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Electronic structure and structural phase stability in BaS, BaSe, and BaTe

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The self-consistent scalar-relativistic band structures for BaS, BaSe, and BaTe in NaCl-type and CsCl-type structures were obtained using the tight-binding linear muffin-tin orbital method. From atomic-sphere approximation (ASA) total-energy calculations the structural phase stability in these compounds has been studied. The equilibrium lattice constant for all three compounds agrees well with the experimental results. The pressures at which these compounds undergo a structural phase transition from NaCl-type to CsCl-type were calculated. The calculated pressures and volumes at transition agree well with the experimental results. The energy band gaps at ambient conditions in the NaCl-type structure and the volume dependence of band gaps in the CsCl-type structure were calculated. In addition the pressures and the volumes at which band overlap metallization occurs were also calculated and compared with experimental and other theoretical results.

I. INTRODUCTION

In recent years, pressure-induced structural phase transition in alkaline-earth chalcogenides has been studied extensively. Under normal conditions these compounds crystallize in the NaCl-type ($B1$) structure with sixfold coordination and are insulators. With the application of pressure these compounds undergo a structural phase transition to CsCl-type ($B2$) structure with eightfold coordination. Among the IIa–VI compounds, barium chalcogenides (BaX, X=S, Se, Te) are found to exhibit a structural phase transition even with the application of moderate pressures of 65, 60, and 55 kbar, respectively.[1–3] Apart from this, these compounds exhibit an interesting phenomenon of metallization with the application of further pressure.[3–5] Here metallization is described due to band broadening with increase in pressure and subsequent overlap of filled valence band (p-like valence band of the chalcogen atom) and the conduction band (d-like conduction band of the cation).[6] Among these compounds BaTe has the lowest band overlap pressure as a result of its smaller bulk moduli and band gap.[7]

To understand some of the physical properties of these compounds, a detailed description of electronic structure of these compounds is needed. In this paper, we present the self-consistent band structure for BaS, BaSe, and BaTe using the tight-binding linear muffin-tin orbital method (TBLMTO).[8]

II. METHOD OF CALCULATION

The band structure for both $B1$ and $B2$ structure and the total energies within the atomic-sphere approximation (ASA) were obtained by means of the TBLMTO, which is the exact transformation of Andersen's linear muffin-tin orbitals[9] to localized short-ranged or tight-binding orbitals. The exchange-correlation potential within the local-density approximation (LDA) is calculated using the parametrization scheme of von Barth and Hedin.[10] The most important relativistic corrections, namely the Darwin's correction and mass-velocity terms were included, while the spin-orbit coupling term is neglected. For both $B1$ and $B2$ structures the calculations were performed for 512 **k** points in the Brillouin zone. The density of states were calculated by the method of tetrahedra.[11]

It is well known that the LMTO method gives accurate results for densely packed structures and since the NaCl-type structure is a loosely packed structure, it becomes necessary to include empty spheres.[12] In particular this becomes important for total-energy calculations where the structural energy difference is only hundredths of a rydberg. Without breaking crystal symmetry two equivalent empty spheres were included at the positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75), whereas the metal and nonmetal atoms occupy the positions (0, 0, 0) and (0.5, 0.5, 0.5). To optimize the calculations, equal sphere radii were chosen for both metal and nonmetal atoms in the case of both $B1$ and $B2$ structures, so that the difference in the potential at the sphere boundaries is minimum. Apart from this the combined correction terms were also included, which accounts for the nonspherical shape of the atomic cells and the truncation of higher partial waves ($l>2$) inside the spheres, so that now the errors in the LMTO method is minimized. For BaTe the following basis orbitals were used, namely, Ba: $6s,6p,5d$; Te: $5s,5p,5d$. In the case of BaS and BaSe, Ba $5p$ bands are treated as fully relaxed valence-band states. The following orbitals were used for BaS and BaSe, Ba; $6s,5p,5d$; Se: $4s,4p,4d$, and S: $3s,3p,3d$. The volume/molecule for BaTe (579 a.u.[3]) is larger when compared to that of BaS (440 a.u.[3]) and BaSe (483 a.u.[3]). Hence the radius of the Ba atom is larger in BaTe, than in BaS or BaSe. Therefore the chemical pressure will be larger for BaTe. Also among these compounds, BaTe has the low value of bulk modulus. Because of these reasons the structural transition and metallization occurs at a low pressure in the case of BaTe. Therefore it does not become necessary to treat Ba $5p$ bands as relaxed valence-band states in the case of BaTe.

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III. TOTAL-ENERGY CALCULATIONS

In order to study the structural phase stability[13] for each of the compounds, the total energies were calculated for both $B1$ and $B2$ structures by changing the volume from about 1.1 V_0 to 0.7 V_0, where V_0 is the equilibrium volume. The variations of total energies with volume for all the three compounds are given in Fig. 1. The calculated total energies were fitted to the Birch equation of state,[14] to obtain the pressure-volume relation (Fig. 2). The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus

$$B=-V_0\frac{dp}{dv} \tag{1}$$

is calculated from the P-V relation. The theoretically calculated equilibrium lattice constant and the bulk modulus for both $B1$ and $B2$ structures are given in Table I and are compared with experimental[1-4] and earlier theoretical work.[15-17] In the case of BaTe, the equilibrium lattice constant agrees well with the experimental value, whereas in the case of BaS and BaSe the calculated value is 1.4 and 1.2 % smaller than the experimental value. For the $B1$ phase the calculated bulk modulus agrees with the experimental values and also with other theoretical work for all three compounds. The bulk modulus decreases from BaS to BaTe. The variation in the bulk modulus is similar to that of pure chalcogen atom bulk moduli.

The structural phase stability is determined by calculating Gibb's free energies (G) (Ref. 18) for the two phases $B1$ and $B2$:

$$G=E_{\text{tot}}+PV+TS\ . \tag{2}$$

Since in the theoretical calculations, we are considering

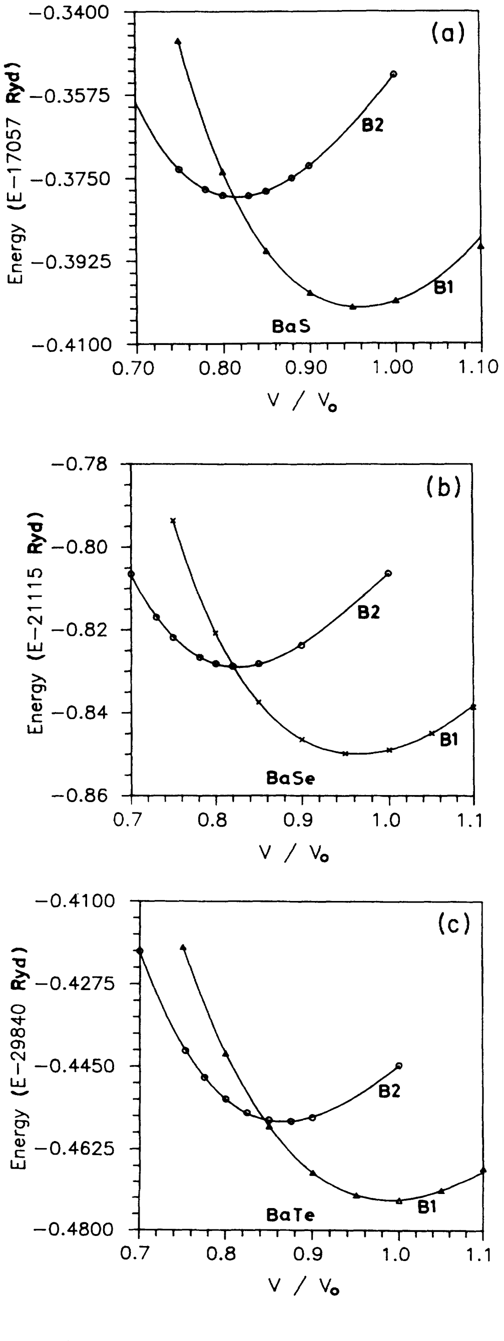

FIG. 1. Calculated total energies as a function of volume in the $B1$ and $B2$ structure for (a) BaS, (b) BaSe, and (c) BaTe.

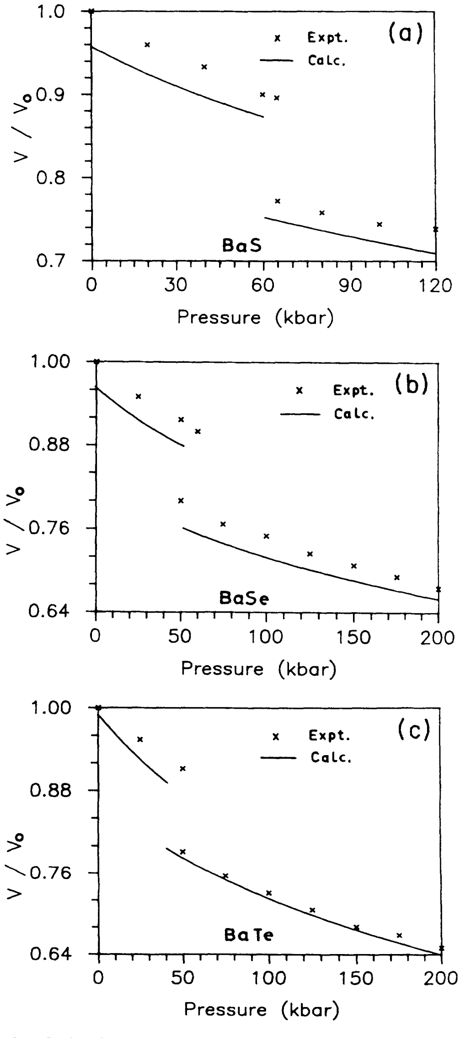

FIG. 2. Calculated pressure volume relation in the $B1$ and $B2$ structures for (a) BaS, (b) BaSe, and (c) BaTe.

TABLE I. Equilibrium volume (V) and bulk modulus (B) for $B1$ and $B2$ phases of BaS, BaSe, and BaTe. ASW is augmented spherical wave. LAPW is linear augmented plane wave.

	BaS			BaSe				BaTe				
	Expt.[a]	TBLMTO	ASW[b]	Expt.[c]	TBLMTO	LAPW[e]	ASW	Expt.[f]	TBLMTO	LAPW	ASW	LMTO[g]
a (a.u.)	12.074	11.894		12.463	12.299			13.242	13.186			
$V(B1)/V_0$	1.0	0.956	0.84	1.0	0.963	0.978	0.85	1.0	0.99	0.997	0.84	1.000(7)
$B(B1)$ kbar	394.2	524.6		434±26[d]	454.1	468		294[d]	337.5	354		356
$V(B2)/V_0$		0.817	0.78	0.878	0.824	0.835	0.8	0.907	0.871	0.857	0.81	
$B(B2)$ kbar	340.2	608.4		419±140[d]	529	486		275[d]	394.1	391		

[a] Reference 1.
[b] Reference 15.
[c] Reference 2.
[d] Reference 4.
[e] Reference 16.
[f] Reference 3.
[g] Reference 17.

only the zero-temperature limit, Gibb's free energy becomes equal to the enthalpy (H)

$$H = E_{\text{tot}} + PV \ . \tag{3}$$

At a given pressure a stable structure is one for which enthalpy has its lowest value and the transition pressures are calculated at which the enthalpies for the two phases are equal. The transition pressure from the $B1$ to the $B2$ structure, the transition volumes, and the volume reduction are given in Table II and are compared with earlier literature.[1–3,16,17] From the table it can be seen that the transition pressures agree well with the experimental results.

IV. BAND STRUCTURES

The self-consistent scalar-relativistic band structure for all three compounds were calculated for both $B1$ and $B2$ structures. The band structure for the $B1$ phase at ambient conditions is given in Fig. 3. The overall band profile is found to be same for all three compounds and is in agreement with earlier work.[19–21] In the case of the $B1$ structure the gap is always indirect, with the top of the chalcogen valence p band occurring at Γ_{15} and the bottom of the Ba $5d$ bands occurring at X_3. The shape of this conduction band is similar to that of the fcc noble or transition metals which is due to the fact that the Ba atoms constitute a fcc sublattice. The calculated value of band gap at normal conditions is given in Table III along with the experimental value[22] and the other theoretical work.[15,16] The band gap is 40–50 % smaller than the experimental value. This is mainly due to the errors introduced by the LDA which underestimates the band gap. However, the calculated values agree with the other theoretical results.

The band structures for the $B1$ and $B2$ phases at the transition volume are given in Figs. 4 and 5. From the figures it can be seen that the structural transition induces a large reduction in the band gap. Just after the structural transition the band gaps are still indirect except that now the valence p bands of the chalcogen atom occurs at M and the bottom of Ba $5d$ conduction bands at Γ. The gaps are positive even after the structural transition indicating that the metallization occurs only after structural transition. The band structure at the metallization volume is given in Fig. 6. In the case of BaTe, the indirect gap remains the same until band overlap occurs, however, in the case of BaS and BaSe the gaps transform from an indirect to direct gap between the p-like valence band of the chalcogen atom at Γ_{15} and d-like Ba conduction band at Γ_{12} before metallization. At metallization the band gap closes due to the overlap of the Ba $5d$ conduction bands and the chalcogen valence p bands which arise due to the broadening of the bands with increase in pressure. At ambient conditions the Ba $5p$ bands are lower in energy than the chalcogen atom s band for all

TABLE II. Transition pressures and transition volumes for the $B1$–$B2$ transformation in BaS, BaSe, and BaTe.

	BaS		BaSe			BaTe			
	Expt.[a]	TBLMTO	Expt.[b]	TBLMTO	LAPW[c]	Expt.[d]	TBLMTO	LAPW	LMTO[e]
P (kbar)	65	60.25	60	52	56	48	39.5	32	38
$V_1(B1)$	0.896	0.873		0.88	0.89		0.894	0.925	
$V_2(B2)$	0.773	0.773		0.762	0.76		0.798	0.8	
$\Delta V/V_1(B1)$	13.7	13.8	13.9	13.4	14.6	13.2	10.7	13.5	

[a] Reference 1.
[b] Reference 2.
[c] Reference 16.
[d] Reference 3.
[e] Reference 17.

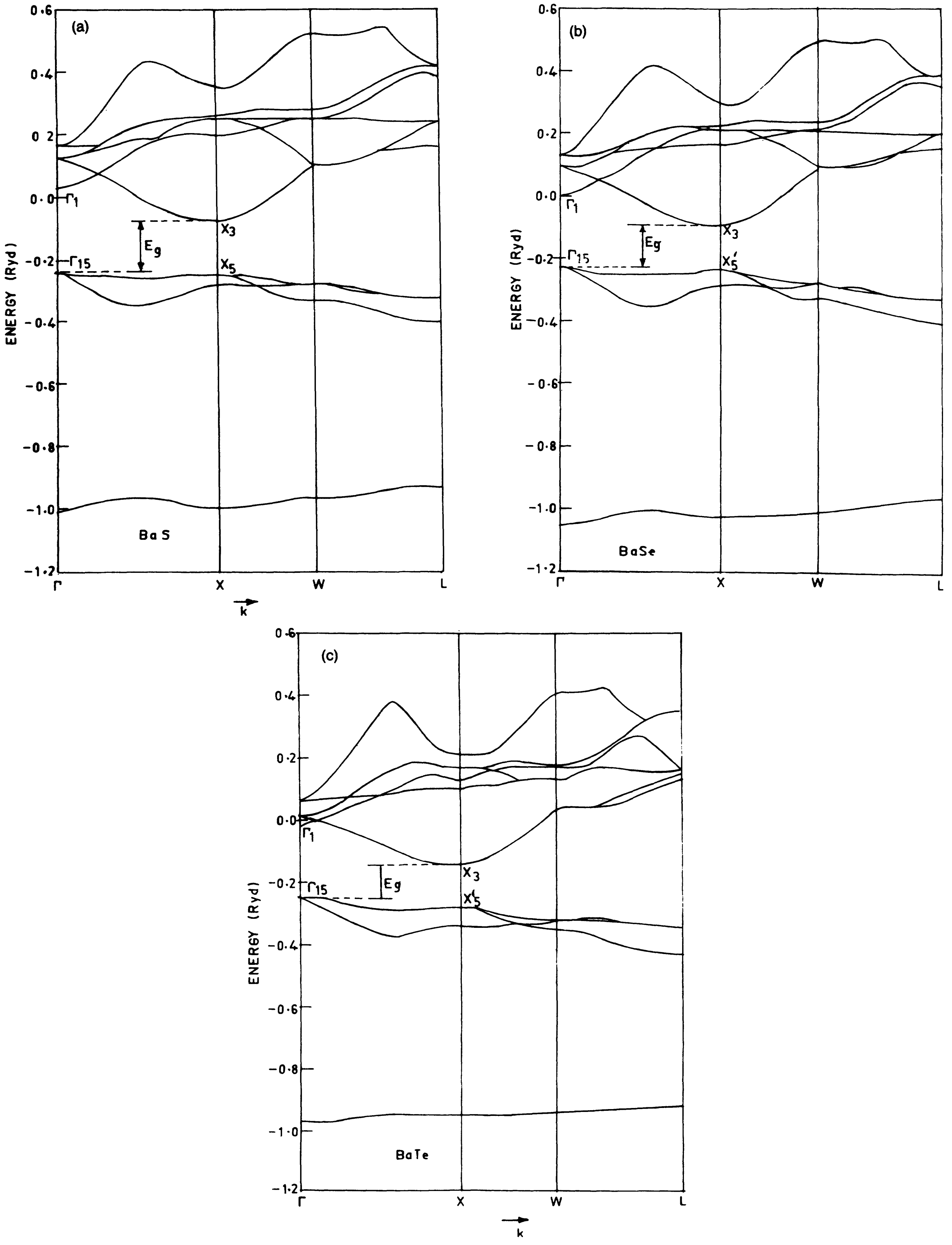

FIG. 3. Band structure in the *B*1 phase at equilibrium volume for (a) BaS, (b) BaSe, and (c) BaTe.

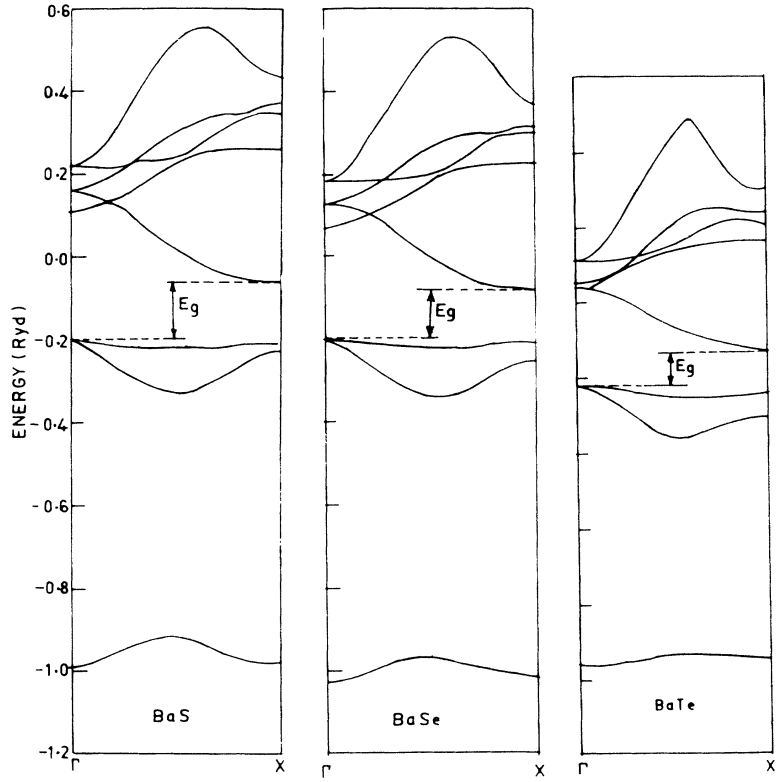

FIG. 4. Band structure in the $B1$ phase at transition.

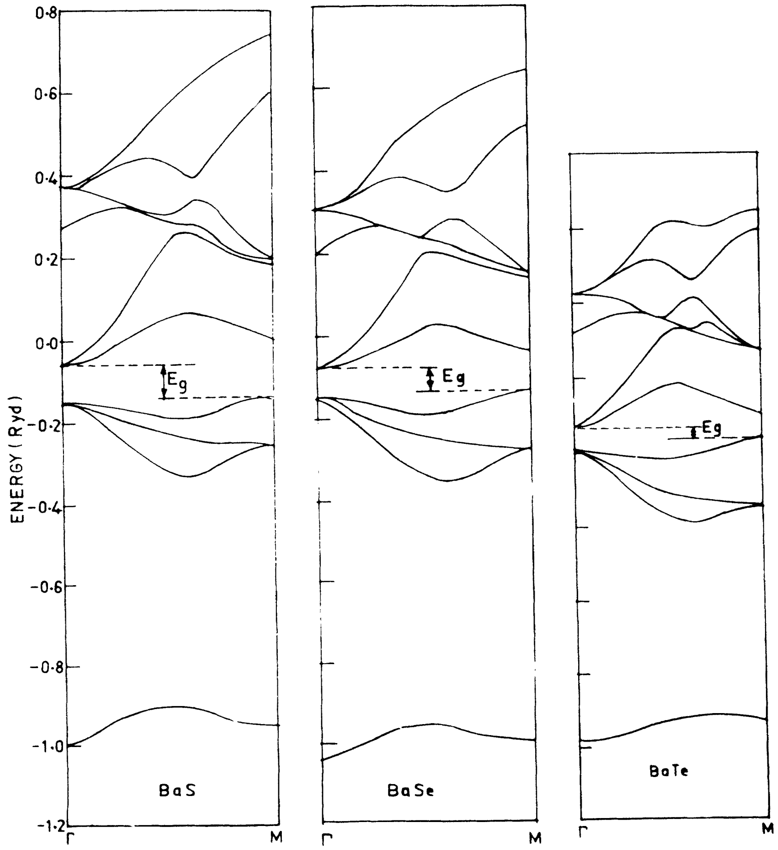

FIG. 5. Band structure in the $B2$ phase at transition.

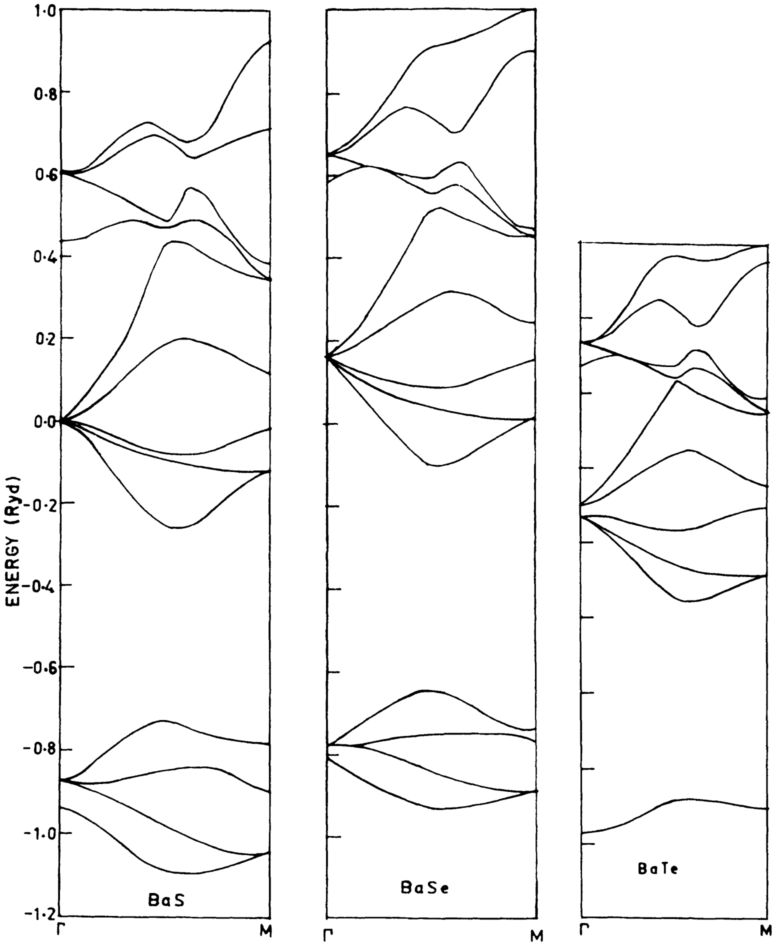

FIG. 6. Band structure in the $B2$ phase near the metallization volume.

the three compounds. With the application of pressure the Ba $5p$ bands move up. Since in the case of BaS and BaSe metallization occurs at a higher pressure compared to BaTe, the Ba $5p$ band moves up more and near metallization it is higher in energy than the chalcogen s band which can be seen from Fig. 6. The volume dependence of the band gaps in the CsCl structure is shown in Fig. 7. The band gaps for all three compounds decrease monotonically with volume. The volume and pressures at which the band gap becomes zero are given in Table IV along with experimental[3,5] and other theoretical work.[15–17]

TABLE III. Energy band gap Eg (eV) in the NaCl structure.

	Expt[a]	TBLMTO	LAPW[b]	ASW[c]
BaS	3.9	2.3		2.1
BaSe	3.6	2.01	1.8	1.8
BaTe	3.4	1.58	1.45	1.4

[a]Reference 20.
[b]Reference 16.
[c]Reference 15.

V. RESULTS AND DISCUSSION

The electronic properties of rare-earth metal compounds BaS, BaSe, and BaTe have been studied by means

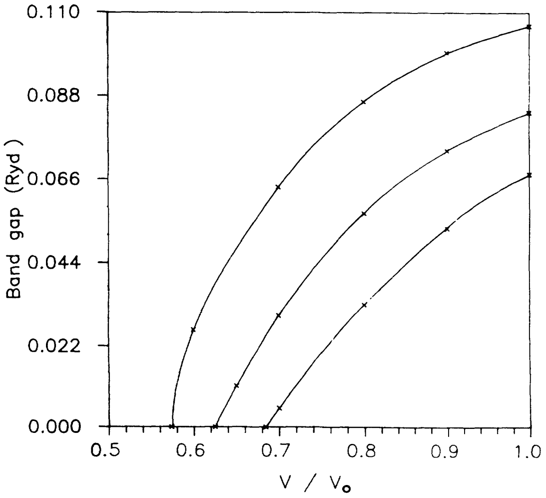

FIG. 7. Volume dependence of band gaps of BaS, BaSe, and BaTe in the $B2$ phase.

TABLE IV. Transition pressures and transition volumes for metallization transformation in BaS, BaSe, and BaTe.

	BaS			BaSe				BaTe				
	Expt.[a]	TBLMTO	ASW[b]	Expt.[a]	TBLMTO	LAPW[c]	ASW	Expt.[d]	TBLMTO	LAPW	ASW	LMTO[e]
V_m/V_0		0.574	0.62	0.555	0.625	0.61	0.66	0.65	0.684	0.67	0.77	0.71
Pressure	800	491	320	520	310	315	170	200	141	158	40	< 100

[a] Reference 5.
[b] Reference 15.
[c] Reference 16.
[d] Reference 3.
[e] Reference 17.

of the TBLMTO band-structure calculations. The scalar-relativistic band structures were obtained for $B1$ and $B2$ structures. The overall band profile for all three compounds is the same, and is in agreement with earlier band-structure results. Using the total-energy calculations the structural phase stability in these compounds has been studied. At normal conditions all the three compounds are stable in the $B1$ structure. The calculated equilibrium lattice constant for the $B1$ structure is in agreement with experimental values. For BaS and BaSe it is 1.4 and 1.2 % less than the experimental results. The calculated pressure at which these compounds undergo a structural transition from a $B1$ to a $B2$ structure agrees well with experimental results. However, the calculated band gaps at ambient conditions underestimates the measured ones by about 40–50 %. The metallization volumes are slightly higher than the experimental values. The disagreement in the values of the band gap between the experimental and the theoretical values is due to the errors introduced by the local-density approximation[23] (LDA) to the exchange-correlation potential. It is usually found that the valence bands of the semiconductors are very well described in this scheme, but the position of the conduction bands relative to the valence bands is not calculated correctly in the LDA, which underestimates the fundamental band gaps in semiconductors and insulators by 30–50 %. Two approaches can be used to rectify this. One is by providing the self-interaction correction energy[24] to the LDA. However, this scheme is applicable to systems in which the bands are narrow compared to the band gap. It is not known how to extend this scheme to problems where the bands are broad compared to the band gap. An alternative approach is to take into account the full nonlocal exchange-correlation potential. It is found that calculations by Norman and Perdew[25] using the Langreth-Mehl-Hu nonlocal exchange-correlation potential[26] yield only small improvements over the fundamental band gap. However, in recent calculations by Christensen and co-workers[27,28] the "corrected" band gaps, which agree well with experimental results, are obtained by adding an empirically calculated external potential at atomic sites.

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