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Optical response and band-structure calculations of alkaline-earth tellurides under pressure

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Optical reflection and absorption spectra of SrTe and BaTe have been measured in the pressure range of 0 to 400 kbar at 300 K. Excitonic transitions related to the lowest direct gap in the rocksalt ($B1$) structure shift to lower energy with increasing pressure and are attributed to a Te $5p$ to Ba $5d$ (Sr $4d$) transition at the X point. In both SrTe and BaTe the optical response indicates a discontinuous decrease of the lowest direct gap by about 1 eV at the pressure-induced structural transitions from the $B1$ to the $B2$ (CsCl-type) structure. The direct optical gap of BaTe ($B2$) closes at pressures near 270 kbar. An upper limit of about 550 kbar is extrapolated for the corresponding band overlap in SrTe. Experimental and previous theoretical results for phase stability, deformation potentials, and metallization in BaTe are compared to fully relativistic self-consistent band-structure calculations using the linear muffin-tin-orbital method in conjunction with the local-density approximation.

I. INTRODUCTION

High-pressure investigations of alkali halides and alkaline-earth chalcogenides have recently attracted interest, because advances in static high-pressure techniques have made it possible to study the approach to a valence-conduction-band overlap in these large-gap insulators. Previous experimental work on the optical properties under pressure was primarily concerned with the high-atomic-number materials CsI (Refs. 1–4 and literature cited therein) and BaTe.[5–7] Among the Ia-VII and IIa-VI compounds these two isoelectronic materials have the smallest degree of polarity and are therefore expected to undergo an insulator to metal or semimetal (I-M) transition at pressures which are lower compared to other compounds from the corresponding family. Earlier theoretical investigations of CsI (Refs. 8–10) and alkaline-earth chalcogenides[11–13] have provided the basis for a more detailed understanding of the changes in energy band structure and bonding at reduced volume. As a general trend the theoretical models predict that the I-M transition in compounds with heavy cations arises from a lowering of cation-derived d-like conduction-band states relative to the top of the p-like valence-band region.

In the experimental part of the present work we report on the optical response of the two alkaline-earth tellurides BaTe and SrTe in the pressure range of 0–400 kbar at $T=300$ K. From the general features of the band structures of ionic monochalcogenides crystallizing in the rocksalt structure[11–14] SrTe and BaTe are expected to be indirect-gap materials at normal pressure. The indirect-gap energies are not known precisely due to the difficulty of preparing these refractory compounds in high-purity stoichiometric form. In BaTe the fundamental absorption edge appears to be close to 2.6 eV.[15] Excitonic structures associated with the lowest direct valence-conduction-band transitions have been observed near 3.6 eV in SrTe and 3.1 eV in BaTe.[16] Both materials undergo a structural transition from the NaCl-type ($B1$) to the CsCl-type ($B2$) structure near 120 and 48 kbar, respectively.[5,17] Here, we use optical reflection and absorption spectroscopy on *single-crystalline* starting materials in order (i) to investigate the effect of pressure and of structural transitions on the low-energy interband excitations and (ii) to follow the approach towards the valence-conduction-band overlap. A preliminary account of the experimental results has been given elsewhere.[7,18]

In the theoretical part of this work we report on self-consistent band-structure calculations of structural stability, deformation potentials, and band overlap metallization in BaTe under pressure. The present theoretical approach differs from earlier calculations[12,13] in that we employ a self-consistent linear-muffin-tin-orbital (LMTO) method[19] in conjunction with the local-density approximation (LDA) (Ref. 20) to exchange and correlation.

II. THEORETICAL RESULTS FOR BaTe

Band-structure calculations are made as a function of volume for both the $B1$ and $B2$ structures. The calculations are fully relativistic and they include the "combined correction term"[19] which corrects for the nonspherical shape of the atomic cells and the truncation of the angular momentum (l) expansions (we include here partial waves with $l=0$, 1, 2, and 3). Further, in each iteration the energy range of occupied states is divided into two linearization regimes (two "panels") in each of which the LMTO band structure is calculated. The lower panel covers the Ba $5p$ and the Te $5s$ states whereas the upper contains the Te $5p$ bands and, in the metallic phase, the occupied part of the Ba $5d$ band.

Since the LMTO method is less accurate for open structures we include two "empty spheres" in the rocksalt structure. This is particularly important for the total-energy calculations, and we consider the omission of these empty spheres in the augmented-spherical-wave (ASW) calculations by Carlsson and Wilkins[12] as the main cause for the relatively poor predictions of the ground-state properties of BaTe.[21] As will be shown below, the present calculations agree well with the results obtained by Wei and Krakauer[13] who used the linear-augmented-plane-wave (LAPW) method. Thus, the different shape approximations used in LMTO and LAPW do not[21] affect seriously the accuracy of the type of calculations at which we aim in the present work.[22]

The calculated total-energy variations for BaTe in the $B1$ and $B2$ structures are shown in Fig. 1 and the corresponding equilibrium volume, bulk modulus and its pressure derivative are given in Table I. The equilibrium volume agrees with experiment. The calculation of Carlsson and Wilkins[12] gave a volume that was 16% too low for the reason mentioned above. The calculated pressure P_T at which the $B1$-$B2$ transition occurs was obtained from the theoretical structural difference in enthalpy, and we find $P_T=38$ kbar. This is close to the value (32 kbar) found in Ref. 13 and in good agreement with experiment (48 kbar, Ref. 5).

In agreement with observation we find that BaTe is insulating in the $B1$ structure and also insulating after the transition to the $B2$ phase. The band structures calculated for BaTe in the two structures at volumes near the $B1$-$B2$ transition are shown in Figs. 2 and 3. In the rocksalt phase we find the gap to be indirect (Γ—X). In the $B2$ structure (Fig. 3), BaTe also has an indirect gap, namely from the Te $5p$ state at M to the bottom of the Ba $5d$ band at Γ. The direct gap at Γ is only slightly larger (0.1 eV), and it cannot *a priori* be excluded that the errors introduced by the local-density approximation (LDA) could be different for the two gaps. It might be hoped that they would have different volume dependences, so that an experimental identification would be easy. However, calculations show that (within LDA) their first-order volume coefficients are very similar (see Table II).

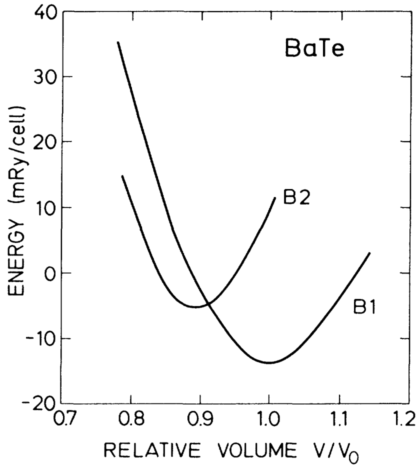

FIG. 1. Total energies of BaTe in the $B1$ and $B2$ structure plotted as a function of relative volume. V_0 is the experimental equilibrium volume.

From the calculation we find that it is the indirect $\Gamma-M$ gap that closes at the band overlap transition. The pressure which we calculate for the I-M transition (less than 100 kbar) is lower than calculated in Ref. 13. Further, the volume V_M at which BaTe in the assumed $B2$ structure becomes metallic is $V_M=0.71V_0$ according to our calculation and is larger than that found by Wei and

TABLE I. Equilibrium volume (V), bulk modulus (B_0), and pressure derivative of the bulk modulus (B_0') of BaTe. The experimental equilibrium volume at 298 K is $V_0=51.64$ cm^3/mol (579 a.u.^{3}). Also given are pressure (P_T) and relative volume (V_T) of the $B1$ phase at the structural $B1$-$B2$ transition.

	Expt.	Calc.			
		ASW[c]	LAPW[d]	LMTO[e]	LMTO[f]
V/V_0	1.0	0.85	0.997	1.000(7)	0.985
B_0 (kbar)	294[a]		354	356	367[g]
B_0'	7.4[a]		4.64	4.76	5.67[g]
P_T (kbar)	48[b]		32		38
V_T/V_0			0.925		

[a] Reference 23.
[b] Reference 5.
[c] Reference 12.
[d] Reference 13.
[e] "Scalar relativistic," i.e., relativistic but without spin-orbit interaction.
[f] Fully relativistic, i.e., including spin-orbit coupling.
[g] Calculated at the observed volume.

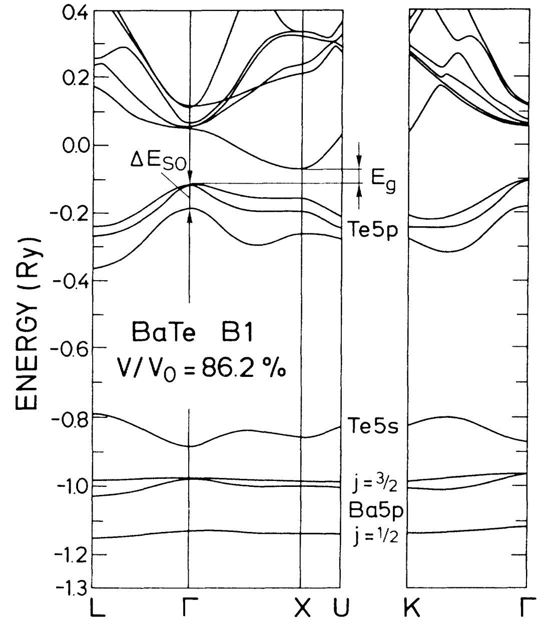

FIG. 2. Relativistic band structure of BaTe in the NaCl-type structure near the $B1$-$B2$ structural transition.

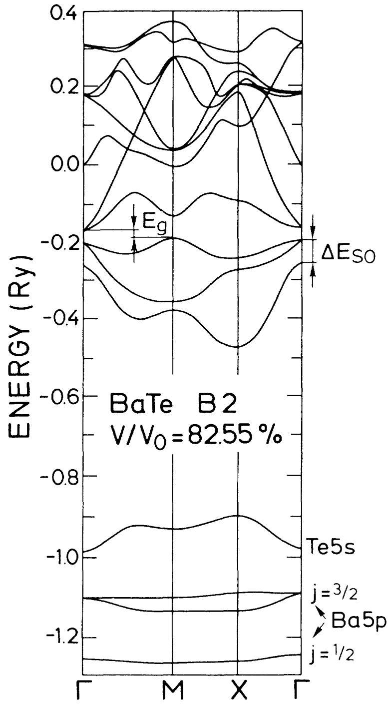

FIG. 3. Relativistic band structure of BaTe in the CsCl-type structure near the $B1$-$B2$ structural transition.

Krakauer ($0.67 V_0$). The experimental value from Ref. 6 is smaller ($0.65 V_0$) and possibly even less according to the present experiment (see Sec. IV).

III. EXPERIMENTAL PROCEDURE

Single crystals of SrTe and BaTe were grown from the melt in tungsten crucibles by using the method of directional solidification. Initial temperatures were about 30° above the melting points which are 2300 °C in SrTe and 2070 °C in BaTe. In the case of BaTe particular effort was made to purify the starting Ba metal in a distillation process. SrTe and BaTe crystals of about 5 mm dimensions were transparent to visible light with a slightly brownish and greenish color, respectively. The lattice parameters are 666.0 pm (SrTe) and 700.1 pm (BaTe). Although the samples could be handled in air without visible degradation over a period of several minutes (in contrast to powdered material), all manipulations were performed under insert gas atmosphere.

High-pressure optical experiments were performed by using a gasketed diamond window cell[24,25] in combination with the ruby luminescence method for pressure determination.[26] Reflection and transmission spectra were measured in the spectral range from 0.5—3.5 eV using a microoptical system similar to that described earlier.[25] A small crystal of about 20-μm thickness was mounted in the gasket with a freshly cleaved surface in direct contact with one of the diamond windows. The remaining cell volume was filled with KCl, which served as a pressure

TABLE II. Volume coefficients $D = dE_G/d\ln V$ of indirect and direct gaps in BaTe ($B2$). Also given are pressure P_M and relative volume V_M at band overlap.

	Expt.	LMTO[c]	LAPW[d]
D(dir) (eV)	5.7[a]	2.44[e]	
D(indir) (eV)		2.81[e]	2.7[e,f]
P_M (kbar)	<270[a] 200[b]	<100	158
V_M/V_0	>0.62[a] 0.65[b]	0.71	0.67

[a] Present experiment.
[b] Reference 6.
[c] Present calculation, fully relativistic.
[d] Reference 13.
[e] Calculated near the $B1$-$B2$ transition volume.
[f] From Fig. 2 of Ref. 13.

medium providing quasihydrostatic pressure conditions. Absolute reflectivities (denoted R_d) were measured at the sample-diamond interface. We note that for these materials the absolute values of R_d are considerably lower compared to the reflectivity R_0 at the sample-vacuum interface due to differences in the refractive index step.

IV. EXPERIMENTAL RESULTS FOR BaTe

Absorption and reflection spectra for BaTe at different pressures are shown in Fig. 4. In the $B1$ phase a broad absorption edge shifts towards lower energy with increasing pressure [Fig. 4(a)]. Superimposed on a smooth absorption behavior there is a weak structure which exhibits a small blue shift, as indicated by arrows in Fig. 4(a). This latter structure is tentatively attributed to defect absorption with F-type centers being possible defect states. The broad absorption edge of BaTe ($B1$) would be consistent with an indirect band gap which according to the band-structure calculations (see Fig. 2) is expected to arise from $\Gamma - X$ transitions. The sizeable defect absorption near the interband edge makes it difficult to extract the indirect band gap from the present room-temperature absorption measurements. From more detailed absorption studies of BaTe single crystals[15] the indirect gap would be close to 2.6 eV.

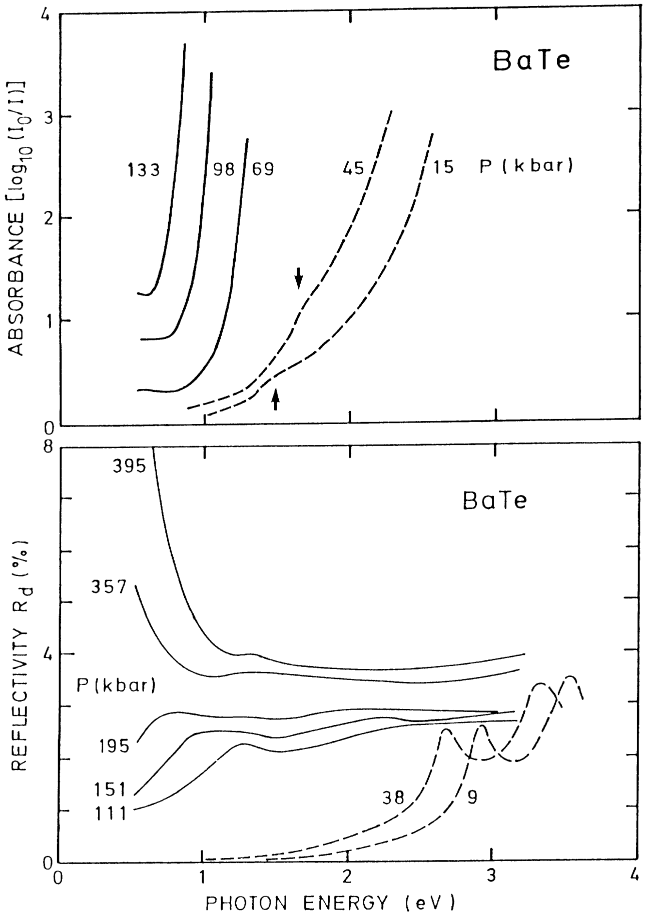

FIG. 4. Absorption and reflection spectra of BaTe at different pressures. Dashed and solid lines refer to NaCl-type and CsCi-type structure, respectively. Arrows mark a defect absorption band. For dotted lines see text.

Reflection spectra of BaTe ($B1$) (Fig. 4b) exhibit two sharp peaks in the near-uv, which are separated by roughly 0.6 eV. In accordance with thin film absorption studies of BaTe at normal pressure[16] these reflection bands are interpreted as excitonic transitions where the 0.6-eV separation results from spin-orbit splitting. With increasing pressure both reflection bands shift almost in parallel to lower energy, which clearly identifies the excited state as $5d$-like. Furthermore, the relativistic band structure of BaTe ($B1$) (see Sec. II) suggests that the transition occurs between states near the X point (X_6^--X_3 and X_7^--X_3, with double-group notation being used for valence-band states only). This assignment agrees with the interpretation of optical investigations of other alkaline-earth chalcogenides at normal conditions.[27] For comparison, the calculated spin-orbit splitting at X (X_6^--X_7^-) is 0.63 eV at $V/V_0=0.826$.

At the $B1$-$B2$ transition the dominant optical absorption-edge shifts to the near-infrared spectral range and becomes significantly steeper [Fig. 4(a)]. At the same time the lowest-energy structure in reflection shifts discontinuously from about 2.6 eV ($B1$) to 1.6 eV ($B2$). This indicates a considerably smaller direct gap in the $B2$ phase. From the theoretical band structure of BaTe ($B2$) in Fig. 3 the lowest direct gap is now expected at the Γ point (Γ_8^--Γ_{12}).

With increasing pressure, the steep part of the absorption edge and the low-energy reflectivity edge in BaTe ($B2$) further shift to lower energy. In the reflection spectra a second weak structure is observed at about 1 eV higher energy relative to the low-energy reflectivity edge. This feature is tentatively attributed to the spin-orbit companion of the lowest direct transition at the zone center. For comparison, the calculated spin-orbit splitting at Γ is 0.73 eV at ($V/V_0=0.826$). According to the band-structure calculations (see Fig. 3) additional structure in this energy range may also be expected to arise from the direct gap at the M point.

We shall not attempt a detailed analysis of the reflection spectra, because we would have to make somewhat speculative assumptions about the dielectric response and its pressure dependence at photon energies outside the present experimental range. Instead, we restrict ourselves mainly to a discussion of the pressure dependence of pronounced structures in the reflection and absorption spectra.

Figure 5 summarizes the energies of reflectivity edges in BaTe as a function of relative density, where the experimental pressure-volume (P-V) relation[5] is used for pressure to density conversion. The position of the reflectivity edges is taken from maxima in the first derivative of the reflectivity with respect photon energy. At normal volume, the energies so defined lie about 0.1 eV below the corresponding absorption maxima observed in thin-film measurements.[16] Also included in Fig. 5 are the approximate energies of the dominant absorption edge in the $B2$ phase. These absorption-edge energies are determined by

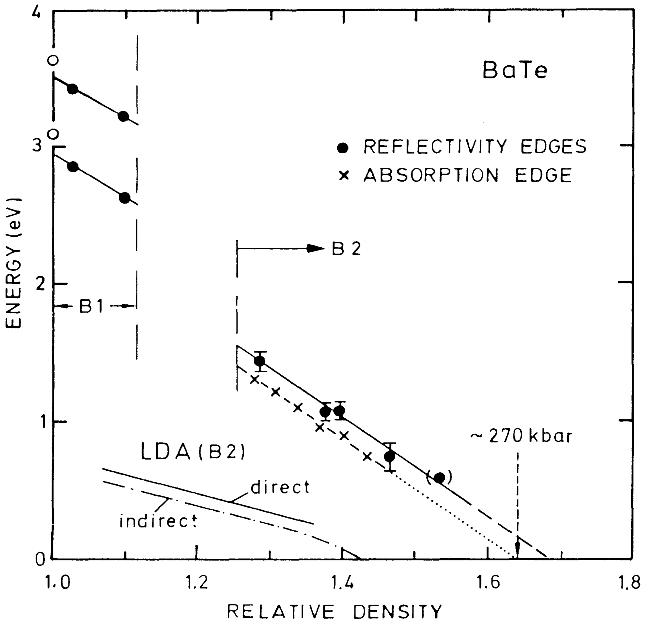

FIG. 5. Energies of direct optical transitions in BaTe plotted as a function of relative density. Open circles represent energies of absorption maxima at normal pressure. Arrow near $\rho/\rho_0 = 1.54$ indicates density at metallization as reported in Ref. 6. Error bars for $B1$ phase are smaller than size of data points.

defining the edge position at 69 kbar as indicated in Fig. 4(a) and by measuring the absorption edge shift at other pressures relative to the 69-kbar spectrum at an absorbance level of 2. In this way, the present absorption-edge data agree with the experimental results reported by Grzybowsky and Ruoff.[6] However, a detailed comparison to the earlier experimental data is not possible, because absorption spectra were not reported in the previous work. The closeness of absorption and reflection edge energies in Fig. 5 suggests that the dominant absorption edge also arises from the direct interband transitions at the Γ point. The experimental deformation potential of the direct gap in the $B2$ phase near the $B1$-$B2$ transition is about 5.7 eV which is larger by a factor of 2 when compared to the theoretical value (see Table II).

A linear extrapolation of the data for the $B2$ phase in Fig. 5 seems appropriate in order to estimate the relative volume ($V/V_0 = 0.62$) at which overlap of the *direct* gap is expected. The corresponding pressure is about 270 kbar. A similar value would be obtained from the absorption-edge data of Grzybowsky and Ruoff,[6] if their extrapolation procedure would include a more realistic value for the zero-pressure fundamental gap. On the other hand, the electrical conductivity measurements of these authors indicate an I-M transition at about 200 kbar. We offer two possible explanations for this apparent discrepancy:

(1) The I-M transition may arise from a closure of the indirect Γ-M gap which, according to the present and earlier band-structure calculations,[12,13] is predicted to be the lowest gap in the $B2$ phase of BaTe. However, as discussed above (Sec. II) this prediction may critically depend on the choice of the crystal potential. Unfortunately, our optical absorption data do not allow for an unambiguous characterization of the nature of the fundamental gap in the $B2$ phase, because of increasing absorption below the dominant absorption edge [see Fig. 4(a)] which is thought to be at least partly due to defect states. The presence of defect induced absorption is further supported by infrared absorption measurements which, after the transition to the $B2$ phase, show a pronounced pressure-dependent absorption tail in the infrared spectral range below 0.3 eV (see Fig. 6). It should be noted that this infrared absorption tail is not related to multiple phonon processes, because isostructural CsI remains transparent under similar conditions.

(2) The observation of defect-related absorption leads to a second possible explanation of the apparent discrepancy in terms of a precursor effect to the band overlap transition, namely the progressing delocalization of the electrons captured at defect sites. A similar mechanism has been proposed to explain the I-M transition in EuO at low temperatures.[28] We thus expect that the chemistry of the starting material as well as the defect structure created at the first-order $B1$-$B2$ transition play an important role in determining the electrical transport properties of BaTe near band overlap, in particular if the starting material is in the highly reactive powder form, as was the case in the transport measurements of Ref. 6.

The calculated direct and indirect gaps for the $B2$ phase of BaTe are also indicated in Fig. 5. As is usual within the LDA the gaps are too small. Thus, it is not unexpected that we find the theoretical value of the metallization volume to be somewhat too large. We will briefly return to this in Sec. VI.

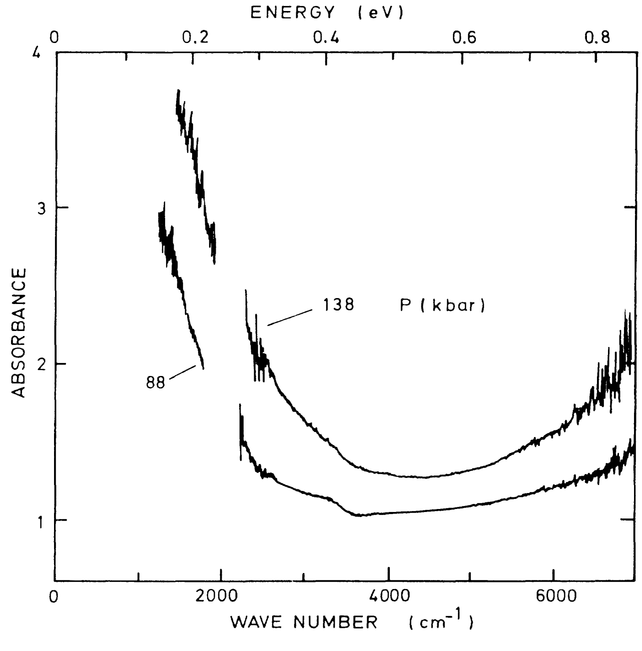

FIG. 6. Absorption spectra of BaTe ($B2$) in the infrared spectral range.

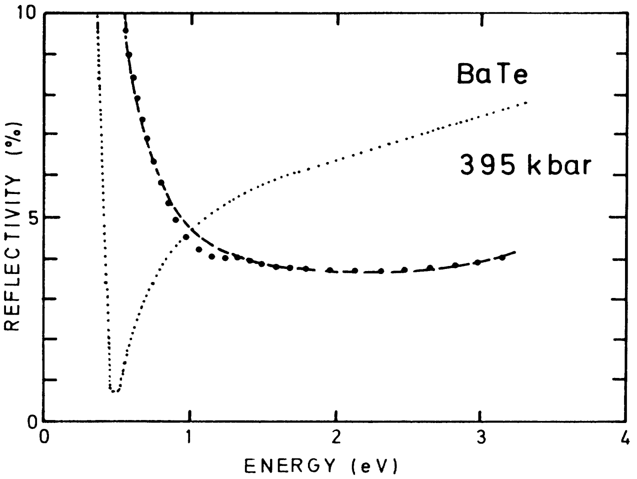

FIG. 7. Reflectivity of BaTe at 395 kbar. Solid dots represent a selection of experimental data points. The dashed line corresponds to the result of a crude Drude-type fit to the experimental data. The dotted line is the corresponding reflectivity for a hypothetical sample-vacuum interface.

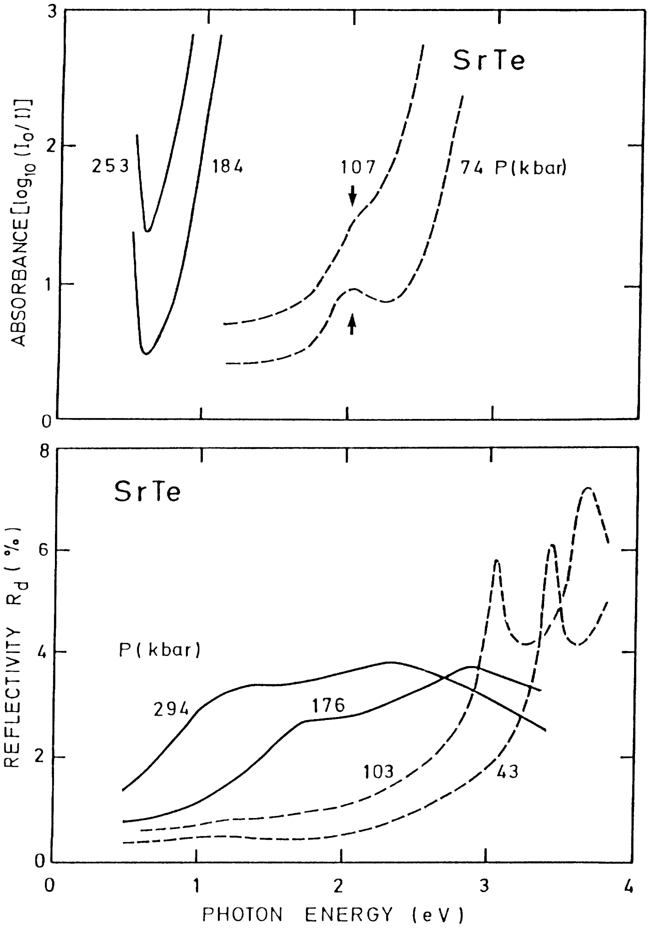

FIG. 8. Absorption and reflection spectra of SrTe at different pressures. Dashed and solid lines refer to NaCl-type and CsCi-type structure, respectively. Arrows mark a defect absorption band.

At pressures above 300 kbar BaTe shows an increase of the near-ir reflectivity [see Fig. 4(b)], as would be expected beyond the band overlap transition. In this situation, direct interband transitions extend down to very low energies, and a simple interpretation of the ir reflectivity in terms of a free-electron-like plasma reflection edge would not be fully adequate. However, this does not invalidate a crude analysis by using a Drude-type expression for the complex dielectric constant[29] and by fitting the corresponding reflectivity to the experimental data as shown in Fig. 7 for the spectrum at 395 kbar. A reasonable fit is obtained by assuming a background dielectric constant of 2.8 at photon energies above 1.5 eV. In this way we obtain an estimate of the total oscillator strength f in the ir spectral range (<1 eV) being in the order of $f=0.01$ (electrons) per formula unit. Thus, the optical response is consistent with a rather low density of states near the Fermi level, as might be expected from the calculated results for the related compound CsI near band overlap.[10]

In Fig. 7 we also illustrate how the fitted reflectivity near 400 kbar would look like for a hypothetical sample-air interface. In this case we would expect to observe a relatively sharp plasma reflection edge in the ir followed by a pronounced reflectivity minimum. This behavior is reminiscent of the ir optical response of highly doped semiconductors.

V. EXPERIMENTAL RESULTS FOR SrTe

Qualitatively, the optical behavior of SrTe under pressure is similar to that of BaTe. Absorption and reflection spectra are shown in Fig. 8. In SrTe ($B1$) one again finds a defect absorption band near the absorption edge [see arrows in Fig. 8(a)]. As in the case of BaTe, the two pronounced reflectivity peaks observed near 100 kbar [Fig. 8(b)] are separated by 0.6 eV, which supports the interpretation in terms of a spin-orbit splitting. Comparison of the absorption and reflection spectra indicates that the presumably indirect band gap of SrTe ($B1$) is about 0.5 to 1 eV below the direct gap at the X point.

At the transition to the $B2$ phase SrTe becomes opaque to visible light. The dominant absorption edge shifts discontinuously into the near-infrared spectra range. At energies below this absorption edge the optical density increases again, indicating a defect absorption which is even stronger compared with the present samples of BaTe under similar conditions.

Figure 9 shows the reflectivity edge energies in SrTe as a function of density, where the experimental P-V relation[17] is used for a pressure-density conversion. At the $B1$-$B2$ transition the position of the low-energy reflectivity edge shifts from about 2.9—1.8 eV. The reflection spectra of SrTe ($B2$) exhibit a second peak at about 1.1 eV above the low-energy structure, which may again be related to the valence-band splitting at Γ and to M point transitions.

Comparison of the absorption spectrum at 184 kbar and the reflection spectra at 176 kbar indicates, that the ab-

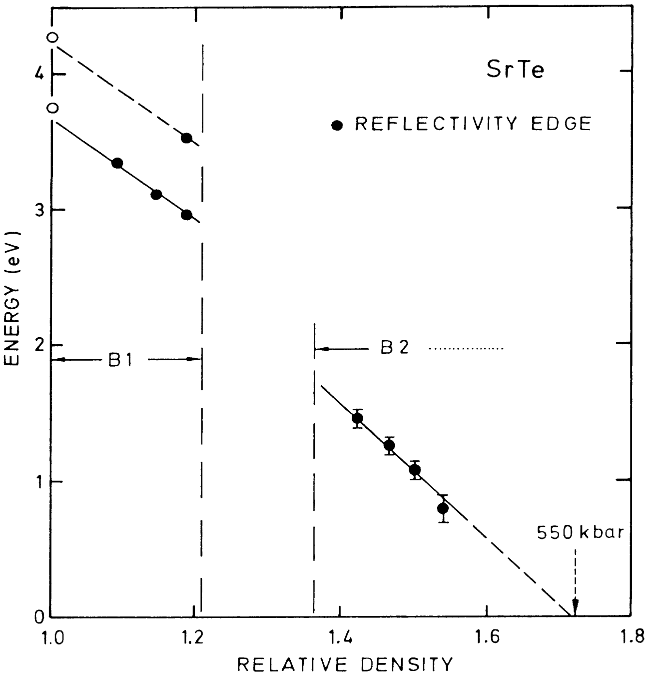

FIG. 9. Energies of direct optical transitions in SrTe plotted as a function of relative density. Open circles correspond to absorption maxima at normal pressure (from Ref. 16).

sorption edge in SrTe ($B2$) is about 0.5 eV below the reflectivity edge at pressures near 200 kbar. This is different from the case of BaTe ($B2$) where the dominant absorption edge lies much closer to the reflectivity edge. Thus, near 200 kbar SrTe ($B2$) seems to have an indirect optical gap well below the zone-center transition. The absorption and reflection spectra in Fig. 8 furthermore indicate that the zone-center direct gap closes at a faster rate with increasing pressure compared with the indirect gap.

From the dependence of the reflectivity edge in SrTe ($B2$) on density we estimate an upper limit of about 550 kbar for the zone-center band overlap transition. Here it is assumed that the $B2$ phase remains stable and that an extrapolation of the experimental P-V relation[17] is valid up to this pressure.

VI. SUMMARY AND CONCLUSIONS

We summarize the present results as follows:

(1) The equilibrium volume, bulk modulus, its pressure derivative, and the $B1$-$B2$ transition pressure of BaTe as calculated from fully relativistic LMTO band structure calculations are found to be in good agreement with experiment and with earlier calculations[13] which employed the LAPW scheme.

(2) The calculated volume coefficients for optical gaps in BaTe are found to be somewhat too small (by a factor of 2) when compared to experiment. The calculated metallization volume of BaTe is slightly larger than the experimental values derived from both electrical transport measurements[6] and from the present optical data.

(3) The pressure dependence of the optical reflectivity identities the double-peak structures in the near-UV reflection spectra of SrTe and BaTe ($B1$) as spin-orbit split exciton transitions associated with the lowest direct (p-d) gap at the X point. This interpretation is supported by the fully relativistic band-structure calculations for the $B1$ phase of BaTe. The indirect gaps in SrTe and BaTe ($B1$) are about 0.5—1 eV *below* the X-point excitonic transitions. This feature has been overlooked in the interpretation of previous experimental[6] and theoretical[13] results.

(4) At the structural $B1$-$B2$ transition the lowest direct gap decreases discontinuously from about 2.6 to 1.6 eV in BaTe and from 2.9 to 1.8 eV in SrTe. From the optical data for the $B2$ phases around 200 kbar we find an experimental indication for an indirect gap in SrTe, whereas BaTe seems to have a direct (or close to direct) fundamental gap.

(5) The zone-center direct gap in BaTe ($B2$) closes near 270 kbar. We extrapolate an upper limit of about 550 kbar for the corresponding band crossing in SrTe ($B2$).

(6) The strong defect-induced absorption in BaTe ($B2$) suggests that the metallic conductivity observed near 200 kbar (Ref. 6) may arise from a continuously progressing ionization of defect states, this being a possible precursor effect to the band overlap transition.

A final comment concerns the comparison between experiment and theory. It is well known that the gaps obtained for insulators and semiconductors are too low[30] when calculated from band models using the LDA. Nevertheless, two apparently conflicting observations have been made in a number of such calculations. Firstly, in spite of the underestimated gap values it appears[10,13] that the errors *gradually* decrease as metallization is approached. This might be expected, since the LDA should predict correctly dimensions of the Fermi surface of a metal and thus give correctly the conduction bands once the volume is so small that they have overlapped the valence bands. The second observation is that the deformation potentials of gaps in tetrahedral semiconductors seem to be determined correctly[31] by LDA calculations. Obviously, these two conclusions must in some sense be contradictory, when applied to band overlap metallization in compounds such as BaTe and CsI. Apparently, one of them (or both) do not hold near the metallization volume. The theoretical and experimental results for the band overlap conditions in BaTe and CsI seem to indicate a general trend, namely that LDA calculations underestimate the volume reduction required for a band overlap transition.[32] This would be in accordance with a previous notion by Trickey and co-workers.[33]

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