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The Effect of Hydrostatic Pressure on the Optical Properties and Electron Energy Levels in Thallous Halides

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ABSTRACT

Measurements have been made on the optical absorption of freely mounted thin crystals of TlBr, and evaporated films of TlCl, TlBr and TlI, from room temperature down to 4°K. The shift with pressure to 6 kbars of the sharp excitonic features has been followed at 80°K and 274°K. All the exciton peaks move to lower energies with pressure, but the spin–orbit doublet moves at a slower rate than the other peaks. The pressure coefficient of the energy of the first exciton peak (minimum gap) rises sharply with temperature above the Debye temperature (*ca.* 130°K). From these measurements information on the electron lattice interactions and deformation potentials has been obtained. A model for the band structure of TlBr and TlCl has been outlined, based on an analysis of the optical spectra, pressure shifts and band structures of isoelectronic compounds.

§ 1. INTRODUCTION

INFORMATION concerning electron energy levels in solids can be gained by studying optical absorption spectra over a broad energy range. These energy levels are affected by a change in the volume of the crystal, which can be brought about by the application of pressure. Paul (1961) pointed out that interband transitions corresponding to the same pair of symmetry states have approximately the same rate of energy change with pressure (pressure coefficient). Thus the use of pressure in conjunction with optical absorption measurements provides some insight into the symmetry properties of energy levels, and at the same time allows comparisons to be made between different solids.

The thallous halides are basically ionic solids and crystallize in either the cubic CsCl (TlCl, TlBr) or the distorted orthorhombic (TlI) structure. They are isoelectronic with the group IV–VI (PbSe) compounds and the group V (Bi) elements. In contrast to the electrical and optical properties of compounds isoelectronic with Ge, a number of 'unusual' properties has been found in previous studies on this family of compounds. These are exemplified by the sharpness of exciton absorption peaks, a positive temperature coefficient (Zinngrebe 1959, Tutihashi 1960, Lefkowitz, Lowndes and Yoffe 1965, Bachrach and Brown 1968, 1970) and a negative pressure coefficient (Zahner and Drickamer 1959, Brothers and Lynch 1969) for the minimum gap energy, and a very high static dielectric constant (Lowndes and Martin 1969). This paper is concerned with a quantitative

study of the effects of temperature and hydrostatic pressure on energy bands associated with transitions both at the minimum gap and at higher energies (< 6 ev). There is also a discussion on a proposed band structure for TlBr, which should also hold for TlCl.

Previous studies on the optical properties of thallous halides have used evaporated films, or thin single crystals on substrates. It is clear from these studies that 'strain' in the crystals (or films) produces serious difficulties in determining the absorption spectra, particularly in the accurate position and the shape of the exciton peaks at low temperatures. In the present investigation, 'freely mounted' single crystals of TlBr prepared by cutting have been used in the transmission measurements, which have been carried out to photon energies of 6·2 ev. In the experiments on TlCl and TlI, evaporated films were used, and only measurements of pressure coefficients have been made in order to compare the results with those for TlBr.

In the absence of thin single crystals, it has been customary to determine the pressure coefficient from the shift of the absorption edge (absorption coefficient $\alpha = 50 \sim 500\,\mathrm{cm}^{-1}$) with pressure: see for example Zahner and Drickamer (1959) and Brothers and Lynch (1969). It is thought, however, that there will always be an inherent uncertainty in the pressure coefficient obtained in this way since both broadening as well as a shift of band edges can be induced by pressure. A pure shift of energy band edges can be obtained only if measurements are made at the peak of exciton absorption ($\alpha = 10^4 \sim 10^5\,\mathrm{cm}^{-1}$), where the change with pressure in the binding energy (B) of the exciton is negligibly small, and this is likely to be true when B is very much smaller than the minimum gap energy.

In the past there has been a good deal of interest in the effect of temperature on electron energy levels and interband transitions (Fan 1951). Using the pressure coefficient and the elastic constants determined elsewhere, the contribution to the temperature coefficient due to lattice expansion (or contraction) can be isolated, thus enabling the term due to electron–lattice interaction to be evaluated. This has been carried out at 80°K, 198°K and 274°K for single crystals of TlBr. As will be shown later, both the pressure coefficient and the deformation potential, defined as the change in an energy level per unit strain (Bardeen and Shockley 1950) vary drastically at higher temperatures, approximately doubling as the temperature is raised from 198°K to 274°K. This would seem to be the first time such an effect has been reported and it should be taken into account when applying Paul's empirical rule (1961) to different solids.

§ 2. Preparation of Specimens and Experimental Methods

Single crystals of TlBr of thickness ranging from about 800 Å to several microns, suitable for optical transmission measurements, were cut directly from a bulk single crystal, which had been grown from powder of 4N8 purity, using an L.K.B. ultramicrotome. Examination in an electron microscope showed that the cut plane coincided with the (110) plane of the