Exciton Magnetic Circular Dichroism of PbI_2

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The excitons of PbI_2 can be accurately described in terms of two overlapping Wannier series and, by means of magnetic circular-dichroism measurements, it is shown that the effective mass of an electron in the conduction band and of a hole in the valence band are $m_e^* = 0.27$ and $m_h^* = 0.40$, respectively.

The use of a magnetic field has proved a very useful tool in understanding the optical properties of electrons in solids as shown, e.g., by Roth, Lax, and Zwerdling,[1] and Roth.[2] In addition, the effect of a magnetic field on excitons has been discussed by Elliott and Loudon,[3] and by Knox.[4] Here we consider the circular dichroism induced by a magnetic field on the optical properties of PbI_2 and show that remarkable information about the nature of the excitons in this crystal is achieved. To these measurements we have also added a careful analysis of existing optical spectra[5-11] which can now be understood fairly well without previous inconsistencies which affected their interpretation.

The samples discussed in this paper were thin films of PbI_2, approximately 0.1 μm thick, which had been deposited on glass substrates. According to reported data[8] the films used here had their c axis perpendicular to the substrate surface. Thicker films were not employed, since in the main exciton peak they showed some structure apparently due to the presence of crystallites of different orientation.[8]

Magnetic circular-dichroism (MCD) measurements were performed at 18 kG on samples held at ~80°K. The state of polarization of the light falling onto the samples was changed periodically from right to left circular by means of a KD_2PO_4 electro-optical light modulator driven by an electric field at ~20 kHz. The light transmitted from the sample was analyzed by means of a monochromator, and its dc and ac (rms) components I and ΔI, respectively, were detected with an electrometer and a lock-in amplifier. It is easy to show that

$$\Delta I/I = t\Delta\alpha/2\sqrt{2}, \quad (1)$$

where t is the sample thickness and $\Delta\alpha$ its absorption coefficient variation induced by the magnetic field.

The $\Delta I/I$ ratio was recorded as a function of wavelength while keeping I constant through a feedback loop acting on the light source supply. The MCD of PbI_2 is shown in Fig. 1. The exciton peak energy falls at ~2.53 eV, where the MCD curve crosses the horizontal axis, and is thus in agreement with reported film absorption data.[8] In Fig. 1 is shown also the derivative of the optical density with respect to photon energy E, and good agreement is found between this curve and the MCD data when the magnetic-field–induced shift, taken from the zero-field peak, is

$$\Delta E = 21 \pm 1\ \mu\text{eV}.$$

This splitting energy can be used to obtain the value of the effective gyromagnetic factor g^* of the exciton according to

$$\Delta E = g^*\mu_B H,$$

where μ_B is the Bohr magneton, and in this way we get $g^* = 0.20 \pm 0.01$.

We find then that in order to interpret our MCD data it is necessary to re-examine some electron properties of PbI_2 in the region of the lowest

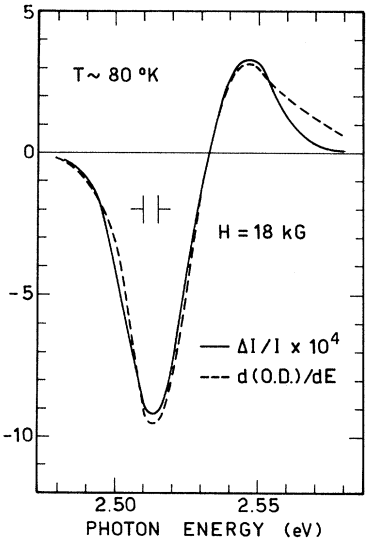

FIG. 1. Measured magnetic circular dichroism of PbI_2 films (solid) and energy derivative of the $H=0$ optical density (dashed, arbitrary units).

excitons in the absence of external fields. The optical data on PbI_2, which are reported in Fig. 2 and Tables I and II, had been previously interpreted as a very anomalous Wannier series in which the $n = 1$ line did not fit the expected sequence.[6,11] In fact, the $n = 1$ exciton was assumed to lie at energies lower than predicted from the remaining peaks, in contrast to the behavior observed in other systems.[12] Since it appeared unlikely to us that, because of the large dielectric constant of PbI_2 ($\epsilon \sim 6.2$), the Wannier-Mott scheme did not fit, we then studied the data of Fig. 2 and found that a consistent interpretation of the spectra between 2.5 and 2.6 eV could be given in terms of two overlapping series of excitons: A,

$$\hbar\omega_n = E_g - G/n^2$$

and B,

$$\hbar\omega_n' = E_g + \Delta - G/n^2,$$

where $\Delta \simeq B_1 - A_1 \simeq B_2 - A_2$, as from Table I. The two series show a very close analogy with the spectrum of solid krypton between 10 and 13 eV.[13]

In fact, when using the data of Nikitine *et al.* (see Table I), we get $B_1 - A_1 \cong B_2 - A_2 \cong 25$ meV, where the subscripts refer to the exciton-envelope quantum numbers. Furthermore, the assumption of the reduced-mass scheme for the lines A_1 and A_2 proves successful since it predicts the energy gap $E_g(A)$ (Table II), exactly where it is found—the hump labeled A_∞ of Fig. 2.

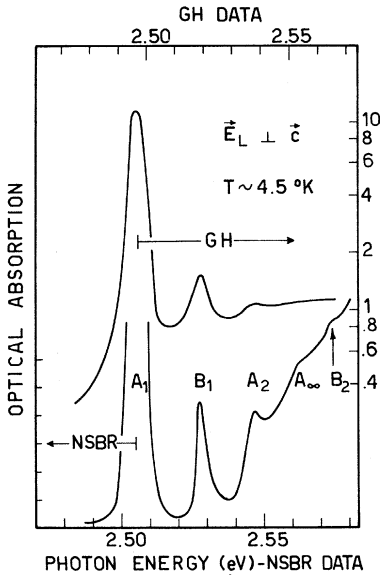

FIG. 2. Optical-absorption spectra according to Nikitine *et al.* (NSBR, Ref. 6) and to Gähwiller and Harbeke (GH, Ref. 11).

Table I. Peak energies, in meV, of PbI_2 optical spectra.

	NSBR (Ref. 6)	GH (Ref. 11)
A_1	2506	2496
A_2	2551	2537
A_∞	2566	•••
B_1	2531	2520
B_2	2577	•••
$B_{1,2} - A_{1,2}$	25	24

The Rydberg, or exciton binding energy, is found to be essentially the same for both series, ~60 meV with the use of the data of Nikitine *et al.*,[6] and 55 meV with the use of Gähwiller and Harbeke's data.[11]

The shape of the spectrum of Fig. 2 can be reproduced fairly well by employing Elliott's formula for exciton and interband transitions.[14] It is also found that employing linewidths Γ of the order of 6 meV, such as those observed, no line with $n \geq 3$ can be resolved, as can be seen in Fig. 2. In fact, it is easy to show that the inequality $G/\Gamma \leq n^2(n+1)^2/(2n+1)$ gives the quantum numbers of the lines that cannot be resolved. Here G/Γ is ~10.

We examine now the cause of splitting between the two exciton series by noting, first, that the energy $\Delta \sim 24.5$ meV is of the order of that found in the fine structure of alkali-halide spectra which was attributed to exciton-phonon interaction.[15] Infrared studies on PbI_2 have shown that the TO phonons should lie at ~16 meV.[16] Now, since this crystal is only slightly ionic, i.e., the optical and static dielectric constants are almost equal,[17] the LO phonons, which have a strong coupling with the electrons, should have energies only slightly higher than those of the TO phonons. Therefore on the basis of such phonon energies it appears fairly hard to justify

Table II. Values of exciton parameters calculated according to this paper. Energies in meV, masses in free-electron units, and radii in angstroms.

Exciton parameters	NSBR (Ref. 6)	GH (Ref. 11)
$E_g(A)$	2566	2551
$G_A \sim G_B$	60.5	55
$\mu_A \sim \mu_B$	0.17	0.16
$r_A \sim r_B$	19	21
$E_g(B)$	2592	•••

the observed exciton-series splitting Δ by means of the mere sum of an exciton plus a LO phonon.

It remains to consider the existence of a splitting in the upper valence band which has been suggested by several authors who have given values ranging from 10 to 48 meV.[7,8,18] Selection rules should allow only transitions from the higher of the two bands when the electric vector of light is polarized perpendicularly to the c axis as in the spectra of Fig. 2. It may occur, however, that because the light beam impinging onto the crystal is not parallel, the "forbidden" series might also be excited to such an extent as to give the weaker B lines. Or, it may occur that mixing between the two bands takes place via phonons of proper symmetry to render partially allowed the transitions arising from the lower band. Further experimental results are required in order to specify the actual process which determines the observed splitting.

If we assume that the energy bands of PbI_2 are parabolic and isotropic, then we can describe the MCD measurements in terms of g^* which has been shown to be given by[1,2]

$$g^* = \frac{2E_{s.o.}}{3E_g + 2E_{s.o.}}\left(\frac{1}{m_e^*} - \frac{1}{mm_h^*}\right), \qquad (2)$$

where $E_g(A)$, m_e^* and m_h^* have their usual meanings and the spin-orbit energy $E_{s.o.} = 0.81$ eV.[7,11] This expression has been employed also for magneto-optical studies of Ge,[1,2] CdSe,[19] and thallous halides.[20]

In the reduced-mass approximation we have

$$1/m_e^* + 1/m_h^* = 1/\mu, \qquad (3)$$

and from (2)

$$1/m_e^* - 1/m_h^* = C_g^*, \qquad (4)$$

where $C = 5.74 \pm 0.02$ according to the values of Table II. By solving Eqs. (2) and (3) for m_e^* and m_h^* we get $m_e^* = 0.275 \pm 0.015$ and $m_h^* = 0.04 \pm 0.03$.

In the above equations we have employed film data which do not resolve all peaks. In Fig. 2, however, we see that the dominant contribution to the optical spectra is A_1, and therefore the MCD data of Fig. 1 can be essentially related to the main peak.

In conclusion, the results discussed in this note, after leading to accurate estimates of the band gap and of the exciton binding energy, have given, for the first time, the values of the electron and hole effective masses of PbI_2.

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