are canted relative to the crystallographic axis.

[11] This potential barrier can be quite low, as it only arises from anharmonic effect [U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) A238, 425 (1957)].

[12] For an isolated octahedron μ is the oxygen mass, 16 amu. In this case we find $x_0 = 0.15$ Å for YAG:Mn^{3+} and 0.35 Å for Al_2O_3:Ni^{3+}. However, there is some evidence from the concentration dependence of acoustic loss (see reference 3) that cooperative Jahn-Teller effects are significant even at quite low concentrations. It follows that more than the nearest-neighbor oxygen ions are involved, so that μ is greater than 16 amu, and x_0 is correspondingly less.

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POLARITON ABSORPTION LINES

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(Received 18 May 1965)

When light is weakly absorbed in a crystal ($\alpha\lambda \ll 1$), the observation of a sharp absorption line at energy E is generally taken to mean that there is an excitation level at an energy E whose energy could be, in principle, calculated from a many-body Hamiltonian in which the electron-electron interaction is the simple Coulomb potential. This Letter reports the observation and interpretation in ZnO of sharp, weak absorption lines whose energies cannot be so calculated.

The band structure of hexagonal ZnO has been previously reported.[1,2] The present work was stimulated by an interesting recent report by Park et al.,[3] in which a somewhat modified interpretation of the original results was proposed.

The exciton energy-level structure of ZnO near 3.38 eV is shown in Fig. 1(a). Levels marked A and B come from "1S" excitons from

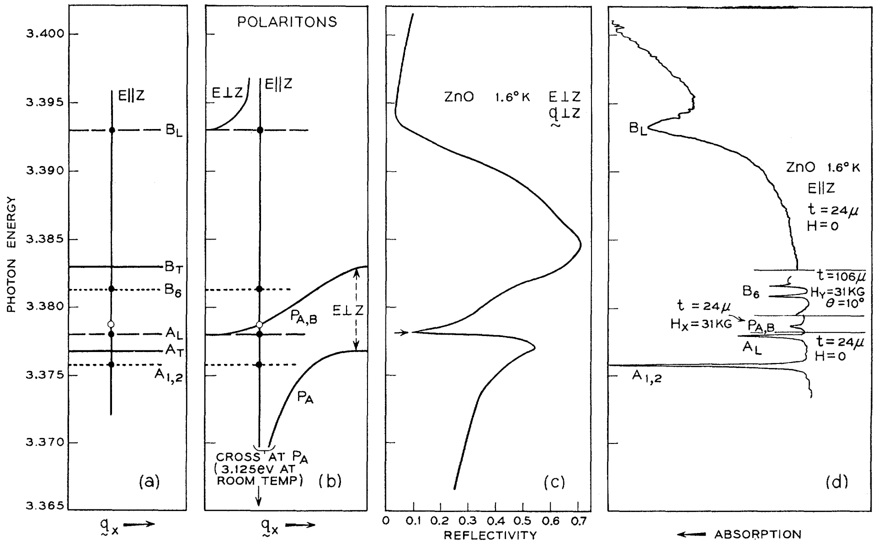


FIG. 1. (a) The intersections between exciton dispersion curves and light with $E \parallel z$ for the A and B excitons in ZnO. (b) The same as (a) except that polariton states have been drawn in place of excitons. Absorption lines can occur in $E \parallel z$ at level crossings. (c) The reflectivity of ZnO for $E \perp z$ light. (d) A composite display of the absorption of $E \parallel z$ light in ZnO. t is the crystal thickness. The curves are microphotometer traces taken from photographic plates.

the first and second valence bands, respectively. Exciton A consists of two sets of states which arise from the two relative orientations of electron and hole spin. One set itself consists of a degenerate pair and is the short-dashed line in Fig. 1(a) labeled $A_{1,2}$. It does not interact strongly with light for its formation involves spin flip. The other set can couple to light polarized in the x-y plane (the z direction being defined as the hexagonal axis). For wave vectors $\vec{q}$ in the x direction, these states are dipole coupled (exchange), and split into a longitudinal state A_L (dashed line) and a transverse state A_T (solid line).[4] The same statements are true for exciton B with the notation change of $A_{1,2}$ to B_6. The effects of the finite exciton mass, which is to produce curvature in the $E(\vec{q})$ lines is not observable on the scale drawn.

Light polarized with $E \parallel z$ couples at most only very weakly to all these states. The six intersections of the solid line, labeled $E \parallel z$ in Fig. 1(a), with the exciton dispersion curves then give possible absorption line energies. While all but $A_{1,2}$ of these intersections represents a forbidden transition in the long wavelength limit, finite wave-vector effects, crystal strains and inhomogenities and weak applied magnetic fields might be expected to lower symmetry sufficiently to produce absorption lines in $E \parallel z$ as a result of weak coupling. Only the four intersections marked with heavy dots have, in fact, been observed. $A_{1,2}$ (which was previously labeled A_m)[1] is weakly allowed. The line B_6 is forbidden and so has only been seen by applying a magnetic field in a nonprincipal direction; it then occurs as a split line [Fig. 1(d)]. The g value of B_6 is approximately given by $g \approx 3.9 \cos\theta$, where θ is the angle between the magnetic field H and the z axis. The g value of $A_{1,2}$ is 3.7 for $H \parallel z$, and 0 for $H \perp z$. Combination of these results with the electron g value[5] of 1.93 shows that the orbital contribution of the valence band to the hole g value in excitons is very small, and both hole valence bands will have $g_{h\parallel} \approx 2, g_{h\perp} \approx 0$.

The relevant experimental results are shown in Figs. 1(c) and 1(d). Figure 1(c) shows the reflection results for $E \perp z$, and from these have been derived the energies marked A_T and B_T. The reflection curves are undoubtedly distorted from ideal shapes by the effects of spatial dispersion.[6] Indeed, for light with $\vec{q}$ parallel to z, a weak spatial dispersion reflectivity peak has been seen at the energy of A_L marked by an arrow in Fig. 1(c). In Fig. 1(d) is shown a composite display of the absorption results for $E \parallel z$. The $A_{1,2}$, A_L, and B_L crossings are observed for $H = 0$. The B_6 absorption as explained above is brought in by H with $\theta \neq 0$. An additional line $P_{A,B}$ was observed at an energy 0.0007 eV above A_L, and at a position corresponding to no known energy level in the scheme of Fig. 1(a). In good geometry and in the absence of a magnetic field, this line is weakly observable in many crystals. With the propagation vector somewhat cocked, or in good geometry with an appropriate magnetic field [as shown in Fig. 1(d)], this line is observable in all crystals of suitable thickness. Figure 2(a) shows examples of the zero-field observation of $P_{A,B}$. Under no circumstances have absorption lines been seen at the positions of A_T or B_T.

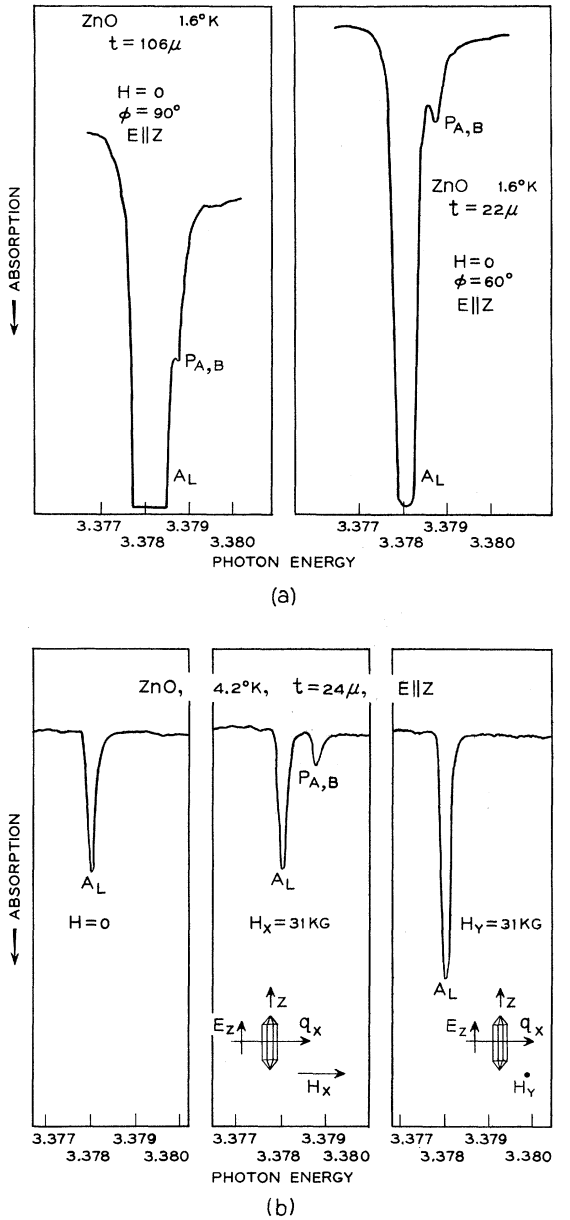
The presence of a line $P_{A,B}$ and the absence of the two anticipated transverse lines follow from the nature of the true normal modes. The actual normal modes of the crystal are polaritons[7] i.e., mixtures of excitons and the photons with which they interact. Since A_T and B_T interact strongly with photons polarized perpendicular to the hexagonal axis, one should really examine the crossings of light $E \parallel z$ with the polariton dispersion relation. These crossings are shown in Fig. 1(b). The two nonobserved crossings of Fig. 1(a) no longer exist. Instead, they are replaced by other crossings. One of these is the crossing of the line $P_{A,B}$ with $E \parallel z$ denoted by an open circle on Fig. 1(b). Other crossings occur beyond the energy scale shown.

The polariton dispersion relation[4] in this geometry is given by

$$\frac{c^2 q_x^2}{\omega^2} = \mathcal{E}_\perp(\omega),$$

while the crossing frequencies (absorption lines) will occur at $\mathcal{E}_\perp(\omega) = \mathcal{E}_\parallel(\omega)$. $\mathcal{E}_\parallel(\omega)$ is readily obtained from the reflectivity for $E \parallel z$.[1] All the relevant parameters for the determination of $\mathcal{E}_\perp(\omega)$ are available,[4] and so, the energy at which the polariton absorption line should occur can be directly calculated and is 0.000 64 eV above A_L, in satisfactory agreement with experiment.

Within the framework of classical optics, a magnetic field in appropriate geometry should



(a)

(b)

FIG. 2. (a) Two examples of the polariton line $P_{A,B}$ seen in zero magnetic field. Φ is the angle outside the crystal between the light beam and the hexagonal z axis. (b) The effects of a magnetic field on some exciton absorption lines. H_x enhances $P_{A,B}$, H_y enhances A_L.

produce couplings at these polariton crossings by the same mechanisms that produce Voigt and Faraday effects in cubic crystals. Because a magnetic field mixes the two components of polarization perpendicular to the field, a magnetic field in the y direction in these experiments couples $E \parallel z$ with the states A_L and B_L. Thus, H_y is expected to enhance, for instance, the absorption line A_L. A magnetic field in the x direction (parallel to $\vec{q}$), however, mixes $E \parallel z$ with the transverse polariton and enhances this additional line. These effects have been seen and are shown in Fig. 2(b).

Another polariton line, much easier to observe, has been seen at room temperature in ZnO and also in CdS. It happens that just below the band gaps of these materials there is a crossing of the $E(\vec{q})$ curves for propagating modes polarized parallel and perpendicular to z, just as there is a crossing at $P_{A,B}$ in Fig. 1(b). It also happens that the absorption coefficients of the $\parallel$ and $\perp$ modes are different at this isotropic point. It is possible, therefore, to choose a crystal thickness such that one polariton (which is the one polarized $\perp C$), does not propagate all the way across the crystal, whereas the $\parallel$ polariton does. Consequently, at the isotropic point, a polariton absorption line might be expected to be observed for $E \parallel z$ light. In $E \perp z$, a complementary enhancement of transmission is expected. These expectations have been verified. The lines can sometimes be seen weakly in zero magnetic field, which again must be due to inhomogeneities or higher order wave-vector effects. A magnetic field H_y has no effect on the lines, but in exact analogy to $P_{A,B}$, a field H_x markedly increases the strength of the line. These effects are shown for ZnO and CdS in Figs. 3(a) and 3(b) respectively. The magnetic field effect clearly marks the absorption as a polariton absorption line.

The results may be summarized as follows. The observation of the B_6 line together with previously reported results confirms that in ZnO, the A exciton arises from the Γ_7 valence

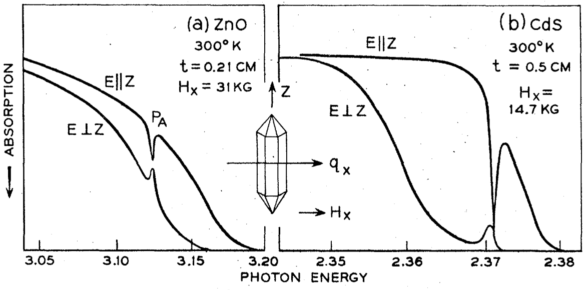


FIG. 3. Polariton effects produced by a magnetic field H_x at room temperature in (a) ZnO and (b) CdS. For $H=0$ there are sometimes very weak anomalous polariton effects. H_y produces no effects.

band, and the B exciton from the Γ_9 band. Since spin-spin splittings and the valence band spin-orbit splitting are all small compared to the exciton binding energies (about 0.059 eV[1]), it follows that the Γ_7 band lies about 0.005 eV above the Γ_9 band. The existence of two polariton absorption lines has completed the observation of the set of level crossings which can occur. The absence of absorption at the transverse exciton energies in the "wrong" mode is now seen to be a simple consequence of the importance of polariton effects.

The existence of polariton absorption lines with $H \parallel \vec{q}$ is a classical effect in anisotropic crystals. The fact that such lines appear even in the absence of magnetic fields and masquerade with or without a field as weak absorption lines, displaced from the transverse exciton states they have replaced, makes them a nontrivial feature of optical investigations of anisotropic crystals.

We wish to thank R. T. Lynch and E. D. Kolb for supplying the ZnO crystals.

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[6] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

[7] See, for example, Robert S. Knox, Theory of Excitons (Academic Press, Inc., New York, 1963), p. 133.

ELECTRON-NUCLEAR DOUBLE RESONANCE STUDY OF THE SELF-TRAPPED HOLE ASSOCIATED WITH LITHIUM IN NaF[*]

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(Received 27 May 1965)

Electron spin resonance (esr) and electron-nuclear double resonance (ENDOR) studies have shown that self-trapped holes (V_K centers) in NaF doped with lithium associate with the Li ions. This complex, in addition to being a new color center, is of interest because of the close resemblance of its esr spectrum to that of the center in LiF identified by Känzig[1,2] as the antimorph of the F center (V_F center).

The esr[3,4] and optical properties[5] of the V_K center have been investigated in several alkali halides. These studies led to the molecule-ion model in which the hole is shared by two adjacent halide ions to form a negatively charged diatomic molecule, e.g., F_2^-, oriented along a [110] crystalline axis. An ENDOR study of the V_K center in LiF by Gazzinelli and Mieher[6] has provided definite verification of this model. A similar ENDOR study has been made of the V_K center in NaF.[7]

In this Letter, the name V_{KA} center will designate the complex consisting of a V_K center associated with an alkali impurity.[8] The lithium V_{KA} center in NaF, which is the subject of this Letter, is shown schematically in Fig. 1.

These centers are produced in crystals grown from a melt of reagent-grade NaF doped with ≈1% LiF by weight. A sample is x irradiated (50 kV, 30 mA, ≈24 hr) at 77°K to produce V_K centers. Upon warming, the onset of conversion to V_{KA} centers is observed at ≈140°K, and the conversion is complete at ≈160°K. The V_{KA} centers are stable at 160°K. No trace of the V_K-center esr remains upon recooling to 77°K. The conversion efficiency based on esr amplitude ratios appears to be near 100%. Attempts were made to orient the V_{KA} centers by optical methods which were successfully used to orient V_K centers in NaF and LiF. However, the V_{KA} centers were dissociated with a consequent regeneration of V_K centers.

The V_{KA}-center esr spectrum, like that of the V_K center in the alkali fluorides, is characterized by a large, anisotropic hyperfine interaction between the unpaired electron and the two nuclei of the molecule. There are, in general, four esr lines corresponding to the four possible combinations of the spins of the two fluorine nuclei ($m_I[\mathrm{F}] = \pm 1, 0, 0$). The separation between the $m_I[\mathrm{F}] = \pm 1$ lines is ≈1800 G