

Ground-state properties and high-pressure phase of beryllium chalcogenides BeSe, BeTe, and BeS

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(Received 22 April 1996)

We present an *ab initio* pseudopotential study within the local density approximation of the ground-state and high-pressure phases of BeSe, BeTe, and BeS. We analyze the zinc-blende, NaCl, CsCl, NiAs, and β -Sn structures. By calculating the total energy, atomic forces, and stress tensors we determine the structural parameters (lattice constants, bulk moduli, etc.) of these compounds and the transition pressure from the zinc-blende (*B3*) to the NiAs (*B8*) phase. The structural parameters and transition pressure for BeSe and BeTe compare quite well with recent experimental results. For BeS our results are predictions.

[S0163-1829(96)04038-6]

I. INTRODUCTION

Little is known about beryllium chalcogenides BeS, BeSe, and BeTe. Recent experimental results¹ report the existence of a first-order transition between zinc-blende and NiAs phases in BeSe and BeTe at pressures of 61.36 GPa and 39.36 GPa, respectively. Among the IIA-VI compounds experimentally investigated so far only for BeSe and BeTe has a first-order phase transition from the zinc-blende phase to the NiAs phase been reported; for the rest a phase transition between the NaCl and the CsCl structure has been observed² except for BeS where no experimental data are available. The beryllium compounds BeSe, BeTe, and BeS crystallize in the cubic zinc-blende structure. The rest of the chalcogenides of group IIA adopt the cubic NaCl structure except for BeO and MgTe, which have the wurtzite (hexagonal) structure. BeSe, BeTe, and BeS are particularly similar to the boron compounds BN, BP and BAs, having at ambient conditions the same crystal structure, wide band gap, and high bulk moduli. The zinc-blende compounds BN, BP, and BAs have an unusual behavior when compared to the other III-V compound families due to the small core size and the absence of *p* electrons. Thus the study of the Be compound could help in the understanding of the behavior of the B compounds.

In this work we concentrate our efforts in the theoretical study from *ab initio* pseudopotential theory of the structural phase transition of beryllium chalcogenides BeSe, BeTe, and BeS under pressure. We analyze the ground-state zinc-blende structure (ZB) and the sixfold coordinate cubic NaCl, the hexagonal NiAs, the cubic CsCl, and the tetragonal β -Sn structures. The calculations are performed in the framework of the density functional theory with *ab initio* norm-conserving pseudopotential.³ It is well known that this method is capable of giving accurate results for ground-state properties of a wide variety of semiconductors and metal materials. The *ab initio* pseudopotential method for total energy calculations has been shown to be capable of predicting structural properties for group-IV elements^{4,5} and III-V compounds.⁶⁻⁸ Although the agreement between experiment

and theory for group-IV elements is quite impressive, notable discrepancies appear for some III-V compounds. Some difficulties arise from the fact that there is little experimental knowledge about the structure of the high-pressure phases and the incomplete theoretical study of these phases.

The paper is organized as follows: In the next section we briefly describe the method of calculation and in Sec. III we present the study of the structural properties of the ground-state and high-pressure phases of BeSe, BeTe, and BeS. Finally our conclusions are given in Sec. IV.

II. METHOD

We have used a first principles pseudopotential method within the local density approximation (LDA) formalism³ to calculate the total energies of zinc-blende, NaCl, NiAs, CsCl, and β -Sn phases for the beryllium compounds BeSe, BeTe, and BeS. The Ceperley-Alder form of the local density approximation for the exchange correlation⁹ was used. Norm-conserving nonlocal pseudopotentials were constructed with the Kerker scheme.¹⁰

We need to calculate small energy differences between phases. A basis set containing all plane waves up to the cutoff energy of 30 Ry was used for BeSe and BeTe which is sufficient to describe the energy difference between different phases with an accuracy of 1 meV/molecule; for BeS we need to increase the cutoff up to 90 Ry due to the hard potential of the sulfur atom. The Brillouin zone integrations were replaced by discrete **k** space summations. We use the standard **k**-points technique of Monkhorst and Pack.¹¹ In order to perform accurate Brillouin zone integrations for the semiconducting zinc-blende phase we use 28 **k** points and 168, 120, 110, and 100 **k** points for the NiAs, CsCl, NaCl, and β -Sn phases, respectively.

The β -Sn and NiAs structures have a single degree of freedom, which we take to be the *c/a* ratio. For these structures we minimize the energy with respect to the internal degrees of freedom at each volume considered. For the hexagonal NiAs structure we determine the two lattice constants *a* and *c* as follows. First we choose a unit cell volume *V* and

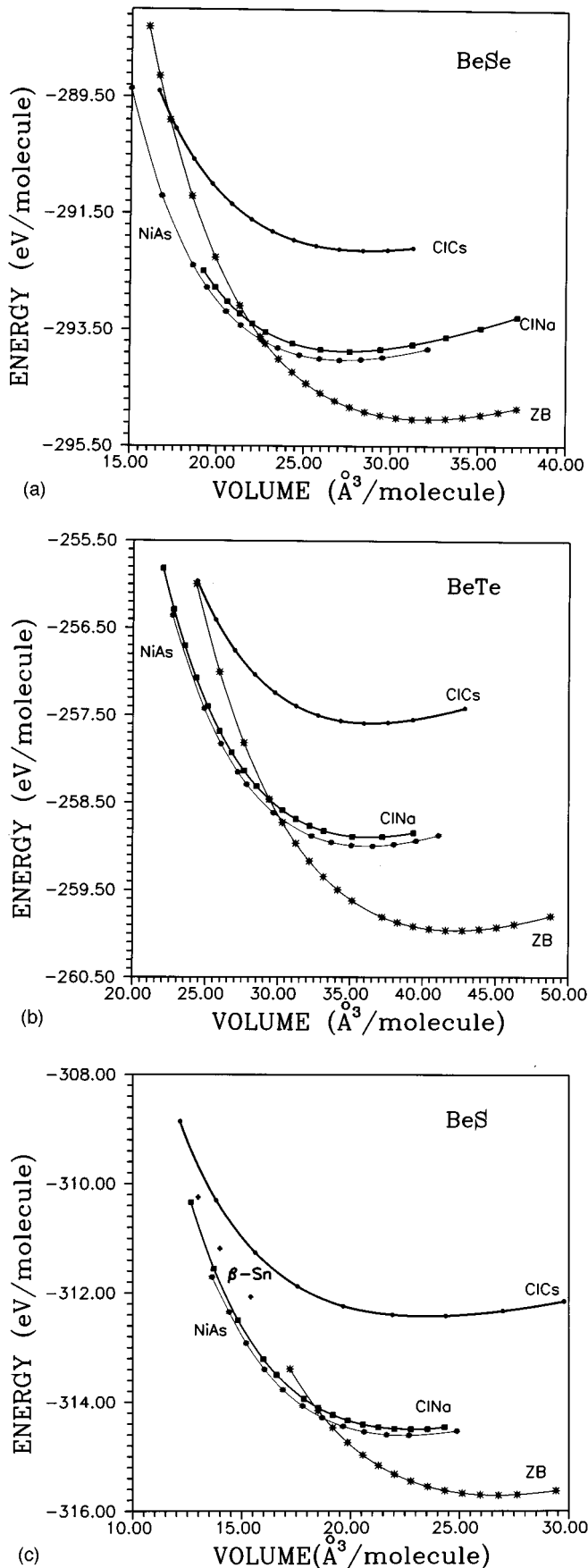


FIG. 1. Calculated total energies per molecule as a function of volume for (a) BeSe, (b) BeTe, and (c) BeS; some results for β -Sn are indicated by crosses.

TABLE I. Lattice constant a_0 , structural parameters c/a , bulk moduli B_0 , and pressure derivative of B_0 and B_0' for the different phases analyzed for BeSe, BeTe, and BeS.

	Structure Phase	a_0 (Å)	c/a	B_0 (GPa)	B_0'	
BeSe	ZB	5.037	-	98.8	3.106	
		5.139 ^a	-	92.2 ^b	-	
	NiAs	3.421	1.578	94.7	3.852	
	ClNa	4.795	-	91.2	4.032	
BeTe	ZB	3.057	-	74.6	3.383	
		5.531	-	70.6	3.377	
	5.625 ^a	-	66.8 ^b	-		
	NiAs	3.774	1.556	76.6	3.716	
BeS	ZB	ClNa	5.252	-	79.2	3.567
		3.314	-	69.9	3.537	
	4.745	-	116.0	3.220		
	4.865 ^a	-	-	-		
NiAs	3.198	1.587	135.6	3.980		
ClNa	4.492	-	127.5	3.201		
ClCs	2.867	-	76.0	3.250		

^aReference 16.

^bReference 1.

with the stress theorem¹² we calculate the difference $\sigma_{xx} - \sigma_{zz}$ of the stress in the x and the z directions. This difference is related to a generalized force. Then we minimize $\sigma_{xx} - \sigma_{zz}$ to obtain the c/a ratio that minimizes the force and the energy. This procedure is repeated for all the volumes we consider in our study. A similar procedure is used to study the tetragonal β -Sn structure.

III. RESULTS AND DISCUSSION

BeSe, BeTe, and BeS crystallize in the zinc-blende structure. In this work we analyze the zinc-blende structure and the structures candidates to the high-pressure phase (NaCl, NiAs, β -Sn, and CsCl); this means that we do not exclude the possible existence of other, more stable structures. The total energy curves per molecule as a function of volume for the five phases are plotted in Figs. 1(a)–1(c). These curves are fitted to the Murnaghan's equation of state.¹³

TABLE II. Transition volumes and transition pressures for the zinc-blende (ZB) to NiAs structures. Volumes are normalized to the calculated equilibrium volumes in the zinc-blende structures.

	V_T (ZB)	V_T (NiAs)	P_T (GPa)
BeSe	0.759	0.659	42.76
BeTe	0.758	0.665	32.21
BeS	0.757	0.651	52.35

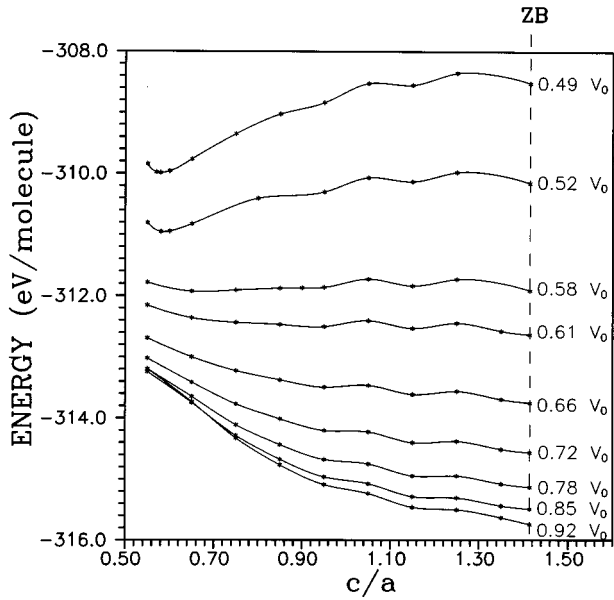


FIG. 2. Calculated total energies as a function of the c/a ratio for several volumes for the β -Sn structure for BeS.

The calculated static properties, equilibrium lattice constant a_0 , bulk modulus B_0 , and pressure derivative of B_0 (B'_0) are given in Table I for the zinc-blende phase and the possible structures of BeSe, BeTe, and BeS at high pressure. The comparison with the experimental available results is in good agreement, with an overestimation of the bulk modulus B_0 .

It is clear from our phase diagram that the NiAs structure is the high-pressure phase of BeSe, BeTe, and also for BeS. The NiAs structure can be viewed as the NaCl distorted along the [111] direction. In the range of volumes considered the total energy curve of rocksalt structure lies above that of NiAs. Then the rocksalt is not the high-pressure phase for these compounds. We observe the CsCl structure is at higher energy than the other structures; then it does not compete as a high-pressure phase. We have also considered the β -Sn structure as a possible candidate to the high-pressure phase. The β -Sn structure can be obtained from the zinc-blende structure by changing the c/a ratio of the tetragonal cell which for the zinc-blende is equal to $\sqrt{2}$ while in the β -Sn it is approximately 0.55. With a similar procedure to the one used for the NiAs phase we obtain the c/a ratio that minimizes the forces and the energy. For all the compounds examined the β -Sn is unstable at low pressure. Similar trends have been reported in diamond¹⁴ and BN.¹⁵ The β -Sn structure is stable, however, at very high pressure. As a prototype of the results we obtain when we analyze the β -Sn structure in Fig. 2 we show the total energy of BeS for a wide range of c/a ratios for volumes between $0.49V_0$ and $0.92V_0$, where V_0 is the equilibrium volume for the zinc-blende structure. At small pressures the E_{tot} versus c/a ratio curve has no local minimum around $c/a=0.55$ but for volumes $0.58V_0$ and higher the β -Sn structure becomes metastable; for a volume of $0.52V_0$ the c/a ratio is approximately 0.58.

To determine the transition pressure, the Gibbs free en-

ergy $G=E+PV-TS$ should be considered. From experimental data the pressure-induced phase transition is independent of the temperature, and so the contribution of the last term can be neglected, and we work with the enthalpy $H=E+PV$. The common tangent between the zinc-blende and the NiAs total energy curves determines the transition path between both structures. The slope of this tangent give the theoretical transition pressure, which is defined as the pressure where the enthalpies of both structures are equal. The results for the transition pressure and volume are given in Table II. For BeTe the zinc-blende phase transforms to the NiAs phase at 32.2 GPa with a relative volume decrease of 12.41% at the transition. Our theoretical results for the BeTe are in excellent agreement with recent experimental results of 39 ± 5 GPa.¹ For BeSe the transition pressure is $P_t=42.7$ GPa lower than the experimental one of 56 ± 5 GPa and the relative reduction of volume at the transition is 13.25%. Finally for BeS we obtain a P_t from zinc-blende to NiAs structure of 52.3 GPa and a relative volume decrease of 14.03% at the transition. We want to emphasize that our results for BeS are a prediction due to the lack of experimental results, but it was suggested by the experimental trends a transition pressure of 69 GPa (Ref. 1) from zinc-blende to a NiAs phase.

For the three Be compounds the transition is accompanied by a relatively small volume decrease while the typical reduction volume for II-V compounds is around (17–20)%.

The NiAs phases of BeS, BeSe, and BeTe remain stable in a very large pressure range as can see in their respective phase diagrams. From our results, with the well-known limitation of the LDA (under estimation of the gap) we obtain that for BeTe the NiAs phase is metallic as is usual in the first-order structural changes for the III-V and II-VI compounds. However, for the BeSe and BeS our study shows that both remain semiconductors at the high-pressure NiAs phase.

IV. CONCLUSIONS

In this work we have analyzed the relative stability of several structures candidates to the high-pressure phase of BeSe, BeTe, and BeS. We have studied five different structures, zinc-blende, rocksalt, β -Sn, NiAs, and CsCl. Our results show that under pressure the three Be compounds transform from the zinc-blende structure to the hexagonal sixfold coordinated NiAs phase. The transition pressure for BeSe is 42.76 GPa and 32.21 GPa for BeTe. The NiAs phase of BeTe is metallic and for BeSe and BeS this phase is semiconductor. For BeS we predict a transition pressure of 52.35 GPa. The decrease in volume is 13.25% and 12.41% for BeSe and BeTe, respectively, and 14.03% for BeS.

ACKNOWLEDGMENTS

This work has been partially supported by the Consejería de Educación del Gobierno Autónomo de Canarias.

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