DIRECT OBSERVATION OF EXCITON MOTION IN CdS†

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Several authors have recently described or predicted a number of rather unusual optical effects connected with the exciton spectra of crystals. Gross and Kaplyanskii[1] have shown that the weak forbidden transition to the $n = 1$ state of an exciton in cubic Cu_2O has absorption and polarization properties which depend upon the direction of the exciting light in the crystal. Pekar and Tsekvava[2] have predicted that cubic crystals can show birefringence near exciton absorption peaks if the exciton has an anisotropic mass. In CdS oriented with the hexagonal c axis perpendicular to a magnetic field H, and with the light traveling at right angles to both, Hopfield and Thomas[3] found that the exciton spectra depended markedly on the sign of H. These effects are, however, not peculiar to excitons, since quadrupole transitions of atoms in a crystal field can exhibit analogous behavior. Some effects peculiar to excitons are the result of excitons having an energy versus crystal momentum curve which is not flat. Thus Pekar[4] has shown theoretically that for wavelengths close to a suitable exciton transition, light of the same frequency and polarization can be propagated in the same direction with different refractive indices; Brodin and Pekar[5] have offered evidence of this effect in anthracene crystals at 20°K. In this Letter we report on a new experiment which gives a direct observation of the curvature of the $E(k)$ relation for excitons.

In reference 3 it was pointed out that an intrinsic direct exciton created from a photon must have the same crystal momentum vector as the photon. As a result of its momentum the exciton has a velocity $\hbar\vec{k}/M$, where $\vec{k}$ is the wave vector of the light in the medium and M is the exciton mass. In a magnetic field this velocity gives rise to an additional term in the exciton Hamiltonian equivalent to a quasi-electric field $\vec{E}_q = \hbar\vec{k} \times \vec{H}/Mc$. Stark effects on excitons are in general even functions of the electric field. This will be true for an applied electric field for $H = 0$. However, in the presence of a magnetic field the effective electric field is the sum of the applied and quasi-fields. When the applied electric field, the magnetic field,

and $\vec{k}$ are all mutually perpendicular the effect of the quasi-field should be to shift the plane of symmetry of the Stark effect by an amount E_q. From E_q and $\vec{k}$ the exciton mass can be directly calculated.

The Stark effect has been observed on the $n = 2$ exciton states derived from the top valence band of CdS at 1.6°K in light polarized paralled to c. The Stark effect of the $n = 2$ states is used since it is much larger than the effect expected for the $n = 1$ states. CdS is piezoelectric and so an electric field could affect the spectra by changing the band gap; however, for all fields used no change in the positions of the $n = 1$ lines could be detected, indicating that the piezoelectric effects are negligible. The crystals were 5-10 microns thick and several mm long; the electric field was applied by placing the crystals between the plates of a condenser to which a symmetrical square wave was applied, thus avoiding the necessity of making contacts. The crystals were illuminated with nearly monochromatic light from a Perkin Elmer monochromator with a mean wavelength equal to that of the exciton transition. This ensured that the crystal was exposed to the minimum light intensity so that the photoconductivity was as small as possible and the effective dielectric relaxation time as long as possible. The transmitted light was photographed with a high-dispersion Bausch and Lomb grating spectrograph; in front of the entrance slit there was a revolving sectored disk which served the dual purpose of switching the square wave by means of a separate light source and photomultiplier, and of exposing the photographic plate during only one phase of the square wave. Hence a spectrum could be observed for the electric field in either of the two possible directions.

Figure 1 shows the effect of the electric field on the separation of two pairs of lines of the Zeeman pattern of the $n = 2$ exciton state in CdS with $c\perp H$ and $H = 31\,000$ gauss [the symbols are identified in reference 3]. The two curves are for the two directions of H which, as explained above, give different spectra. This orientation of H with
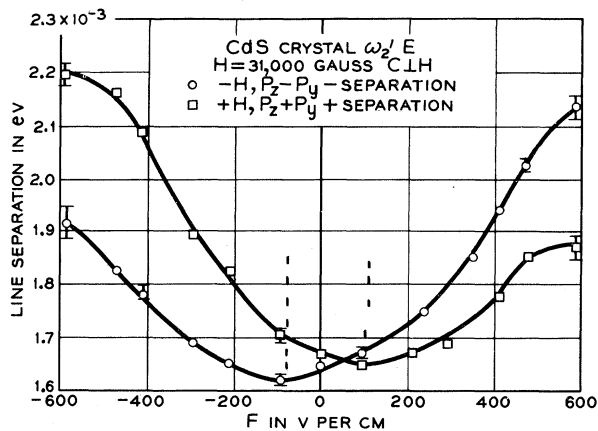
FIG. 1. The separation between two pairs of lines in the Zeeman spectra of the $n = 2$ exciton state in CdS at $1.6°K$, as a function of the applied electric field. The pair of lines P_z^-, P_y^- are two lines in the absorption spectrum with H in one direction, and the pair of lines P_z^+, P_y^+ are two analogous lines for H in the other direction. The light is polarized parallel to the hexagonal c axis.

respect to c was chosen as it gave the most clearly defined lines. The duration of the square-wave cycle was 400 μsec in these experiments. In order to show that the frequency is high enough to prevent appreciable screening of the electric field by polarization of the crystal, a square-wave generator was used without chopping the light. It was found that for $H = 0$ there was no change in the effect as the duration was changed from 1.6 milliseconds to 20 μsec. It is seen that the two curves are approximately symmetrical with their planes of symmetry on either side of the plane of zero applied field. In the absence of a magnetic field no such asymmetry was found. The mean displacement of the planes of symmetry from the center point is about 95 ± 10 v/cm. The directions of the displacements were found to be in accord with the theory described above. At high applied electric fields the lines become broadened and there is evidence that the field in the crystal is reduced. If E_q equals 95 v/cm then M is found to be $1.1 m_e$. (The refractive index for $E \parallel c$ at the frequency of the $n = 2$ transition is estimated from the reflectance spectra to be 2.2; this value was used to calculate the photon momentum inside the crystal.) A recent analysis[6] of the exciton Zeeman spectra of CdS has yielded an exciton mass in a direction perpendicular to c equal to $0.9 m_e$, where m_e is the

free electron mass. The observation of the effect and its agreement in sign and approximate magnitude with the predicted values demonstrate the exciton momentum and show that this exciton "mass spectroscopy" experiment can be used to determine exciton masses.

In some crystals the Stark effect was found to be considerably larger than shown in Fig. 1 and the apparent value of E_q considerably less, in one case only 30 v/cm, although with the correct sign. These effects can be understood by supposing that at $1.6°K$ and 31 000 gauss in some crystals tangent (Hall angle) > 1, i.e., that $\omega_c\tau > 1$, where ω_c is the cyclotron resonance frequency of the highest mobility carriers (presumably electrons) and τ is the relaxation time. Under these circumstances a transverse Hall field exceeding the applied field can form across the thin dimension of the crystal in the direction of the light propagation. This field can be formed before the longitudinal field is screened out because screening of the longitudinal field by surface charge is much less efficient than that of the transverse field. Presumably at sufficiently high frequencies the Hall field would not be established, but such frequencies were not available to us. In one crystal, analysis of the results showed that $\omega_c\tau \sim 1.7$. This indicates that cyclotron resonance may be observed in CdS but only in selected crystals at fields in excess of about 20 000 gauss. From the magnitude of the Stark shift shown in Fig. 1, it is estimated that $\omega_c\tau \sim 0.5$ for this crystal and that the Hall field shifts the position of the symmetry planes by about 20%. The calculated exciton mass is therefore expected to be somewhat too high.

The method of determining the exciton mass described here could be of use in determining the individual masses of holes and electrons since the reduced exciton mass comes from the exciton ionization energy. Interest also derives, however, from the fact that due to polaron and other effects the exciton mass may not be simply the sum of electron and hole masses. Provided the exciton lines are sharp, which was the case for the crystal used in Fig. 1, the method is easiest to apply when $\omega_c\tau < 1$. Finally, the inclusion of the $\hbar \vec{k} \times \vec{H}/Mc$ term in the Hamiltonian is of importance in analyzing the Zeeman effect of excitons, particularly for the higher quantum number exciton states.

technical assistance.

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PROTON MOTIONS IN AMMONIUM HALIDES BY SLOW NEUTRON CROSS-SECTION MEASUREMENTS*

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The motions of ammonium ions and the order-disorder transitions in their salts have been investigated extensively by a variety of techniques. These include specific heat measurements,[1-4] crystal structure studies by neutron diffraction,[5] infrared spectroscopy,[6-8] and nuclear magnetic resonance.[9-11] The results of the investigations reported here show that cross-section measurements for neutrons of subthermal energy also provide a valuable criterion for determining the type of proton motion and the strength of chemical binding in the ammonium halides or other compounds of hydrogen.

Using a crystal spectrometer[12,13] at the Brookhaven reactor, total neutron cross-section measurements were made at room temperature for NH_3 gas at 115 psia and for the following ammonium halide salts: NH_4F, NH_4Cl, NH_4Br, and NH_4I. In Fig. 1 the cross sections per hydrogen atom, corrected for neutron absorption,[14] are plotted as a function of neutron wavelength. Since the scattering cross section for hydrogen is large and primarily incoherent, Bragg interference effects are relatively small and do not contribute significantly to the total cross section. A series of closely spaced cross-section measurements in the neighborhood of the most intense Bragg peak for NH_4Br indicated that the Bragg effects were small and could be neglected.

At short wavelengths $(\lambda_n \rightarrow 0)$ the scattering cross sections approach the values for the free atoms. At long wavelengths the predominant inelastic scattering process is one in which the neutron gains energy from the crystal or molecule. The scattering cross section then becomes proportional to the wavelength, λ_n, and may be represented by $\sigma_s = a + b\lambda_n$. The slopes, b, of the cross-section curves in Fig. 1 were determined in the long-wavelength range by a least-squares fit to the data. The dashed line is the theoretical
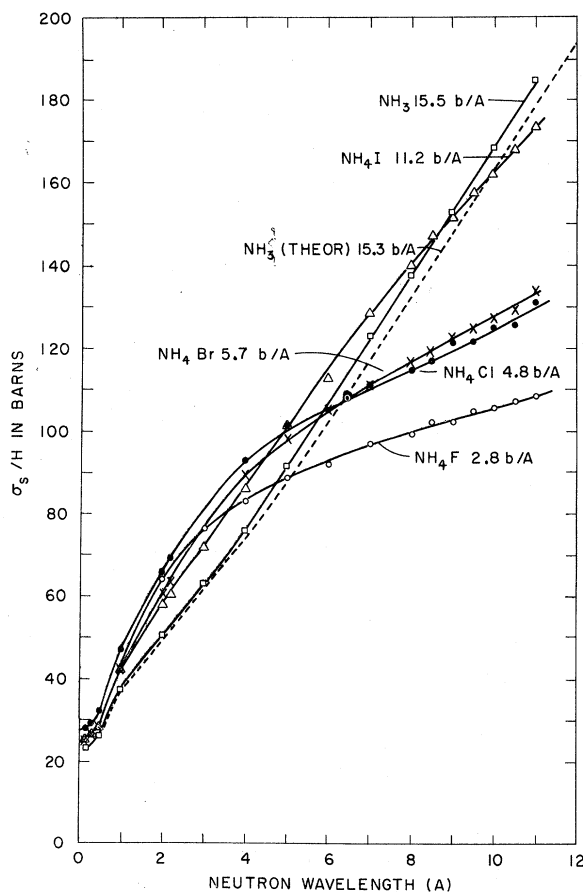

FIG. 1. Neutron scattering cross section per hydrogen atom for ammonia and the ammonium halides.