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Band-Overlap Metallization of BaS, BaSe, and BaTe

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Abstract

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 1) smaller than those corresponding to the $NaC\ell \rightarrow CsC\ell$ structural transitions, but, 2) 10-15% larger than those obtained by the Herzfeld dielectric theory. The calculated equilibrium energy gaps in the $NaC\ell$ structure underestimate the measured ones by 50-60%.

I. Introduction

The availability of diamond anvil pressure cells and synchrotron X-ray radiation permit precise optical and structural studies of the pressure-induced metallization of closed-shell compounds. The metallization is usually described[1] within the 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[2,3,4] 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 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 numerical 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 tht 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 two. 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 to 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 6s5p5d4f, S 3s3p3d4f, Se 4s4p4d4f, and Te 5s5p5d4f. 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[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 Section 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 sub-
lattice. 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 appro-
priate 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 starred value (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 obtained 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 2. The theoretical gaps are 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 1/2 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$\rightarrow$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[2,3,4] V_{CsCl}^{struc} immediately after the structural transition are given in Table 3. All of the gaps are positive, indicating that the band overlap 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 third column of the table. As expected, the amount of compression required to induce the transition increases with the zero pressure band gap (cf. Table 2). 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[14,15,16] 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 4, 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 4, 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 two 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 potential which give more accurate equilibrium volumes than the local density approximation.

Acknowledgements

Footnotes and References

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21. For each compound, in the CsCℓ structure, the total energy is minimized at the observed equilibrium volume $V_{NaCℓ}^{expt}$ in the NaCℓ structure, and at a volume close to the band overlap transition. For other volumes, f_{Ba} is obtained by linear extrapolation or interpolation. Because of the large number of calculations required in this procedure, we employed the spd rather than the spdf basis to obtain the optimal sphere radii. The resulting expressions for f_{Ba} are: BaS, $f_{Ba} = 0.48 = 0.23 (1-V/V_{NaCℓ}^{expt})$; BaSe, $f_{Ba} = 0.46 - 0.16 (1-V/V_{NaCℓ}^{expt})$; BaTe, f_{Ba} 0.43 - 0.04 $(1-V/V_{NaCℓ}^{expt})$. In the NaCℓ

structure, f_{Ba} is obtained by interpolation or extrapolation from values at $V_{NaC\ell}^{expt}$ and $0.95\ V_{NaC\ell}^{expt}$. The expressions for f_{Ba} are:

BaS, $f_{Ba} = 0.32 - 0.13\ (1-V/V_{NaC\ell}^{expt})$; BaSe, $f_{Ba} = 0.31 - 0.12$ $(1-V/V_{NaC\ell}^{expt})$; BaTe, $f_{Ba} = 0.30 - 0.10\ (1-V/V_{NaC\ell}^{expt})$. The resulting total charge in the Ba sphere varies from -1.3 to -1.9 $\left|e\right|$ in the CsCℓ structure and -1.7 to -2.2 $\left|e\right|$ in the NaCℓ structure.

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Table Captions

Table 1. Sensitivity of calculated band gap in BaTe to the fraction f_{Ba} of unit cell volume occupied by Ba sphere, for fixed volume (578 a_0^3/atom pair) in both NaCl and CsCl crystal structures. Starred volumes minimize the total energy.

Table 2. Comparison of calculated and experimental band gaps in NaCl structure. $E_{g_0^*}^{th}$ obtained using the sphere radii which minimize the total energy.

Table 3. Quantities relevant to structural and band overlap transitions. V_{NaCl}^{expt} is the measured equilibrium volume in the NaCl structure. The Herzfeld criterion[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.

Table 4. Calculated and measured equilibrium volumes in the NaCl and CsCl structures. V_{NaCl}^{expt} given in a_0^3/atom pair.

Table 1

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 2

	$E_g^{th,max}$(eV)	E_g^{expt}(eV)	$E_{g,*}^{th}$(eV)
BaS	2.1	3.9	1.6
BaSe	..8	3.6	1.3
BaTe	1.4	3.4	0.9

Table 3

	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] Ref. 2   [b] Ref. 4

Table 4

	v^{expt}_{NaCl}	$\dfrac{v^{th}_{NaCl}}{v^{expt}_{NaCl}}$		$\dfrac{v^{expt}_{CsCl}}{v^{expt}_{NaCl}}$	$\dfrac{v^{th}_{CsCl}}{v^{expt}_{NaCl}}$	
		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

Figure Caption

Fig. 1. Volume dependence of band gaps of Ba chalcogenides in the CsCℓ structure. $V_{NaC\ell}^{expt}$ is the measured equilibrium volume in the NaCℓ structure (Ref. 23). Filled circles denote calculated points. Pressures at band-overlap transitions are 320 Kbar for BaS, 170 Kbar for BaSe, and 40 Kbar for BaTe.
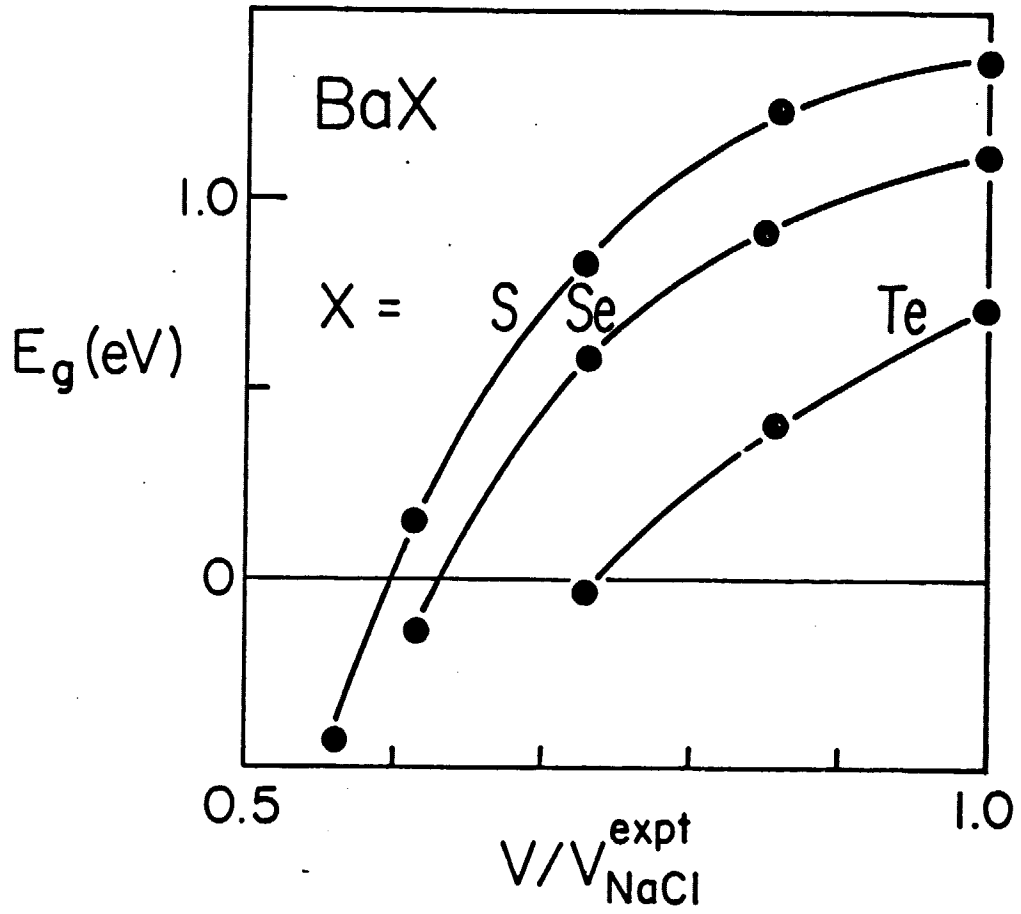
Fig. 1