

Local-Density-Functional Calculation of the Pressure-Induced Metallization of BaSe and BaTe

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Local-density-functional total-energy calculations are reported for both the structural and metallization transitions of BaSe and BaTe. Good agreement with recent experimental results for BaTe confirms the band-overlap mechanism in this and related closed-shell systems. A metallization pressure of about 400 kbar is predicted for BaSe. These calculations represent the first convincing demonstration of the ability of the local-density-functional approximation to predict band-overlap metallization accurately.

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The pressure-induced structural phase transition and metallization of closed-shell compounds are of great current interest.^{1,2} In a recent Letter, Grzybowski and Ruoff² reported the metallization of BaTe, which is the first case of metallization in a closed-shell system for which the pressure and volume at metallization were accurately measured. Prior to metallization, BaTe first undergoes a first-order phase transition from the sodium chloride structure to the cesium chloride structure at 48 kbar, while metallization occurs in the cesium chloride structure at 200 kbar.² In this Letter, we report for the first time theoretical local-density-functional total-energy calculations which are in good agreement with these recent experimental results for BaTe and which confirm the band-overlap mechanism³ in these closed-shell systems. In addition, we report similar theoretical predictions for the related compound BaSe. These calculations represent the first convincing demonstration of the ability of the local-density-functional approximation to predict band-overlap metallization accurately.

Metallization is often described^{3,4} in terms of the single-particle band states as the overlap of the filled valence band and the unoccupied conduction band. The band gaps in these closed-shell insulating materials are expected to decrease as the pressure increases, until finally the empty *d*-type conduction band drops in energy below the top of the filled *p*-type valence bands. Among these systems BaTe and BaSe are currently under extensive experimental study,^{1,2} since they are expected to have the lowest band overlap pressures as a result of their smaller bulk moduli and band gaps.⁵ It is well known, however, that for many insulators and semiconductors the local-density-functional approximation⁶ seriously underestimates the zero-pressure band gaps.^{7,8} Local-density-functional predictions of the insulator-metal transition (IMT) thus appear to be a contradiction in terms. On the other hand, recent work of Wang and Pickett and Levine and Louie⁸ indicates that the local-density band gap might be expected to vanish at a volume which is close to the experimental metallization volume. Thus,

fairly accurate estimates of the IMT pressure and volume might still be possible within the local-density-functional approximation, even though the zero-pressure band gaps are incorrect. An earlier calculation, however, using the augmented spherical-wave (ASW) method,⁹ predicted BaTe metallization at a much larger specific volume and much lower pressure than observed. The calculated equilibrium volume⁹ was also much smaller than experiment. It is not clear whether the failure in these predictions is mainly due to the local-density-functional approximation or whether it is due to other approximations (spherical shape approximations in the potential, the neglect of relativistic effects, etc.).

To investigate this question, we have used a self-consistent linearized augmented plane-wave (LAPW) method¹⁰⁻¹² which is free from any shape approximations of the potential and charge density. This method has been applied successfully to heavy *d*-band metals¹¹ and semiconductors¹³ to compute structural and vibrational properties.¹² We only briefly describe the method here. The band states are computed scalar-relativistically (without spin-orbit coupling). The core electrons are treated fully relativistically with use of an atomic-type calculation which employs only the spherical part of the potential. There is a slight overlap of the Ba *5p* core states between neighboring atoms, and these overlapping spherical atomiclike charge densities are treated exactly in both interstitial and muffin-tin regions.¹¹ All states, including core states, are recomputed in each iteration. The potential and charge density are represented by shape-unrestricted expansions, and the total energy is calculated with high accuracy and numerical stability.¹⁴ The Hedin-Lundqvist¹⁵ exchange correlation functional is used. A basis set of about 200 LAPW that provides good convergence is used; i.e., increasing the basis set and extrapolating¹⁶ to infinite basis set yields a decrease of less than 2 mRy in the total energy relative to the actual basis set used. It is found that sufficiently accurate Brillouin zone integrations can be performed by use of ten special¹⁷ *k* points in the *B*1-structure irreducible Brillouin

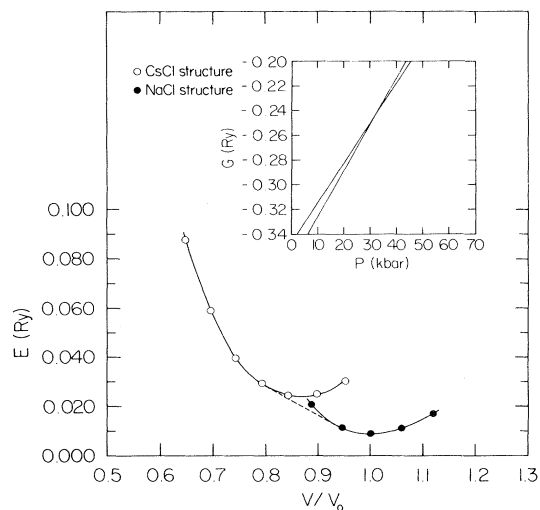


FIG. 1. Calculated total energy (plus 29848.370 Ry) of BaTe in the $B1$ and $B2$ phases. The solid lines are fits by Murnaghan's equation of state. The dashed common tangent line indicates the $B1$ - $B2$ transition. The inset shows the Gibbs free energy in the region of the phase transition.

zone and twenty special k points for the $B2$ structure. In the $B1$ structure, the number of k points was increased to 60 at the zero-pressure volume, and the change in the total energy was found to be only 0.8 mRy. In the $B2$ structure, going from four to twenty k points at all the different volumes changed the total energy by about 3 mRy at zero pressure and by about 4.8 mRy at a specific volume of 0.65. The band gap is essentially unchanged. This increase does not significantly change the energy-minimum position or the curvature, however.

Total energies are obtained for up to 60% of the experimental equilibrium volume. The calculated total energy and Gibbs free energy for BaTe are plotted in Fig. 1 (similar plots are obtained for BaSe), and the

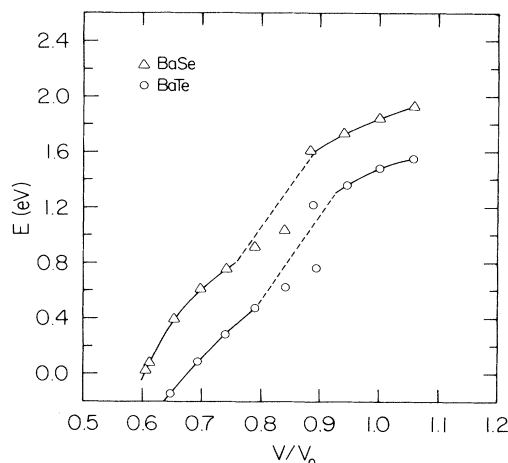


FIG. 2. Volume dependence of the band gap in BaSe and BaTe. The dashed lines indicate the $B1$ - $B2$ phase transition.

volume dependence of the band gaps is plotted in Fig. 2. Numerical results are tabulated in Tables I-III. It is found that the NaCl structure is stable at ambient pressure for both BaSe and BaTe. The difference in the cohesive energy between the NaCl and CsCl phases at zero pressure is 23 mRy (15 mRy) for BaSe (BaTe). The calculated total energies are fitted by Murnaghan's equation of state,²⁰ and the rms error in these fits is less than 0.1 mRy. Three quantities obtained in the fit are the equilibrium volume, bulk modulus B , and pressure derivative of the bulk modulus, B' , at zero pressure. The calculated ground-state properties are summarized in Table I and compared with experiment and the earlier ASW results.⁹ The calculated equilibrium volume in the $B2$ phase of BaTe is about 5% smaller than the room-temperature experimental values obtained by backwards extrapolation of the equation of state measured beyond the structural phase transition.² The calculated

TABLE I. Equilibrium volume, bulk modulus, and pressure derivative of the bulk modulus of BaSe and BaTe in the NaCl ($B1$) and CsCl ($B2$) phases. V_0 is the experimental volume at ambient pressure. For BaSe $V_0 = 483$ a.u.³, and for BaTe $V_0 = 579$ a.u.³. The bulk modulus, B , is in kilobars. B' is the pressure derivative of the bulk modulus.

	BaSe			BaTe		
	LAPW	ASW ^a	Expt. ^b	LAPW	ASW	Expt. ^c
$V(B1)/V_0$	0.978	0.84	1.0	0.997	0.84	1.0
$B(B1)$	468	...	400 ^d	354	...	294 ^d
$B'(B1)$	6.56	4.64	...	7.4 ^d
$V(B2)/V_0$	0.835	0.79	...	0.857	0.80	0.907
$B(B2)$	486	391	...	275
$B'(B2)$	4.84	4.65	...	4.6

^aReference 9.

^bReference 1.

^cReference 2.

^dReference 18.

TABLE II. Transition pressures and transition volumes for the *B1-B2* phase transformation in BaSe and BaTe. The volumes are given as fractions of the room-temperature zero-pressure volume as in Table I.

	LAPW	BaSe ASW ^a	Expt. ^b	LAPW	BaTe ASW	Expt. ^c
<i>P</i> (kbar)	56	...	60	32	...	48
<i>V</i> (<i>B1</i>)	0.89	0.925
<i>V</i> (<i>B2</i>)	0.76	0.78	...	0.80	0.78	...
<i>DV/V</i> (<i>B1</i>)	0.146	...	0.139	0.135	...	0.132

^aReference 9.

^bReference 1.

^cReference 2.

larger bulk moduli and smaller volumes are partly due to the effects of temperature and the zero-point motion which we have not included. Inclusion of these effects^{5,21} will tend to increase the volumes by about 1–2% and decrease the bulk moduli by about 10%. The differences between these results and the ASW results deserves some comment. Two possible sources are (1) the use of shape approximations in the ASW, and (2) the neglect of relativistic effects in the ASW calculations. Since the ASW results for the *B2* structure are in somewhat better agreement with the LAPW results, and since the *B2* structure is more close packed than the *B1* structure, the use of shape approximations is probably responsible for most of the difference in ground-state properties. This is consistent with the fact that the ASW metallization specific volume (Table III) for BaSe is in good agreement with the LAPW method. The somewhat worse agreement in the case of the BaTe metallization volume is probably due to the fact that neglect of scalar-relativistic effects, as discussed below, tends to reduce the band gap by lowering the (chalcogenide) valence-band maximum, and this effect is larger for the heavier Te atom.

BaTe and BaSe undergo a first-order phase transition from the NaCl structure to CsCl structure before metallization.^{1,2} The calculated band gaps at the volumes immediately before and after the structural phase transition are all positive, which indicates that

metallization occurs after the structural phase transition, in agreement with experiment. The theoretical and experimental results for the *B1-to-B2* phase transition are summarized in Table II. The *B1-B2* transition pressure of 32 kbar for BaTe is somewhat lower than the 48-kbar experimental value. The very good agreement in the transition pressure for BaSe is probably fortuitous, since the transition pressure is more difficult to determine than the transition volume. For example, including the zero-point motion can increase the transition pressure by about 5 kbar.⁵ However, the experimental trend of decreasing transition pressure with increasing atomic number is reproduced in this calculation.

We now turn to the metallization transition. Table III presents the theoretical and experimental results for the metallization transition, and the band gap is plotted as a function of volume in Fig. 2. In the NaCl phase the gaps are always indirect between the top of the Se (Te) 4*p* (5*p*) valence band at Γ and the bottom of the Ba 5*d* band at *X*. The calculated band gaps of 1.8 eV (1.5 eV) for BaSe (BaTe) at the equilibrium volume are much smaller than the experimental values of 3.6 eV (3.4 eV).² These are typical local-density-functional approximation errors.^{7,8} There are two sources for this discrepancy: (1) a *local*-density functional is used rather than a more general nonlocal functional, and (2) even if the exact nonlocal functional were employed, there would remain a discrepan-

TABLE III. Transition pressures and transition volumes for metallization transformation in BaSe and BaTe. The volumes are given as fractions of the room-temperature zero-pressure volume, as in Table I. The pressure is given in kilobars.

	LAPW	BaSe ASW ^a	Expt. ^b	LAPW	BaTe ASW	Expt. ^c
<i>P</i>	315	170	...	158	40	200
<i>V</i>	0.61	0.63	(0.59–0.62)	0.67	0.74	0.65

^aReference 9.

^bReference 19.

^cReference 2.

cy of unknown magnitude.^{7,8} Wang and Pickett and Levine and Louie⁸ have examined the excitation spectrum via a calculation of the self-energy. Specifically, their work indicates that the magnitude of this second source of discrepancy decreases with decreasing density-functional band gap. This indicates that the local-density-functional approximation band gap might be expected to vanish at a volume which is close to the experimental metallization volume and provides the motivation for the present work. Relativistic effects can also have a significant effect on the band gap, especially in cases like Ge or GaAs where the top of the valence band is a p state while the bottom of the conduction band is nearly a pure s state. In an earlier LAPW calculation for GaAs, for example, scalar relativistic effects reduce the band gap¹³ from 0.9 to 0.25 eV by dropping the s -conduction minimum relative to the p -valence maximum. As a result, the discrepancy between the local-density band gap and the experimental band gap at zero pressure is much greater for the heavier Ge atom than for the lighter Si atom. Although relativistic effects are significant, especially in BaTe near the metallization transition, the direct effect on the gap is smaller, since the gap is between a valence p band and a conduction d band. In fact, this relativistic effect is in the opposite direction in BaSe and BaTe: a nonrelativistic calculation for BaSe results in a small reduction in the band gap of 0.1 eV at zero pressure, and a reduction of 0.23 eV near metallization. This corresponds to a decrease of metallization pressure by about 70 kbar and an increase of transition volume about 3% (note the relative insensitivity of the volume). Although we have not repeated this test for BaTe, this relativistic effect for the heavier Te atom should be even larger. This scalar-relativistic effect is included in the present calculation.

As seen in Fig. 2, the structural transition induces a large reduction in the band gap. Just after the structural transition the band gaps are still indirect between the top of the chalcogenide valence p bands at M and the bottom of the Ba $5d$ bands at Γ . For BaTe this indirect gap is kept until band overlap, but for BaSe at specific volume of about 0.65 it changes to be a direct gap between the p -like Se Γ_{15} states and the d -like Ba Γ_{12} states. Our calculated band-overlap volumes are within 2% of the experimental data, but the transition pressure of 158 kbar for BaTe is somewhat smaller than the experimental value of 200 kbar. It should be noted, however, that the transition pressure is more difficult to predict than the transition volume. For example, the 2% decrease in the volume needed to bring the LAPW value into agreement with experiment would increase the transition pressure by 40 kbar for BaTe and by 65 kbar for BaSe. Different forms of local-density-correlation functionals now in common use can easily lead to variations of this magnitude in the volume. The Hedin-Lundqvist correlation formula

used here, for example, tends to yield smaller equilibrium volumes in Si and GaAs than does the Wigner interpolation formula,¹³ and smaller equilibrium volumes yield smaller predicted transition pressures. Assuming the 65-kbar increase in the predicted transition pressure for BaSe due to the (probably) slightly too large theoretical transition volume, we predict that the IMT for BaSe should be seen closer to 400 kbar rather than at the calculated value of 315 kbar. In view of these considerations, the agreement with experiment for the metallization volume and pressure is very good, and demonstrates the ability of local-density-functional theory correctly to predict band-overlap metallization in closed-shell systems. It will be interesting to see if similar results can also be obtained for related rare-earth chalcogenides.

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