Band-Overlap Metallization of BaTe

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Energy-dispersive x-ray diffraction studies have been made on BaTe to 410 kbar. It undergoes a first-order phase transition from the sodium chloride structure to the cesium chloride structure at 48 kbar. P(V) data were obtained over the entire range. Optical studies indicated by extrapolation that metallization will occur for $V/V_0 \sim 0.65$ while resistivity studies show directly that band-overlap metallization occurs at $V/V_0 = 0.65$ and P = 200 kbar. The resistivity of the semimetallic phase is $600 \ \mu \Omega$ cm at 300 K; the resistivity of the semimetallic phase varies linearly with temperature between 200 and 300 K.

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The pressure-induced metallization of xenon by Nelson and Ruoff¹ generated great interest in the study of xenon and in the possible metallization of other closed-shell systems. It was subsequently shown by workers from the same group² that the pressure actually presented in the indentor-anvil system was very much greater than that stated earlier.

The metallization of members of the isoelectronic series of barium telluride, cesium iodide, and xenon are of great current interest.³ The band gaps in these insulating materials are expected to decrease as the pressure increases (or as the volume decreases), until finally band overlap occurs.^{3,4} Of these three materials, it is expected that barium telluride will exhibit band overlap at the lowest pressure.⁵

In the present study, lattice parameter, optical absorption edge, and resistivity measurements were made as a function of pressure. A sixteen-sided anvil tip with a diameter of 640 μ m was used with a stainless steel gasket with a 150- μ m-diam hole obtained by drilling the pre-indented gasket. Ruby was used to measure the pressure based on a linear scale.⁶ The sample had purity greater than 99.5% but required extensive hydrogen treatment to remove a second phase. Sample preparation and the placement of the sample in the gasket are described elsewhere.⁷ Initially (after H₂ treatment) BaTe appeared yellow with a lattice parameter of 7.005 ± 0.01 Å.

Equation-of-state studies were made using energy dispersive x-ray diffraction techniques in the Cornell High Energy Synchrotron Source⁸ with propanol as the pressure medium. BaTe underwent a phase transition from the sodium chloride type structure to the cesium chloride type structure at 48 ± 3 kbar; optical studies were used along with diffraction experiments to help define this pressure. The cesium chloride structure then persisted to the highest pressure used, 410 kbar. In many cases, seven or eight diffraction peaks of the highpressure phase were present. The reduced volume versus pressure curve is shown in Fig. 1. The data were fitted by a first-order Birch equation of state. This involves B_0 and B'_0 which are the bulk modulus at zero pressure and the first pressure derivative of the bulk modulus at zero pressure. When fitting the data for the cesium chloride phase, there are three parameters, B_0 , B'_0 , and V_0 (CsCl); in this case V_0 (CsCl) is the fitted volume of the cesium chloride phase at zero pressure. We obtain $V_0(\text{CsCl}) = 0.907 V_0$. Table I shows B_0 and B'_0 for each phase. The volume changes at the transition are also shown in Table I. Unless otherwise stated, V_0 will subsequently correspond to the zeropressure volume in the original NaCl phase.

Optical absorption was studied as a function of wavelength to obtain absorption edges. In these studies no pressure medium was used. There was, therefore, some pressure gradient across the sample, but judging from the color variation at a given



FIG. 1. Volume fraction vs pressure for BaTe at 296 K. The data for the NaCl phase were obtained in the first experiment by one of us (T.A.G.) and unfortunately this low-pressure range was not studied further. The data for the high-pressure phase comes from later experiments and is considered accurate.

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 TABLE I. Transition and equation-of-state data for the NaCl and CsCl phases of BaTe at 296 K.

 Compound
 $P_{\rm c}(khar)$ AV/V(NaCl) $B_{\rm c}(khar)$ $B'_{\rm c}$

Compound	P_t (kbar)	$\left[\Delta V/V(\text{NaCl})\right]_{p_t}$	B_0 (kbar)	<i>B</i> ₀ '		
BaTe(NaCl) BaTe(CsCl)	48 ± 3	0.132	294 ± 2 ^a 275 ± 9 ^b	7.4 ± 0.2^{a} 4.6 ± 0.66^{b}		
^a Ref. 9.		^b Based on $V_0(\text{CsCl}) = 0.907V_0$.				

pressure in BaSe, which we have also studied, this was not large. The optical data were obtained over the entire sample cross section. For the wavelength region of 0.4–1.1 μ m a silicon diode or GaAs photomultiplier tube was used as a detector while for longer wavelengths, cooled PbS or PbSe photoconductive detectors were used. A tungsten light source was used in these experiments. Absorption edge values were estimated by a linear extrapolation of the higher energy end of the optical-densityversus-energy plots to zero optical density. The results of these studies combined with the x-ray studies are shown in Fig. 2. We have assumed that the absorption edge corresponds to the energy band gap. The theoretical results of Carlsson and Wilkins¹⁰ show curvature in the E_g vs V/V_0 curves with the slope increasing as $E_g \rightarrow 0$. The solid curve was obtained as follows: We assumed that the Lorentz-Lorenz equation

$$(n^2 - 1)/(n^2 + 2) = R/V$$
(1)

applies and that the molar refraction R does not vary with the molar volume, V, or pressure; here nis the refractive index. Since $n \to \infty$ as $V \to V_m$, the metallization volume, it follows that $R = V_m$



FIG. 2. Absorption edge vs volume fraction at 296 K. The solid line is fitted to Eq. (4). 490

and that

$$(n^2 - 1)/(n^2 + 2) = V_m/V$$
 (2)

We then used an empirical relation due to Ruoff¹¹ who noted that the closed-shell systems consisting of the alkali halides, the alkaline chalcogenides, and the rare-gas solids closely obey the relation

$$n^2 E_{\mathbf{g}}(eV) = D, \tag{3}$$

where $D = 21.1 \pm 2.4$. This relation with D as an adjustable parameter was combined with Eq. (2) to obtain

$$E_{g} = D(V - V_{m})/(V + 2V_{m}).$$
(4)

This was fitted to the experimental data including the point at $V = V_0$,¹¹ resulting in a value of D = 22.7 eV and $V_m/V_0 = 0.655$. A straight-line fit gave $V_m/V_0 = 0.643$. From these results, it appears that the band gap goes to zero in the neighborhood of $V/V_0 \sim 0.65$. Extrapolations are always dangerous (even small ones) so extrapolation of optical measurements, even for smaller band gaps than measured here, must be taken only as one indication of when band-gap closure may possibly occur. Electrical resistivity measurements are needed to clarify the issue.

Four electrical leads were sputtered to the face of one diamond. These leads were extended up the sides of the diamond, where wires were attached. Electrical insulation was provided by a modification of the method used elsewhere.¹² A mixture of Al₂O₃ and NaCl was used as the electrical insulation barrier between this tip and a metal girdle produced by punching out the flat center region of a $500-\mu$ mthick preindented stainless-steel gasket. This compressed composite also serves as the gasket material between the diamonds. A circular hole in this composite insulator contains the sample. See Fig. 3. The sample is a circular disc with, effectively, four leads attached at the edges (although there is a small overlap). Van der Pauw's method¹³ of fourprobe measurement on a disc of uniform thickness was used to obtain the resistivity when metallization had occurred. It is believed that this is the first ap-



FIG. 3. (a) Schematic of resistivity arrangement. Each of the four electrical leads sputtered *on* the diamond extend from the tapered sides of the diamond onto the tip. (b) Electrode configuration on the tip. The leads extend just slightly into the sample region which is shown by the dashed circle.

plication of van der Pauw's method to measure resistivity in the diamond anvil cell. This makes possible resistivity measurements on samples, e.g., which are not solids when the experiment begins, or are not solid bars of fixed geometry when the experiment begins or which change their dimensions when the experiment is performed. The sample thickness at pressure must be known. A paper on the details of the electrode and gasket fabrication is in preparation.

During the present experiment the crosssectional area, A, of the sample was measured. Upon completion of the experiment, the area is again measured at atmospheric pressure; then the thickness of the sample at atmospheric pressure, t_f^0 , is carefully measured. From t_f^0 , A, and the P(V)lation shown in Fig. 1, the actual thickness at a given pressure (or fractional volume) can be computed. From this and the appropriate measurements of currents and potential differences, as required by van der Pauw's technique, the resistivity at metallization was obtained. Figure 4 shows the results of log(resistance) versus fractional volume for one experiment. Three separate experiments were performed, with a new sample in each case, with extremely close results in the three cases. In all cases the experiments were carried to 300 kbar or above; in one experiment the studies were made to 495 kbar. Metallization occurs at V/V_0 $= 0.65 \pm 0.01$ (which corresponds to a pressure of 200 ± 16 kbar); using the methods described previously, we find that the resistivity at metallization is $\rho_M = 600 \ \mu \Omega$ cm. Taking into account random errors, possible errors in measuring the thickness t_f^0 and the areas and errors in the P(V) relation, and possible errors introduced by the fact that our leads are not attached exactly along the vertical walls of the circular sample disc, we conclude that our absolute experimental error is less than 100 $\mu\Omega$ cm. (The volume fraction at metallization is in good agreement with that found in our earlier two-lead resistance measurement¹⁴). The temperature variation of the resistivity was studied between 140 and 300 K. The resistivity divided by the resistivity at 296 K of the metal was found to increase linearly with temperature with a coefficient of 0.002/K for pressures above the transition pressures.



FIG. 4. Electrical resistance vs volume fraction at 296 K. The smallest volume fraction shown in this experiment corresponds to a pressure of 304 kbar. The resistivity for the metallic phase computed from van der Pauw's equations and table is $600 \ \mu \Omega \ cm$.

Compound	Optical	Resistivity	Theory ^a	Herzfeld ^b	
ВаТе	~ 0.65(200)	0.65(200)	0.74(90)	0.623(249)	
^a See Ref. 10.	^b See Ref. 15.				

TABLE II. Values of V/V_0 for band overlap. The corresponding pressures in kilobars (from our experimental equations of state) are shown in parentheses.

Our results for band overlap are shown in Table II. BaTe exhibits band overlap metallization at a volume fraction of 0.65 and a pressure of 200 kbar. Also shown are the values computed by Carlsson and Wilkins¹⁰ and, finally, the values computed from the Herzfeld (dielectric model) criterion for metallization.¹⁵ The theoretical calculations¹⁰ give overlap at a much higher volume fraction (or lower pressure) than the values obtained from the experiment; however, the latter are near to the values obtained from the Herzfeld criterion. The metallization of BaTe described here is the first case of metallization in a closed-shell system (rare-gas solids, alkali halides, alkaline chalcogenides) for which the pressure and volume at which metallization occurs are accurately known. The actual overlap process occurs without any observed change in crystal structure.

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²K. S. Chan, T. L. Huang, T. A. Grzybowski, T. J.

Whetten, and A. L. Ruoff, Phys. Rev. B 26, 7116 (1982). ³T. A. Grzybowski and A. L. Ruoff, Mat. Res. Soc. Symp. Proc. 22, Pt. III, 43 (1984).

⁴J. Aidun and M. S. T. Bukowinski, Solid State Commun. **47**, 855 (1983).

⁵J. Aidun, M. S. T. Bukowinski, and M. Ross, Phys. Rev. B **29**, 2611 (1984).

⁶J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

⁷T. A. Grzybowski and A. L. Ruoff, Phys. Rev. B 27, 6502 (1983).

⁸M. A. Baublitz, Jr., V. Arnold, and A. L. Ruoff, Rev. Sci. Instrum. **52**, 1616 (1981).

⁹P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940).

¹⁰A. E. Carlsson and J. W. Wilkins, Phys. Rev. B **29**, 5836 (1984).

¹¹A. L. Ruoff, Mat. Res. Soc. Symp. Proc. **22**, Pt. I, 279 (1984).

¹²R. L. Reichlin, Rev. Sci. Instrum. 54, 1674 (1983).

¹³L. J. van der Pauw, Philips Res. Rep. 13, 1 (1958).

¹⁴A. L. Ruoff and T. A. Grzybowski, in *Solid State Physics Under Pressure*, edited by B. Okai (Academic Publications, Tokyo, 1984).

¹⁵K. Herzfeld, Phys. Rev. 29, 701 (1927).