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Elastic constants and electronic structure of beryllium chalcogenides BeS, BeSe, and BeTe from first-principles calculations

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We use an *ab initio* total energy pseudopotential technique within the local-density aproximation to determine the full set of first-order elastic constants of BeS, BeSe, and BeTe, which have not been established experimentally. For BeS we obtain C_{11}=1.84, C_{12}=0.75, and C_{44}=0.99 Mbar. For BeSe and BeTe we obtain C_{11}=1.49, 1.11; C_{12}=0.59, 0.43; and C_{44}=0.81, 0.60 Mbar, respectively. We also calculate the bulk modulus, the optical phonon frequency at Γ, and we present a study of the electronic band structure of those compounds. The calculated bulk moduli agree well with previous experimental and theoretical values. [S0163-1829(97)06921-X]

I. INTRODUCTION

In view of the increasing need of potentially good semiconductors for various electrical and optical devices, group IV and group III-V compounds have been extensively studied. More recently, the study of the II-VI compounds has been carried out with the exception of the three Be compounds BeS, BeSe, and BeTe, presumably because of their toxic nature.

There is presently a great interest in the study of pressure-induced structural phase transitions in II-VI compounds, the Be compounds among them. However, little is known about the ground-state properties of the beryllium chalcogenides. These three compounds are difficult to handle experimentally. As a result of this, theoretical studies of these compounds have also been neglected and there are only a few of them.[1–4]

The beryllium compounds BeS, BeSe, and BeTe are potentially good materials for technological applications. BeS is an interesting material with high hardness and BeTe is a small gap semiconductor. These materials also are interesting for blue-green laser diodes and laser-emitting diodes.[5]

For the beryllium chalcogenides, few experimental data on their electronic structure are known,[6] and although some theoretical calculations are available,[1,2] their results differ considerably. Recent experiments performed by Waag *et al.*[5] report some characteristics of the electronic structure of Be compounds. First-order elastic constants are among the properties not yet established for BeS, BeSe, and BeTe.

In the present work, we obtain the first-principles elastic constants, bulk moduli, frequencies of the TO(Γ) phonon mode, and the electronic band structure for BeS, BeSe, and BeTe. We use the density functional theory within the local-density approximation. Although this approach fails to describe accurately the energy of the excited states, it usually provides a qualitative description of these states.

The method of calculation has been developed by Nielsen and Martin,[16] who computed elastic constants for Ge, Si, and GaAs using direct calculations of the macroscopic stress and force on the atoms in the solid. With the support of previous successful calculations for related materials,[7–9] we believe that our results are just as reliable and can be used to predict the electronic band structure and the elastic properties for BeS, BeSe, and BeTe.

This paper is organized as follows. In the next section we briefly describe the method of calculation. In Sec. III we present our results for the electronic properties and elastic constants of BeS, BeSe, and BeTe. Finally, our conclusions are given in Sec. IV.

II. THE METHOD

We apply a first-principles pseudopotential method based on the density functional formalism with the local-density approximation (LDA).[10] The Ceperley-Alder form of the local-density approximation for the exchange correlation[11] as parametrized by Perdew and Zunger[12] was used. Norm conserving nonlocal pseudopotentials were constructed using the Kerker scheme.[13] The Brillouin zone integrations were replaced by discrete summations over special set of **k** points. We use the standard **k**-points technique of Monkhorst and Pack.[14]

We have calculated the elastic properties by computing the components of the stress tensor for small strains using the method developed by Nielsen and Martin.[16] For a small strain, the C_{11} and C_{12} elastic constants are derived from the harmonic relations $C_{11}= \sigma_1/\epsilon_1$ and $C_{12}= \sigma_2/\epsilon_1$, where σ_i and ϵ_i represent, respectively, the stress and the applied strain. The macroscopic stress in the solid is computed for a small strain by the use of the stress theorem,[16] and the forces on the atoms are derived from the Hellman-Feynman theorem.[17,18] For an ϵ_4 strain (uniaxial strain in the (111) direction) there are internal displacements of the sublattices, and the atomic positions in the unit cell are not determined only by symmetry. Kleinman[19] defines an internal strain parameter ξ that describes the displacements of the atoms. Nielsen and Martin[16] prescribe two independent calculations of stress and force which determine three independent quantities, C_{44}, ξ, and the optical Γ-phonon frequency ω_Γ, with one additional consistency check. They derive a final stress-strain relation

$$\sigma_4=[C^0_{44}-\Omega^{-1}\mu\omega^2_\Gamma(\xi a_0/4)^2]\epsilon_4=C_{44}\epsilon_4,$$

TABLE I. The lattice constant a_0, the elastic constants C_{ij} for BeS, the elastic constant C_{44}^0, the optical Γ-phonon frequency ω_Γ, the bulk modulus B, the shear modulus C_s, and the internal strain parameter ξ.

	a_0 (Å)	C_{11} (Mbar)	C_{12} (Mbar)	C_{44} (Mbar)	C_{44}^0 (Mbar)	ω_Γ (THz)	B (Mbar)	C_s (MBar)	ξ
Theoretical (Ref. 4)	4.773						1.019		
Expt. (Ref. 26)	4.865								
Present calc.	4.745	1.84	0.75	0.99	1.145	18.7	1.11 [a] 1.16 [b]	0.542	0.42

[a] $B=(C_{11}+2C_{12})/3$.
[b] From Murnaghan's equation.

TABLE II. The lattice constant a_0, the elastic constants C_{ij} for BeSe, the elastic constant C_{44}^0, the optical Γ-phonon frequency ω_Γ, the bulk modulus B, the shear modulus C_s, and the internal strain parameter ξ.

	a_0 (Å)	C_{11} (Mbar)	C_{12} (Mbar)	C_{44} (Mbar)	C_{44}^0 (Mbar)	ω_Γ (THz)	B (Mbar)	C_s (MBar)	ξ
Expt. (Ref. 26)	5.139								
Expt. (Ref. 27)	5.137						0.92		
Present calc.	5.037	1.49	0.59	0.81	0.93	16.4	0.89 [a] 0.98 [b]	0.45	0.43

[a] $B=(C_{11}+2C_{12})/3$.
[b] From Murnaghan's equation.

TABLE III. The lattice constant a_0, the elastic constants C_{ij} for BeTe, the elastic constant C_{44}^0, the optical Γ-phonon frequency ω_Γ, the bulk modulus B, the shear modulus C_s, and the internal strain parameter ξ.

	a_0 (Å)	C_{11} (Mbar)	C_{12} (Mbar)	C_{44} (Mbar)	C_{44}^0 (Mbar)	ω_Γ (THz)	B (Mbar)	C_s (MBar)	ξ
Expt. (Ref. 26)	5.625								
Expt. (Ref. 27)	5.617						0.67		
Present calc.	5.531	1.11	0.43	0.60	0.71	14.8	0.66 [a] 0.70 [b]	0.34	0.44

[a] $B=(C_{11}+2C_{12})/3$.
[b] From Murnaghan's equation.

TABLE IV. Summary of important features of band structure of BeS.

	Minimum gaps (eV)			
	Indirect	Direct	Valence bandwidth (eV)	dE_g/dp (meV/GPa)
Theoretical (Ref. 1)	4.17 ($\Gamma_{15}^v \rightarrow X_1^c$)			
Theoretical (Ref. 2)		6.10 (at K)		
Theoretical (Ref. 4)	2.816 ($\Gamma_{15}^v \rightarrow X_1^c$)	5.397 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)		-21.7
Present calc.	2.75 ($\Gamma_{15}^v \rightarrow X_1^c$)	5.51 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)	14.07	-16.62

TABLE V. Summary of the important features of the band structure of BeSe.

	Minimum gaps (eV) Indirect	Direct	Valence bandwidth (eV)	dE_g/dp (meV/GPa)
Theoretical (Ref. 1)	3.61 ($\Gamma_{15}^v \rightarrow X_1^c$)			
Theoretical (Ref. 2)		4.73 (at K)		
Present calc.	2.39 ($\Gamma_{15}^v \rightarrow X_1^c$)	4.72 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)	14.16	-20.43

where C_{44}^0 is the elastic constant in the absence of internal displacements, μ is the reduced mass, a_0 is the equilibrium lattice constant, and Ω is the cell volume.

III. RESULTS

A. Elastic constants

We have performed convergence tests of the total energy and stress at different plane-wave cutoffs and sets of special **k** points for the integration over the Brillouin zone.[14] Following the work of Dacosta *et al.*,[15] we study the isotropic pressure as a function of the energy cutoff. From these results we conclude that for BeSe and BeTe at least a plane-wave cutoff of 30 Ry is needed (≈800 plane waves), while for BeS we must increase the cutoff up to 90 Ry due to the hard potential of the sulphur atom (≈2640 plane waves). The integration over the Brillouin zone for the undistorted lattice is made with a set of ten special **k** points. For the lower symmetry strained lattices, there are 20 and 30 special points for strains applied in the (100) and (111) directions, respectively. The equilibrium lattice constants $a_0 = 4.745$ Å for BeS, $a_0 = 5.037$ Å for BeSe, and $a_0 = 5.531$ Å for BeTe were determined by fitting the total energy with the empirical Murnaghan's equation of state.[20]

To obtain the elastic constants and phonon frequency ω_Γ for BeS, we use strains of $\epsilon_1 = \pm 0.0003$ along the (100) direction to compute C_{11} and C_{12}. To determine ω_Γ, C_{44}, and ξ we use small displacements $u = \pm 0.0002a$ along the (111) direction and strains $\epsilon_4 = \pm\ 0.0003$ along the (111) direction. For BeSe and BeTe, we use $\epsilon_1 = \pm 0.003$ along the (100) direction, $u = \pm 0.0005a$ along the (111) direction, and $\epsilon_4 = \pm\ 0.003$ along the (111) direction. The calculated values for the elastic constants and phonon frequencies are predictions. In Tables I, II, and III we present our results for BeS, BeSe, and BeTe, respectively.

The bulk modulus is defined as $B = (C_{11} + 2C_{12})/3$ and the shear modulus as $C_s = (C_{11} - C_{12})/2$. The bulk moduli obtained (1.11, 0.89, and 0.65 Mbar for BeS, BeSe, and BeTe, respectively) compare quite well with the values obtained by fitting with Murnaghan's equation of state and with previous theoretical results for BeS (1.019 Mbar) (Ref. 4) and experimental values for BeSe and BeTe (0.92 and 0.67 Mbar).[27]

B. Band structure

The important features of the band structures (main band gaps, valence bandwidths, pressure coefficients) for BeS, BeSe, and BeTe are given in Tables IV, V, and VI. Comparison with experiments is difficult because there are few experimental data available. A self-consistent orthogonalized plane wave method[1] has yielded an indirect gap at X for BeS and BeSe, and an indirect gap for BeTe from Γ along Δ. A composite wave variational version of the augmented plane wave method in conjunction with the linear combination of atomic orbitals interpolation scheme[2] reported direct gaps for BeS and BeSe at K, and a direct gap for BeTe from Γ along Σ. Recent first-principles self-consistent local-density calculations of the main band gap for BeS reported an indirect gap $(\Gamma \rightarrow X)$.[4] Here, we obtain indirect gaps $(\Gamma \rightarrow X)$ for the three compounds. Experimental results[5] report that BeTe is an indirect semiconductor with a gap of about 2.8 eV at room temperature, in good agreement with our results.

The present calculations for BeS give an indirect gap $(\Gamma_{15}^v \rightarrow X_1^c)$ of 2.75 eV and a direct gap $(\Gamma_{15}^v \rightarrow \Gamma_{15}^c)$ of 5.51 eV, very close to the value obtained by Van Camp and Van Doren.[4] The valence bandwidth is equal to 14.07 eV and we find that the pressure coefficient (dE_g/dP) is -16.62 meV/GPa. This pressure coefficient agrees well with the value obtained in previous calculations.[4]

Our study yields for BeSe an indirect gap $(\Gamma_{15}^v \rightarrow X_1^c)$ of 2.39 eV and a direct gap $(\Gamma_{15}^v \rightarrow \Gamma_{15}^c)$ of 4.72 eV, while for BeTe we have an indirect gap $(\Gamma_{15}^v \rightarrow X_1^c)$ of 1.80 eV and a direct gap $(\Gamma_{15}^v \rightarrow \Gamma_{15}^c)$ of 3.68 eV. The indirect gap for BeTe is the smallest one we have found in the three beryllium compounds we have analyzed here. The corresponding va-

TABLE VI. Summary of the important features of the band structure of BeTe.

	Minimum Gaps (eV) Indirect	Direct	Valence bandwidth (eV)	dE_g/dp (meV/GPa)
Experimental (Ref. 5)	2.8 (along Γ-X)			
Theoretical (Ref. 1)	2.89 (along Γ-X)			
Theoretical (Ref. 2)		1.49 (along Γ-K)		
Theoretical (Ref. 26)	2.89 ($\Gamma_{15}^v \rightarrow X_1^c$)	1.45 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)		
Present calc.	1.80 ($\Gamma_{15}^v \rightarrow X_1^c$)	3.68 ($\Gamma_{15}^v \rightarrow \Gamma_{15}^c$)	12.63	-24.06

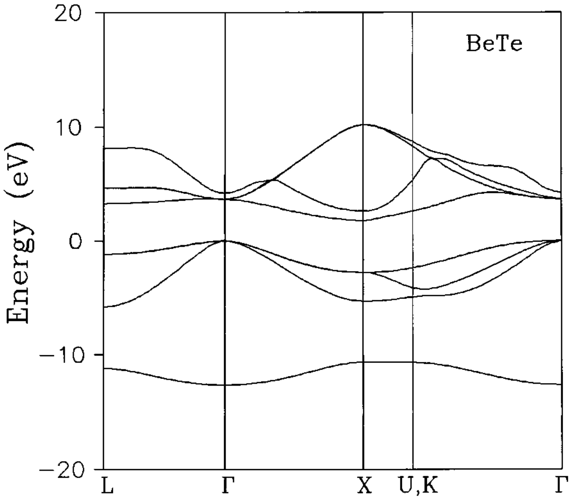

FIG. 1. Electronic band structure of BeTe calculated with a 30 Ry cutoff and a lattice constant $a_0 = 5.531$ Å.

lence bandwidths for these two compounds are 14.16 and 12.63 eV, respectively. We obtain for the pressure coefficients the values -20.43 and -24.06 meV/GPa. In Fig. 1, we present our calculated electronic band structure for BeTe.

The indirect gap for all the three compounds decreases with increasing pressure as indicated in the corresponding tables. It is known that LDA calculations usually underestimate the gap, but the pressure coefficients (dE_g/dP) calculated in the LDA agree quite well with experiments.[21–25]

IV. CONCLUSIONS

We have obtained highly converged total energies, forces, and stresses in BeS, BeSe, and BeTe to arrive at the first-order elastic constants, frequencies of the TO(Γ) phonon mode, and the electronic structure of these materials. For all the calculations we have used the *ab initio* self-consistent pseudopotential method in the framework of the local-density approximation (LDA) with a plane-wave basis. Because all our calculations are *ab initio* with no parametrization, our results should be as accurate as those from previous calculations, and can be considered as reliable predictions for the elastic properties of BeS, BeSe, and BeTe. Our bulk moduli for BeSe and BeTe, obtained using the elastic constants agree quite well with the experimental values.

The calculated band structures yield for the BeS an indirect gap $(\Gamma^v_{15} \rightarrow X^c_1)$ of 2.75 eV and a direct gap $(\Gamma^v_{15} \rightarrow \Gamma^c_{15})$ of 5.51 eV. For BeSe an indirect gap $(\Gamma^v_{15} \rightarrow X^c_1)$ of 2.39 eV and a direct gap $(\Gamma^v_{15} \rightarrow \Gamma^c_{15})$ of 4.72 eV are obtained, and for BeTe the calculated indirect gap $(\Gamma^v_{15} \rightarrow X^c_1)$ is 1.80 eV, while the direct gap $(\Gamma^v_{15} \rightarrow \Gamma^c_{15})$ is 3.68 eV. The indirect gaps of the three Be compounds decrease with increasing pressure as in most semiconductors and insulators. The pressure coefficients obtained in the present calculations compare well with other theoretical values.

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