Band-overlap metallization of BaS, BaSe, and BaTe

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The insulator-metal transition volumes for BaS, BaSe, and BaTe are calculated for the first time, using the self-consistent augmented-spherical-wave technique. The metallization transition volumes are smaller than those corresponding to the NaCl→CsCl structural transitions, but 10—15 % larger than those obtained by the Herzfeld dielectric theory. The calculated equilibrium energy gaps in the NaCl structure underestimate the measured ones by 50—60 %.

I. INTRODUCTION

The availability of diamond anvil pressure cells and synchrotron x-ray radiation permits precise optical and structural studies of the pressure-induced metallization of closed-shell compounds. The metallization is usually described[1] within a one-electron approximation as the broadening and subsequent overlap of a filled valence band and an empty conduction band. The closed-shell Ba chalcogenides are particularly promising compounds for metallization: (1) The fractional compression for metallization should be less than for isoelectronic compounds and elements, such as CsI and Xe, which have larger band gaps, and (2) the metallization pressure should be less than for other divalent chalcogenides (e.g., MgTe), which have larger bulk moduli.

In this paper we describe self-consistent band-structure calculations for BaS, BaSe, and BaTe under compression. The calculations predict band-overlap transition volumes, illustrate the chemical trends in these volumes, and will provide a test of the one-electron approximation used to calculate the band gaps when experimental data on the metallization volumes becomes available. All of the compounds are studied in both the equilibrium NaCl(B1) crystal structure and the CsCl(B2) crystal structures, because they are known[2-4] to transform under pressure into the CsCl structure. This is the first systematic study of the insulator-metal transitions in this series of compounds, taking into account the effects of the structural transitions. The volume-dependent band gap of BaO has previously been calculated[5] by the augmented-plane-wave (APW) method only in the NaCl structure. BaO is not included here because our code does not work correctly for the highly compressed Ba atom close to the band-overlap transition. Furthermore, accurate treatment of strongly localized orbitals such as O $2p$ is difficult within density-functional theory.

II. METHOD OF CALCULATION

The calculations are performed using the self-consistent augmented-spherical-wave method.[6] In this method the one-electron Schrödinger equation is solved approximately using an energy-independent basis set obtained by numeri-

cal integration of the Schrödinger equation inside atom-centered spheres, with boundary conditions which take into account the full symmetry of the crystal. The self-consistent one-electron potential is generated with a local-density approximation[7] for exchange and correlation of the Hedin-Lundqvist form.[8] Relativistic effects are neglected. We now comment briefly on the accuracy of the two primary approximations made in the calculations.

A. The local-density approximation (LDA)

It is well known that for many closed-shell systems the local-density approximation yields theoretical zero-pressure band gaps which are smaller than the experimental gaps by up to a factor of 2. In systems with bands that are very narrow compared to the band gap it is possible to remove a large part of the discrepancy by the use of the self-interaction correction (SIC) scheme.[9] Unfortunately it is not known how to extend the SIC scheme accurately and unambiguously to problems in which the bands are broad compared to the band gap, such as the metallization process of interest here.[10] On the other hand, since the local-density approximation is expected to improve as the system becomes more metallic or free-electron-like, it will be more accurate close the insulator-metal transition than at the equilibrium volume. The discontinuity[11,12] between the *exact* potentials for valence- and conduction-band electrons should decrease with the band gap, and in fact vanishes[12] in a simple model calculation. Furthermore, recent *exchange-only* calculations[13] for atoms have shown that the differences between eigenvalue spacings obtained using the local-density potential and the exact ground-state potential are small. Thus a fairly accurate estimate of the insulator-metal transition volume may result even if the zero-pressure band gap is inaccurate.

B. The use of the ASW basis set

We use the following basis orbitals: Ba $6s\,5p\,5d\,4f$, S $3s\,3p\,3d\,4f$, Se $4s\,4p\,4d\,4f$, and Te $5s\,5p\,5d\,4f$. In our ASW calculations[14] for fcc Xe, and CsI in the CsCl structure, we obtain gaps which differ from APW results[15,16] by less than 0.2 eV. The ASW method is also similar in accuracy to the linear muffin-tin orbital (LMTO) method

with the "combined correction" term.[17] The band structure of Si in the diamond[18] and fcc (Ref. 19) crystal structures has been calculated with the LMTO method. In the diamond structure, empty spheres were included, resulting in eightfold coordination of the spheres. Comparison of the LMTO results with full-potential linear-augmented-plane-wave method[20] and self-consistent pseudopotential[19] results again reveals discrepancies of less than 0.2 eV. Thus the use of the ASW method for solving the one-electron part of the problem does not appear to cause major errors in closely packed structures such as CsCl. However, the NaCl structure results are expected to be more sensitive to the approximations in the ASW method, because of the lower coordination number. The sensitivity tests to be presented in Sec. III confirm these expectations.

III. RESULTS

The relevant particulars of the band structures are as follows: In the NaCl structure the gap is always indirect, between the top of the chalcogen valence p band at Γ and the bottom of the Ba $5d$ band at X. The shape of this d band is similar to that in a fcc noble or transition metal, as would be expected from the fact that the Ba atoms constitute a fcc sublattice. The Ba $6s$ level, doubly occupied in the atom, is empty in the solid because the two $6s$ electrons are transferred to the chalcogen valence p band. The results for the CsCl structure are similar, except that at zero pressure the top of the valence band is at M and the bottom of the conduction band at Γ.

Little quantitative significance can be attached to the calculated band gaps in the NaCl structure, which are too sensitive to the fraction f_{Ba} of the unit cell filled by the Ba sphere. The value of f_{Ba} for each volume and crystal structure is chosen by approximately minimizing[21] the calculated total energy with respect to f_{Ba}. This is a more appropriate variational principle than, for example, minimizing the band gap, since density-functional theory must obtain the correct total energy but not necessarily the correct band gap. As seen in Table I, a change in f_{Ba} of 0.05 in either direction from the value with the asterisk (the value closest to minimizing the total energy), which corresponds to a change of only 6% in the Ba sphere radius, can change the gap for BaTe in the NaCl structure by as much as 0.2 eV. The difference between results ob-

TABLE I. Sensitivity of calculated band gap in BaTe to the fraction f_{Ba} of unit-cell volume occupied by the Ba sphere, for fixed volume ($578a_0^3$/atom pair) in both NaCl and CsCl crystal structures. Asterisks indicate volumes which minimize the total energy.

f_{Ba}	E_g^{NaCl} (eV)		E_g^{CsCl} (eV)	
	$spdf$	spd	$spdf$	spd
0.25	0.75	0.64		
0.30	0.92	0.82*		
0.35	1.12	1.01	0.73	0.64
0.41	1.30	1.18	0.72	0.64*
0.48	1.40	1.28	0.71	0.65

TABLE II. Comparision of calculated and experimental band gaps in NaCl structure. $E_{g,*}^{th}$ obtained using the sphere radii which minimize the total energy.

	$E_g^{th,max}$ (eV)	E_g^{expt} (eV)	$E_{g,*}^{th}$ (eV)
BaS	2.1	3.9	1.6
BaSe	1.8	3.6	1.3
BaTe	1.4	3.4	0.9

tained using an spd basis set and the $spdf$ basis set described above, in this and subsequent tables, illustrates the effects of the Ba $4f$ levels. These should be significant because of the large atomic number of Ba. As seen in the results, the $4f$ effects are small but not negligible. Unless otherwise noted, all stated results are obtained using the $spdf$ basis.

In contrast to the NaCl case, the corresponding changes in the CsCl structure gaps are practically negligible. The higher coordination number in the CsCl structure provides better justification for sphericalizing the Wigner-Seitz cell. We may therefore consider the results obtained for the CsCl structure to be a fairly accurate test of local-density theory rather than of the particular approximation used to solve the effective one-electron Schrödinger equation. To obtain a similar test for the NaCl structure, calculations must be performed using a larger number of ASW spheres or more sophisticated (and computationally costly) band-structure techniques, such as the linear—augmented-plane-wave method.[17]

Despite the sensitivity of the NaCl structure band gaps to f_{Ba}, a reasonable upper bound to the band gap produced by solving the one-electron equations exactly might be obtained by maximizing the gap with respect to f_{Ba} (although we emphasize that there is no justification for believing that this procedure gives the correct band gap). The resulting gaps $E_{g,max}^{th}$ are compared with the experimental values[22] E_g^{expt} in Table II. The theoretical gaps are
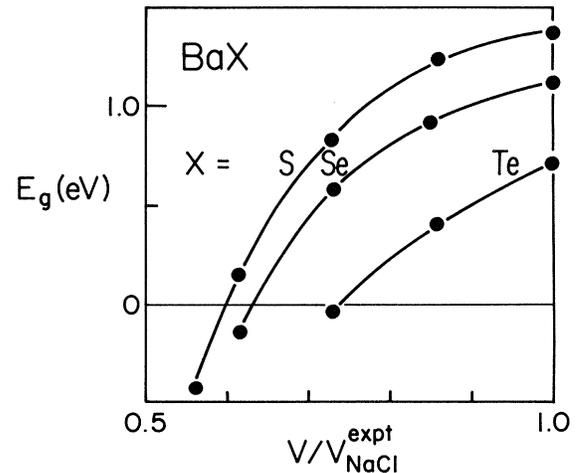
FIG. 1. Volume dependence of band gaps of Ba chalcogenides in the CsCl structure. V_{NaCl}^{expt} is the measured equilibrium volume in the NaCl structure (Ref. 23). Solid circles denote calculated points. Pressures at band-overlap transitions are 320 kbar for BaS, 170 kbar for BaSe, and 40 kbar for BaTe.

TABLE III. Quantities relevant to structural and band-overlap transitions. V_{NaCl}^{expt} is the measured equilibrium volume in the NaCl structure. The Herzfeld criterion (Ref. 1) predicts the metallization volume V^{diel} at which the dielectric constant is infinite in terms of the zero-pressure dielectric constant ϵ and experimental volume V_{NaCl}^{expt} by $(\epsilon-1)/(\epsilon+2)=V^{diel}/V_{NaCl}^{expt}$. Other quantities are defined in the text.

	$E_g^{th}(V_{CsCl}^{struc})$		$\dfrac{V_{CsCl}^{struc}}{V_{NaCl}^{expt}}$	$\dfrac{V_{CsCl}^{BO}}{V_{NaCl}^{expt}}$		$\dfrac{V^{diel}}{V_{NaCl}^{expt}}$
	spdf	*spd*		*spdf*	*spd*	
BaS	1.0	0.8	0.77[a]	0.60	0.62	0.55
BaSe	0.8	0.6	0.78[b]	0.63	0.66	0.58
BaTe	0.2	0.0	0.78[b]	0.74	0.77	0.63

[a]Reference 2.
[b]Reference 4.

low by 50—60 %, a discrepancy larger than the 30—50 % error usually associated with local-density band gaps. However, the experimental trend of increasing band gap with decreasing atomic number is reproduced by the calculations. Furthermore, the absolute magnitude of the error, roughly 2 eV for all three compounds, is not particularly large when compared to results for similar compounds. Recent band calculations[14,16] for CsI, a compound isoelectronic to BaTe, have yielded band gaps too small by 2.5 eV, with a fractional error of 40%.

The last column of the table shows the gaps $E_{g,*}^{th}$ at the values of f_{Ba} which minimize the total energy. All are much smaller than the experimental gaps.

We now turn to the band-overlap transitions and the NaCl→CsCl structural transitions. The volume dependence of the band gaps in the CsCl structure is shown in Fig. 1. All of the gaps drop monotonically and transform from direct to indirect under compression, except for BaTe which remains indirect. The chemical trend in the gaps is unaffected by the compression. The calculated values $E_g^{th}(V_{CsCl}^{struc})$ of the band gaps in the CsCl structure at the volumes[2–4] V_{CsCl}^{struc} immediately after the structural transition are given in Table III. All of the gaps are positive, indicating that the band-overlap (BO) transition occurs after the structural transition. This is consistent with recent band-gap measurements[4] on BaTe and BaSe and previous visual inspections[2] of BaS in the CsCl structure. The volumes V_{CsCl}^{BO} at which the band-overlap transitions occur are given in the fourth and fifth columns of the table. As expected, the amount of compression required to induce the transition increases with the zero-pressure band gap (cf. Table II). Although experimental measurements of V_{CsCl}^{BO} have not yet been made, it is useful to compare our results with the volumes V^{diel} obtained from a simple dielectric theory[1] originally due to

Herzfeld. As seen in the table, the band-theoretic results are consistently higher than the dielectric theory estimates, by 10—15 %, although both estimates show the same chemical trend. Band calculations[14–16] for CsI, Xe, and Ar have predicted band-overlap transition volumes higher than the dielectric theory estimate by roughly the same amount.

At this stage our starting belief that the metallization volume (and hence pressure) would be well predicted is somewhat battered. As shown in Table IV, the calculated equilibrium volumes V_{NaCl}^{th} in the NaCl structure are 16—17 % lower than the experimental values[23] V_{NaCl}^{expt}. The results for the CsCl structure are expected to be more accurate than the NaCl results, because as mentioned earlier the larger coordination number provides more justification for sphericalizing the Wigner-Seitz cell. However, as seen in Table IV, the calculated equilibrium volume V_{CsCl}^{th} in the CsCl structure is still roughly 10% lower than an experimental value obtained[4] by backwards extrapolation of the equation of state measured beyond the structural transition. Since the difference between V_{CsCl}^{BO} and V_{CsCl}^{th} in BaTe is less than the error in V_{NaCl}^{th}, the calculated pressure must be off by more than a factor of 2 in the harmonic approximation, and probably much more when anharmonic effects are included. Nevertheless, we have displayed the calculated pressures in the caption to Fig. 1. To obtain accurate estimates of the transition pressures in the Ba chalcogenides, it will be necessary to devise one-electron potentials which give more accurate equilibrium volumes than the local-density approximation.

Note added in proof. Recent resistivity measurements have indicated metallization volumes of $(0.59-0.62) V_{NaCl}^{expt}$ for BaSe (Ref. 24) and $0.64 V_{NaCl}^{expt}$ for BaTe.[25] The calculated volumes (cf. Table III) exceed these by 2—7 % and

TABLE IV. Calculated and measured equilibrium volumes in the NaCl and CsCl structures. V_{NaCl}^{expt} given in a_0^3/atom pair.

	V_{NaCl}^{expt}	$\dfrac{V_{NaCl}^{th}}{V_{NaCl}^{expt}}$		$\dfrac{V_{CsCl}^{expt}}{V_{NaCl}^{expt}}$	$\dfrac{V_{CsCl}^{th}}{V_{NaCl}^{expt}}$	
		spdf	*spd*		*spdf*	*spd*
BaS	440	0.83	0.84		0.76	0.78
BaSe	483	0.84	0.85		0.79	0.80
BaTe	578	0.84	0.84	0.91	0.80	0.81

16%, respectively. The greater discrepancy for BaTe may be due to the neglect for relativistic effects.

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