed just a little larger than one half the corresponding parameter of the V_K center in KBr (450 G).[9] The width of the individual hyperfine components (160 G) may be compared to the width of the resonance line of the F center[10] in its ground state (146 G) or in its excited state (270 G). The fact that it is close to one half the latter figure seems to be a confirmation of the rather diffuse nature of the electron orbital. Detailed measurements using electron-nuclear double resonance (ENDOR) will be necessary to determine the extension of this wave function more exactly. We have found from preliminary measurements[11] that the D value in RbBr is just a little smaller than in KBr, and that in NaCl it is smaller by an order of magnitude. Lifetime measurements[12] show that in the iodides D is an order of magnitude larger than in KBr. This strong dependence of D on the nature of halides shows that the dipole-dipole coupling contributes little to its value (at least for the bromides and the iodides), and that the main contribution is from spin-orbit interaction. If the electron is assumed to be in a rather diffuse, s-like, orbital, it will contribute to the isotropic part of the g tensor, but not to its anisotropy nor to the D and E values, which can then be predicted in terms of parameters of the V_K centers given by Schoemaker[9] ($E_{1u}, \Delta_u, \delta, \xi$). An extra parameter, the exchange energy, is necessary and has to be fitted experimentally. The spin-Hamiltonian parameters are obtained by calculating the effect of spin-orbit and Zeeman interaction in the second order of a perturbation calculation. From the value of D, one then calculates an exchange energy $W = 7.5$ meV which does not appear unreasonable when compared to the value (43 meV) determined for the unrelaxed exciton in KI.[13] However, the predicted ratio E/D and g-factor anisotropy are in complete disagreement with the experimental values. The first step in improving this model would be to use a more realistic wave function for the electron while keeping a V_K-like wave function for the hole.

It should be noted in Fig. 1 that saturation of the $-1 \longleftrightarrow 0$ transition of the [110] site gives an increase (and not a decrease) of σ_- light. This means that thermal equilibrium is not attained in this spin triplet and that the $M_S = 0$ level is more highly populated than both $M_S = \pm 1$ levels. This is not surprising since the radiative transitions from this $M_S = 0$ level (to the ground state

level) are forbidden. If the lifetime of the $M_S = \pm 1$ sublevels is short with respect to the relaxation time, and if all three sublevels are fed during the pumping cycle, population will indeed accumulate in the $M_S = 0$ level. Similar effects are observed for the $[1\bar{1}0]$ site, which has its axis perpendicular to the field: Saturation of both the $\pm 1 \longleftrightarrow 0$ transitions gives rise to an increase of σ_H light and a decrease of π light; this proves (see Fig. 1) that levels $M_S = \pm 1$ are now more populated than the level $M_S = 0$. This again is not surprising since, in the high-field limit ($g\mu_B H \gg D$), the theoretical lifetimes of the $M_S = \pm 1$ levels are twice that of the $M_S = 0$ level.

Another manifestation of this thermal inequilibrium is the observation[11] at 1.6°K of a level-crossing effect in the circular polarization of the emitted light when the field is applied along [110]. Similar effects were observed[12] in CsI at 4.7°K. It is noteworthy that the unusual population distribution is reached mainly through unequal lifetimes of the Zeeman substates; similar effects described in the literature[3,14] have been attributed to unequal feeding of these substates.

Observation of paramagnetic resonance gives a striking confirmation of the existence of the triplet state of the self-trapped exciton. Extension of these measurements to a series of alkali halides would be helpful for building a phenomenological model of the electron-hole center. Detection of ENDOR by optical techniques seems possible in KBr; such a study would justify development of the theory of the self-trapped exciton. These experiments illustrate very well a particular aspect of the optical technique used to detect the resonance: By changing the conditions of optical observation it was possible to detect one type of paramagnetic center or the other. This feature is very useful for identification of transitions and, when various lines overlap, it may result in a large enhancement of resolution.

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