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Metastable Excitons in CdI_2 and PbI_2

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The fundamental reflectivity spectra of the partially ionic hexagonal layer compounds CdI_2 and PbI_2 measured between 2.5 eV and 10 eV at 300°K and 77°K give evidence of several metastable exciton states as well as of bound excitons and strong one-electron interband transitions. Measurements with linearly polarised light demonstrate the two-dimensional nature of the excitons in PbI_2.

§ 1. Introduction

CdI_2 and PbI_2 are of hexagonal crystal structure, point group D_{3d}. The atomic arrangement is in the form of layers of e.g., Cd- or I-atoms, perpendicular to the *c*-axis, the sequence of the layers is repeated in units of I-Cd-I. Planes of easy cleavage are parallel to the layers. The exciton spectrum of PbI_2 at the absorption edge has been studied by several workers.[1-4] The measurements have been done mostly in absorption on films prepared by different methods or on single crystals and gave fairly contradictory results as to the number and position of observed exciton lines. Excitonic structure in the fundamental optical spectra above the absorption edge of both compounds has been reported by Greenaway and Nitsche[5] and later by Brahms.[6]

§ 2. Experimental Procedure

The techniques of reflectivity measurements in the visible, u.v. and vacuum u.v. region with linearly polarised light have been described elsewhere.[7]

Single crystals of PbI_2 have been grown from a melt of zone-refined material by the Bridgeman method. Platelets of CdI_2 were made by evaporating saturated aqueous solutions of CdI_2. For measurements on cleavage planes normal to the *c*-axis the samples were freshly cleaved prior to measurements. Faces containing the *c*-axis have been prepared by conventional lapping and polishing techniques and subsequent light etching with water.

§ 3. Results and Discussion

Figure 1 shows the reflectivity spectra of PbI_2 between 2 and 12 eV at 300°K and 77°K measured on a cleavage plane. The electric vector of the light is thus normal to the *c*-axis. The spectra consist of broad interband maxima which change very little upon cooling and a number of very temperature sensitive lines. The large changes which take place upon cooling clearly indicate that these lines are of excitonic nature. The position of the line associated with the absorption edge in the pure material at 77°K is 2.495 eV equivalent to 4965Å. It corresponds to the strong absorption line found at 4944Å (4.2°K) in single crystals (for references see[4]) and has a half-width of about 20Å. No other lines or fine structure associated with this strong exciton line have been observed in the present measurements.

At higher energies there are pronounced lines due to transitions into exciton states at 3.26, 4.45 and 5.71 eV. These exciton states are associated with van Hove critical points other than the one of lowest energy. The function of the vertical energy difference between conduction and valence bands $E_{cv}=E_c-E_v$ has critical points where the condition $\nabla_k(E_c-E_v)=0$ is fulfilled. At such a point of energy difference E_0 and wave vector k_0, E_{cv} can be expanded in a Taylor series

$$E_{cv}=E_0+\sum_{i=1}^{3}a_i(k_i-k_{0i})^2\,. \qquad (1)$$

If all coefficients a_i are positive we have an M_0 type critical point and the attractive electron-hole interaction of charge carriers results in the well known hydrogen-like series of bound exciton states lying below the conduction band. Exciton states associated with higher conduction bands are degenerate with a continuum of scattering states in another band giving rise to autoionisation and interference asymmetries in the fundamental optical spectra[8] provided the dielectric screening of the Coulomb interaction is not too strong. Exciton effects therefore predominate over interband transitions in the spectra of materials of low dielectric constants and large lattice parameters such as the alkali halides or solid rare gases.[9] In covalent or weakly polar

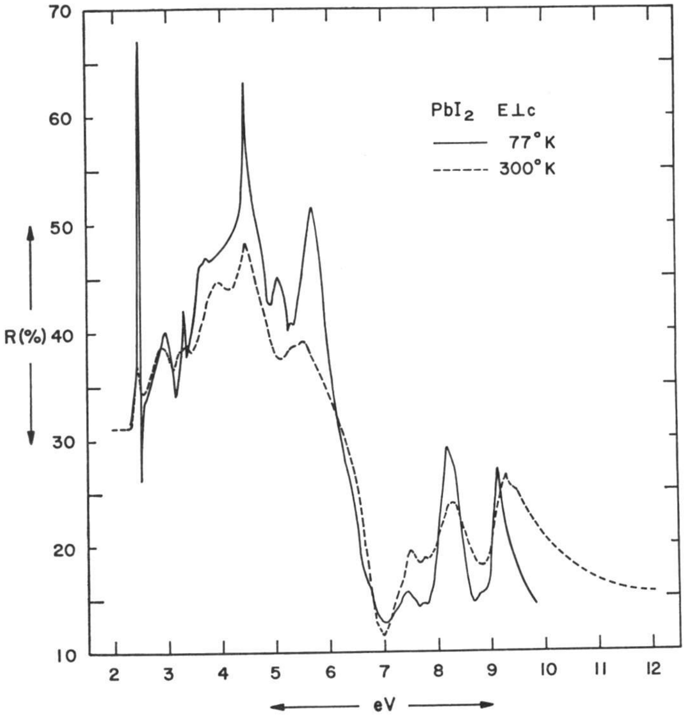

Fig. 1. Reflectivity of PbI_2 at 300°K and 77°K, $E\perp c$.

crystals of higher dielectric constants such as the group IV or III-V semiconductors the Coulomb interaction only modifies the line shape due to interband transitions at critical points. Although it seems that there are also exciton states coupled with M_1- or M_2- type critical points, *i.e.* saddle points where one or two of the coefficients a_i in eq. (1) are negative, there is no rigorous theoretical calculation of bound exciton states at saddle points. The ionicity in PbI_2 is of medium strength (the values for the static and the long-wavelength dielectric constants are 20.8 and 12.25 respectively[10)]) and interband and exciton transitions are therefore of about equal oscillator strength as can be seen in Fig. 1.

There is another remarkable feature common to the three metastable exciton lines mentioned above. Measurements with high resolution reveal a fine-structure pattern of 3 to 5 lines of about equal separation as exemplified by the 3.26 eV peak in Fig. 2. The energies of the fine structure lines are compiled in Table I. It should be emphasized that no such fine structure has been found on the first exciton line where the exciton states are not degenerate with continuum states. We believe therefore that the fine structure reflects the energies of the phonons involved in the exciton decay mechanism. The characteristic energies are different at the three peaks (see Table I) indicating that at each critical point a different set of phonons is required to conserve momentum depending on the relative position of discrete and continuum states in k-space.

Figure 3 shows the 77°K reflectivity spectra of

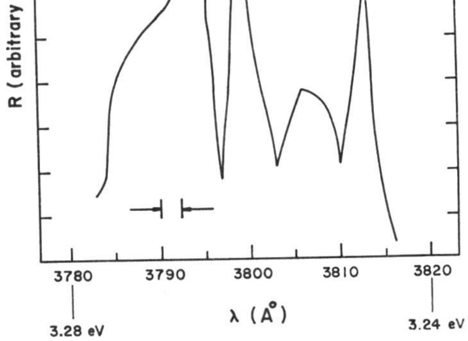

Fig. 2. Fine structure of the 3.26 eV reflectivity peak of PbI_2 at 77°K, $E\perp c$.

Table I. Energies of fine structure lines of exciton peaks in PbI$_2$ in eV.

$E_{\max}$	E	$E_{\max}-E$
3.266	3.261	0.005
	3.255	0.011
	3.249	0.017
4.457	4.470	−0.013
	4.479	−0.022
5.710	5.657	0.053
	5.632	0.078
	5.581	0.129
	5.544	0.166

an etched surface of PbI$_2$ taken with linearly polarised light under the orientations $E\|c$ and $E\perp c$ between 2 and 6 eV. The spectra are different according to the selection rules for the transitions at the critical points depending on the symmetry of the wave functions of initial and final states involved in the transition. This will be used for the discussion of the band structure which is still fairly unknown. The most striking and important result at present is that all exciton lines disappear nearly completely for $E\|c$ whereas the interband structure shows very little difference for both orientations. (The slight indications of the exciton lines for $E\|c$ may be due to the non-zero angle of incidence (~10°) or to a misalignment of the surface layers resulting from the polishing process. For the same reason the absolute and relative heights of the exciton lines differ from those obtained on cleaved surfaces.) The transition into the exciton states thus only occurs if the electric vector of the incident light is parallel to the layers. This result is in accordance with the model of a two-dimensional exciton in layer compounds with the electron and hole confined to the same layer or to adjacent layers so that the dipole moment of the exciton is parallel to the E-vector. This model is equivalent to a two-dimensional hydrogen atom and has been treated by Ralph.[11] The energies of the bound exciton states associated with direct allowed band to band transitions are

$$E_{ex}=E_0-\frac{R}{(n+1/2)^2}\quad \text{for } n=0,1,2\cdots \qquad (2)$$

where R is the exciton Rydberg energy, and the oscillator strengths of the lines are proportional to $(n+1/2)^{-3}$. There appears to be no example in the literature where a series of experimentally observed exciton lines can be fitted by eq. (2). It should however be borne in mind that for the oscillator strengths of the first two lines a ratio of 27:1 is predicted by this theory. The polarization dependence of the exciton lines in PbI$_2$ gives the first clear evidence for the existence of two-dimensional excitons in layer compounds.

Metastable excitons have also been found in CdI$_2$.[5] Figure 4 shows part of the fundamental reflectivity spectrum above the absorption edge

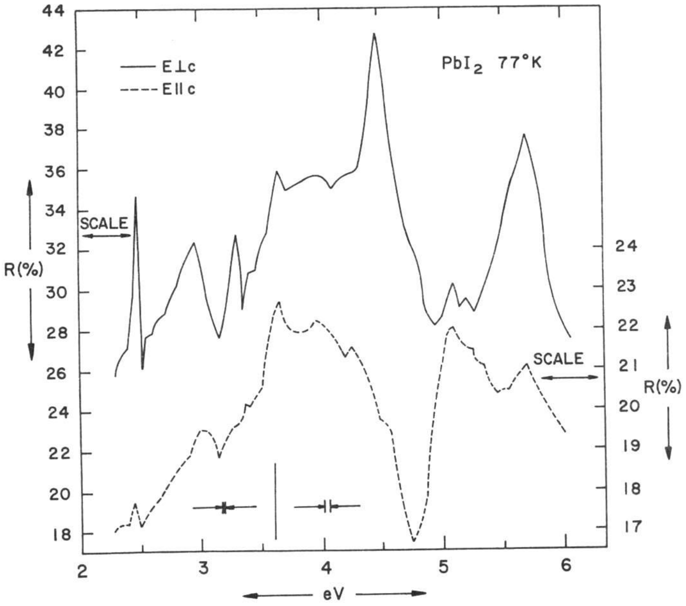

Fig. 3. Reflectivity of PbI$_2$ at 77°K, $E\|c$ and $E\perp c$.

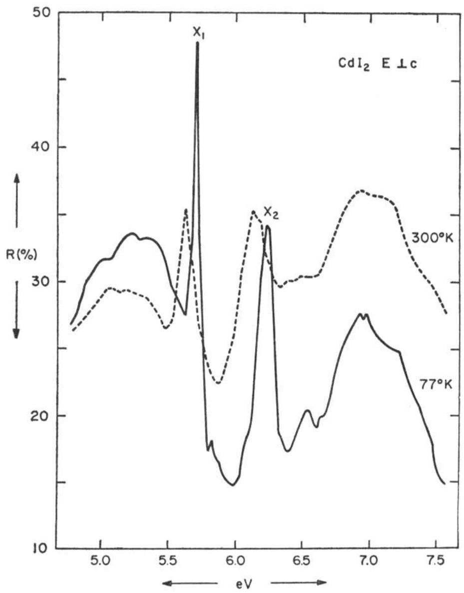

Fig. 4. Reflectivity of CdI_2 at 300°K and 77°K, $E \perp c$.

at 3.2 eV. In this material no exciton structure occurs at the edge. At higher energies we again find broad interband maxima which do not change appreciably on cooling, and excitonic structure with two resonances X_1 and X_2 separated by a symmetrical antiresonance dip. On cooling the excitonic structure sharpens further and reveals satellite peaks at higher energies. In CdI_2 we find that the exciton structure is also present for $E \| c$. In this case the excitons are thus not of two-dimensional character. The lines instead can be fitted with a normal three-dimensional hydrogenic model giving binding energies of 0.17 and 0.41 eV for X_1 and X_2, respectively. The difference in the binding energies as well as different temperature coefficients indicate that X_1 and X_2 are not coupled together by a mechanism such as spin-orbit splitting.

The results show that these partially ionic materials can provide interesting examples of the coexistence of both exciton and interband scattering transitions with large oscillator strength. Clearly much work remains to be done on such materials, particularly from a theoretical point of view, both to interprete the spectra shown here, and to determine the overall electronic band structure.

Acknowledgements

We would like to acknowledge the co-operation of Dr. R. Nitsche who grew the crystals used in this work, and the assistance of Mr. E. Meier who prepared samples and took many of the measurements.

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DISCUSSION

Frederikse, H. P. R.: What is the order of magnitude of the lifetime of these excitons which are subject to autoionization (e.g. the 4.5 eV exciton in PbI_2)?

Harbeke, G.: From the line width we may conclude a lifetime of the order of 10^{-12} sec. No other measurements concerning the lifetime have been performed.

Mooser, E.: I should have expected a two-dimensional character only for excitons associated with the conduction band edge. Can you offer any explanation, why this character should be maintained for excitons which lie up to 3 eV above the band edge?

Harbeke, G.: It should be noted that the density of states function and thus the reflectivity spectra are dominated by critical points. The nature of the exciton states also at high energies is therefore determined by very small regions in *k*-space rather than by the entire conduction band. There is thus no basic difference to the excitons associated with the conduction band edge.

Phillips, J. C.: Several years ago I proposed that hyperfine structure at interband absorption peaks could be taken as evidence that those peaks showed exciton resonance enhancement. The data shown here for PbI_2 exhibit hyperfine structure in excellent agreement with that model. In particular the strong antiresonant interference between the hyperfine components indicates that there is one basic resonance, presumably of electronic character, with an external field (probably phonons) being responsible for the hyperfine structure. It is amusing that similar structure has been observed in nuclear scattering experiments and has been interpreted in a similar manner by Ferrell[1)] using the concept of "hallway states."

Reference

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