PHYSICAL REVIEW B VOLUME 30, NUMBER 12 15 DECEMBER 1984

High-pressure studies of the absorption edges of three thallous halides

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(Received 4 June 1984)

Visible and near-infrared optical-absorption edges of TlCl, TlBr, and TlI were measured as a function of pressure in a diamond anvil cell. The indirect band gap of the three thallous halides shifts red (to lower energy) with pressure and was followed into the near infrared. The direct band gaps of TlBr and TlCl also shift red at a slower rate. The calculated band structures [J. P. Van Dyke and G. A. Samara, Phys. Rev. B 11, 4935 (1975)] of the thallous halides as a function of pressure are quantitatively compared with the experimental results.

INTRODUCTION

Previous high-pressure studies of the thallous halides include optical-absorption measurements,[1,2] conductivity measurements,[3] volumetric measurements,[4,5] and a theoretical study of the effect of pressure on the band structure.[6] Zahner and Drickamer[1] measured the effect of pressure on the optical-absorption edge of three thallous halides and found each to have a large red shift (to lower energy) with pressure. They indicate the transition is direct but noted that a low-energy "tail" was observed. Brothers and Lynch[2] studied the absorption edge of thin films of TlBr and TlCl at 10 K and pressures up to 3.5 kbar. They found a tail which red shifts 20% to 30% faster than the direct-exciton peak. Subsequent theoretical calculations,[6,7] exciton luminescence,[8,9] and optical-absorption studies[10] indicate that the tail is due to a forbidden indirect transition.

Samara and Drickamer[3] measured the effect of pressure on the conductivity of thallous halides and found the conductivity increased nine orders of magnitude for TlI, seven orders of magnitude for TlBr, and five orders of magnitude for TlCl. These results are consistent with a band-overlap insulator to metal transition for all three thallous halides.

Interest in the insulator-to-metal transition stimulated a series of calculations to determine the effect of pressure on the band structure of the three thallous halides.[6] These calculations indicate that the indirect ($X \rightarrow R$) band gap shifts more rapidly than the direct ($X \rightarrow X$) band gap and that the closing of this indirect band gap is responsible for the observed insulator-to-metal transition. These calculations are consistent with existing optical- and electrical-conductivity data; however quantitative comparison was not possible. Van Dyke and Samara used the relativistic orthogonalized-plane-wave (ROPW) method. The crystal potential was based on superposition of neutral-atom charge densities with Slater $\rho^{1/3}$ exchange and contained no adjustable parameters. Accurate measurements of the absorption edges of the thallous halides under pressure offer a unique opportunity for quantitative comparison between experiment and theory.

TABLE I. Murnaghan coefficients.

Crystal	B_0	B'
TlCl	160	7.6
TlBr	197	4.95
TlI	147	5.15

Equation-of-state information is available from piston displacement[4] and x-ray diffraction measurements.[5] This information is crucial for quantitative comparison of theoretical calculations with experimental results because the natural variable for these calculations is the lattice spacing, not the pressure. In this paper all conversions between volume and pressure are based on the two-parameter Murnaghan equation,[11]

$$P=\frac{B_0}{B'}\left[\left(\frac{V}{V_0}\right)^{-B'}-1\right], \tag{1}$$

where B_0 is the bulk modulus at one atmosphere and B' is the pressure coefficient of the bulk modulus. The values of B_0 and B' were fitted to the data of Bridgman[4] and Drickamer *et al.*[5] and are summarized in Table I. For TlI the volume is referred to the cubic phase which is metastable below 5 kbar. To convert data referenced against the orthorhombic phase we divided by 0.96.

EXPERIMENTAL PROCEDURE

Quasihydrostatic pressure was generated in a gasketed Syassen-Holzapfel—type diamond anvil cell (DAC).[12] The sample powder and a ruby chip were loaded into a predented and drilled gasket and fused under a few kilobars of pressure. The TlCl and TlBr samples were Alfa ultrapure grade. The TlI samples were Puratronic 99.9995% pure. Pressures were calculated on the basis of the shift of the dominant R_2 ruby fluorescence line using the linear [0.365 Å/kbar (Ref. 13)] pressure scale.

The visible absorption measurements were performed with a xenon arc or tungsten-halogen light source, a Kratos monochromator (3.3 nm/mm) with its slits set to 0.15 mm and a photomultiplier with photon counting. The near-infrared-absorption measurements were performed with a tungsten-halogen lamp, a Kratos monochromator (6.6 nm/mm) with its slits set to 2 mm, and a lead sulfide detector using standard lock-in techniques. Fiber optics were used to direct the light from the monochromator to the DAC and from the DAC to the detector.

The single-beam design dictates that the absorption coefficient be determined by comparison of the intensity passed through the system with and without a sample in the DAC. The blank runs were performed with NaCl in the DAC. The incident intensity during absorption measurements is assumed to be proportional to the previously measured $I_0(h\nu)$ curve. Extrapolation of the absorbance to zero to determine the indirect gap requires normalization of the $I_0(h\nu)$ curve. Even below the indirect gap there was some attenuation due to scattering by the polycrystalline sample which followed Rayleighs ν^4 scattering law. To account for this the absorption coefficient $\alpha(h\nu)$ was determined using the following equation,

$$\alpha(h\nu)=\frac{1}{L}\ln\left[\frac{I_0S(h\nu)}{I}\right], \qquad (2)$$

where L is the path length, I_0 the incident intensity, I the final intensity, and $S(h\nu)$ normalizes the incident intensity and accounts for attenuation due to light scattering. $S(h\nu)$ has the following form: $S=n\exp(-A\nu^4)$, where n normalizes the incident intensity and A accounts for Rayleigh scattering. Both n and A are determined from data at photon energies well below the indirect gap.

RESULTS AND DISCUSSION

The direct transition appears as a very steep rise to a shoulder on the absorption curve. This structure can be resolved up to 130 kbar for TlCl and up to 118 kbar for TlBr. The TlI absorption edge does not rise as steeply and does not have a sharp shoulder. The direct band gap of TlI could not be determined. The indirect transition appears as a slowly rising absorption tail on the low-energy side of the direct-absorption shoulder. This tail dominates the absorption edges of TlI at all pressures, but is poorly resolved at low pressures for TlCl and TlBr. For both TlCl and TlBr the tail extends further below the direct shoulder as the pressure increases. This is in qualitative agreement with the findings of Brothers and Lynch[2] and with the band-structure calculations of Van Dyke and Samara.[6]

The direct and indirect energy band gaps were extracted from the absorption curves in the following manner. The direct band gap was taken on the low-energy side of the shoulder at $I_0/I=\frac{1}{2}(I_0/I)_{\text{shoulder}}$ where the edge is very steep. This point is about 30 meV below the exciton peak (shoulder) but should give the correct pressure shift. The indirect edge was plotted as both the square root and the cube root of the absorption coefficient versus the photon energy. These energy dependences correspond to indirect-allowed[14] and indirect-forbidden transitions.[10] When the edge was normalized in the vicinity of the indirect band gap but no correction for Rayleigh scattering was made, the extrapolated energy band gap was sensitive to where the curve had been normalized. This problem was overcome by using the data at photon energies below the indirect band gap both to normalize the incident intensity and to calculate a Rayleigh scattering coefficient. The cube-root plots of the corrected absorbance were more linear than the square-root plots which is consistent with the indirect-forbidden transition. The indirect gaps reported here were obtained from extrapolation of the corrected cube-root plots to zero absorption. For TlBr and TlCl these plots were nearly linear from zero absorption up to about 0.1 eV below the direct band gap where the cubic dependence is rapidly exceeded. For TlI the cubic dependence was not exceeded up to 2.3 eV at 5 kbar and the direct band gap could not be determined.

Figure 1 is a plot of the direct and indirect band gaps of thallous chloride as a function of pressure based on three separate high-pressure runs. The results of the ROPW calculations of Van Dyke and Samara[6] at 1 atm and at $V/V_0=0.8$ (which corresponds to about 94 kbar) are also shown for comparison. The curves passing through their calculated energy gaps are based on linear interpolation versus volume. The predicted shifts are qualitatively correct while the predicted relative placement of the direct and indirect band gap is in excellent agreement with the experimental results. The experimental indirect band gap extrapolates to zero at 340 kbar.

Table II contains quantitative comparisons of the shifts for all three thallous halides with the low-pressure results of Brothers and Lynch[2] and with the ROPW calculations of Van Dyke and Samara.[6] The present shifts are marginally larger than those obtained by Brothers and Lynch. The evaporated thin films used by Brothers and Lynch were probably subject to some strain while our applied pressures were not completely hydrostatic, so the agreement is probably as good as can be expected. The low-pressure determination of the indirect band gap in this investigation is less reliable than the results of Brothers and Lynch.

Table III contains the experimental difference between the direct and indirect energy band gaps in comparison to the low-pressure results of Brothers and Lynch[2] and the

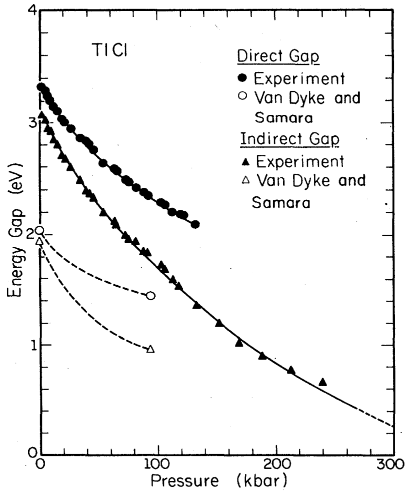

FIG. 1. Direct and indirect band gaps vs pressure for TlCl.

TABLE II. Pressure shifts.

Crystal	Reference	Pressure range (kbar)	Direct-gap shift (meV/kbar)	Indirect-gap shift (meV/kbar)
TlCl	This work	initial	−16	−19
TlCl	Brothers	initial	−14	−18
TlCl	This work	0–94	−11	−14
TlCl	Van Dyke and Samara	0–94	−6.3	−10.4
TlBr	This work	initial	−14	−20
TlBr	Brothers	initial	−13	−16
TlBr	Van Dyke	initial[a]	−13.7	−17.9
TlBr	This work	0–80	−11	−17
TlBr	Van Dyke	0–80	−9.6	−15.1
TlBr	This work	80–137		−14
TlBr	Van Dyke	80–137	−5.6	−9.8
TlI	This work	0–21		−17
TlI	Van Dyke	0–21	−13.6	−24.3
TlI	This work	21–55		−17
TlI	Van Dyke	21–55	−9.1	−18.2

[a] Based on quadratic interpolation versus volume and the Murnaghan equation.

Van Dyke–Samara[6] calculated difference between the X and R conduction-band minima. The calculations are in excellent agreement with the experimental results.

Figure 2 shows the experimental results (from two pressure runs) and the results of the calculations of Van Dyke and Samara[6] of the direct and indirect energy band gaps of TlBr as a function of pressure. The curves passing through the calculated energy gaps are based on quadratic interpolation versus volume and the Murnaghan equation of state. It is clear from Fig. 2 that the predicted shifts and the calculated relative placement of the direct and indirect band gaps are in excellent agreement with the experimental results. The experimental indirect band gap extrapolates to zero at 178 kbar while the calculated indirect band gap of Van Dyke and Samara extrapolates to zero at $V/V_0=0.707$, which corresponds to a pressure of 182 kbar.

TABLE III. Difference between direct and indirect energy gaps.

Crystal	Reference	Pressure	$E_g(D)-E_g(I)$
TlCl	This work	0	0.3
TlCl	Brothers	0	0.24
TlCl	Van Dyke and Samara	0	0.10
TlCl	This work	94	0.56
TlCl	Van Dyke and Samara	94	0.49
TlBr	This work	0	0.2
TlBr	Brothers	0	0.43
TlBr	Van Dyke and Samara	0	0.26
TlBr	This work	80	0.69
TlBr	Van Dyke and Samara	80	0.70

Figure 3 shows the indirect band gap of thallous iodide (from three pressure runs) as a function of pressure along with the results of the calculations of Van Dyke and Samara. The curve passing through the calculated energy gaps is based on quadratic interpolation versus volume and the Murnaghan equation of state. The predicted indirect band gap is a nonlinear function of pressure while the experimental energy gap is nearly linear. The experimental energy gap extrapolates to zero at 114 kbar while the calculated indirect band gap of Van Dyke and Samara interpolates to zero at $V/V_0=0.737$, corresponding to about 109 kbar.

Figure 4 shows the experimental indirect band gaps of

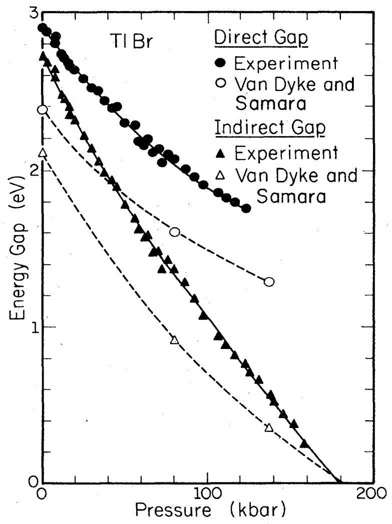

FIG. 2. Direct and indirect band gaps vs pressure for TlBr.

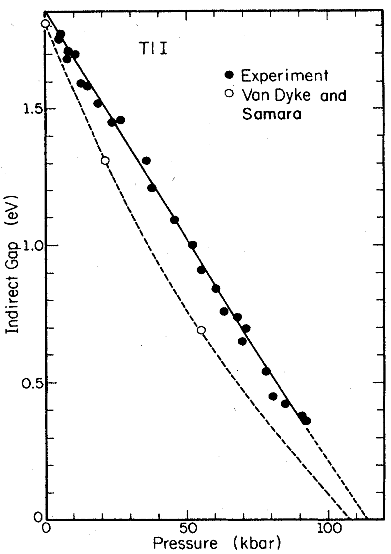

FIG. 3. Indirect band gap vs pressure for TlI.

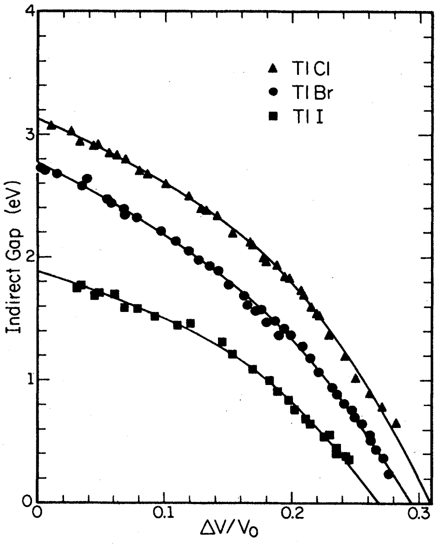

FIG. 4. Indirect band gaps vs $\Delta V/V_0$ for TlCl, TlBr, and TlI.

the three thallous halides versus the change in volume based on the Murnaghan equation. From this plot the indirect band gaps extrapolate to zero at $V/V_0=0.690$, 0.707, and 0.732 for TlCl, TlBr, and TlI, respectively, which correspond to pressures of 332, 182, and 114 kbar.

In conclusion, our results are in reasonable agreement with the low-pressure results of Brothers and Lynch.[2] Our results confirm the prediction of Van Dyke and Samara[6] that the closing of the indirect band gap is responsible for the observed insulator-to-metal transitions. A quantitative comparison of the band structure calculations of Van Dyke and Samara with our results shows that the absolute agreement improves with pressure, the predicted shifts are quite reasonable, and the relative placement of the direct and indirect band gaps is in excellent agreement with experiment.

ACKNOWLEDGMENT

This work was supported in part by the Department of Energy, Division of Materials Sciences under Contract No. DE-AC02-76ER01198.

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[1] J. Zahner and H. G. Drickamer, J. Phys. Chem. Solids **11**, 92 (1959).

[2] A. D. Brothers and D. W. Lynch, Phys. Rev. **180**, 911 (1969).

[3] G. A. Samara and H. G. Drickamer, J. Chem. Phys. **37**, 408 (1962).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

[5] H. G. Drickamer, R. W. Lynch, R. L. Clendensen, and E. A. Perez-Albuerne, Solid State Phys. **19**, 210 (1966).

[6] J. P. Van Dyke and G. A. Samara, Phys. Rev. B **11**, 4935 (1975).

[7] H. Overhof and J. Treusch, Solid State Commun. **9**, 53 (1971).

[8] R. Shimizu, T. Koda, and T. Murahashi, J. Phys. Soc. Jpn. **36**, 161 (1974); **33**, 866 (1972).

[9] J. Nakahara and K. Kobayashi, J. Phys. Soc. Jpn. **40**, 180 (1976).

[10] J. Nakahara, K. Kobayashi, and A. Fujii, J. Phys. Soc. Jpn. **37**, 1312 (1974); **37**, 1319 (1974).

[11] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Wiley, New York, 1951).

[12] G. Huber, K. Syassen, and W. B. Holzapfel, Phys. Rev. B **15**, 5123 (1977).

[13] A. Jayaraman, Rev. Mod. Phys. **55**, 70 (1983).

[14] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), p. 35.