

Ab initio pseudopotential study of the structural phase transformations of ZnS under high pressure

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Using a first-principles pseudopotential approach and the local-density approximation for the exchange-correlation potential, we have calculated the equations of state (EOS's) of the zinc-blende (ZB), rocksalt (RS), β -Sn, and cinnabar structures of ZnS. From these EOS's the high-pressure structural phase transformations (HP-SPT's) of ZnS were investigated. These calculations were performed using two approximations for treating the semicore $3d$ electrons of Zn: as relaxed valence states, and as part of the frozen core and using nonlinear exchange-correlation core corrections (NLCC). It has been found that the NLCC calculations provide a very good description of the structural parameters and the HP-SPT's of ZnS, provided that the Zn pseudopotential is generated from nonrelativistic atomic calculations. The cinnabar structure is found to be an intermediate phase between the ZB and the RS structures of ZnS, a behavior which was previously associated only with the Te- and Hg-based II-VI compounds. The structural parameters of the cinnabar form of ZnS have very similar behaviors as those of the same structure of HgTe and CdTe.

I. INTRODUCTION

The high-pressure structural phase transformations (HP-SPT's) of the II-VI compounds have recently received a lot of interest.¹⁻¹¹ The feature which has emerged in the past few years is the observation of the cinnabar structure as an intermediate phase between the zinc-blende (ZB) and rocksalt (RS) structures in the Te-based II-VI semiconductors.^{8,9} This behavior was previously associated only with the Hg-based II-VI materials. It is worth noting that the cinnabar structure is the ground-state form of HgS.^{12,13} Therefore, it is of great importance to investigate whether the above feature is common for all the II-VI semiconductors or not, which requires careful experimental and accurate theoretical studies for the other (not Te- or Hg-based) II-VI semiconductors. The aim of this work is to investigate theoretically the ZB to the cinnabar HP-SPT of ZnS, using a first-principles pseudopotential plane-wave (PP-PW) method.

At zero pressure, ZnS is known to crystallize in many similar forms (polytypes) with the ZB structure being the most stable one. The available experimental and theoretical data show that the first HP-SPT in ZnS takes place from the ZB to the RS structures at about 15 GPa,^{1,4} and the RS structure remains stable up to about 27 GPa,⁴ where a second HP-SPT takes place to as yet an unknown structure. In this work we will also address the second HP-SPT of ZnS.

The PP-PW technique is one of the most attractive theoretical methods for studying the structural properties of condensed matter, because of its flexibility and accuracy. Very recently, schemes¹⁴⁻¹⁷ have been developed which produce highly optimized pseudopotentials with respect to the PW basis. The schemes and the recently introduced very efficient minimization techniques¹⁸⁻²⁰ have made it possible to extend the range of applications of the PP-PW approach to almost

all the atoms of the Periodic Table, including the group IIB elements.

The HP-SPT are usually determined using the common tangent technique of the equations of states (EOS's) of the considered crystal structures. In this study, four crystal structures of ZnS have been considered, which are the ZB, the RS, the cinnabar, and the diatomic equivalence of the β -Sn structures. The calculations of the EOS's of these forms of ZnS were performed using the PP-PW approach and the local-density approximation (LDA)²¹ for the exchange-correlation potential. Two approximations for treating the semicore $3d$ electrons of the Zn atom have been used: (i) as relaxed states, and (ii) as part of the frozen core and including the nonlinear exchange-correlation core corrections (NLCC).²²

The rest of the paper is organized as follows. In Sec. II we introduce the method of calculation and give the computational details. In Sec. III we report and discuss our results for the structural parameters of the four considered crystal structures of ZnS and its HP-SPT's. Finally, Sec. IV contains a summary of our main results and conclusions.

II. METHOD AND COMPUTATIONAL DETAILS

The calculations were performed using a PP-PW approach and the Ceperley-Alder form²³ of the LDA as parametrized by Perdew and Zunger.²⁴ The Kohn-Sham equations were solved using the Teter, Payne, and Allan conjugate gradient (CG) total energy minimization technique.¹⁹ The RS, the β -Sn, and the cinnabar structures were treated as metals, and in these cases we used the very recently introduced CG method by one of us.²⁰ The Brillouin-zone integration was performed by sampling on a regular $4 \times 4 \times 4$ Monkhorst-Pack (MP) mesh²⁵ for all the considered crystal structures, which gives rise to 10 special k points for the ZB and the RS

structures, and 11 and 12 special k points for the β -Sn and the cinnabar structures, respectively. For the metallic systems, the use of such small numbers of special k points was made possible by using quite large values of the Gaussian smearing parameter²⁶ (1.0, 0.5, and 1.0 eV for the RS, the β -Sn, and the cinnabar structures, respectively) and including the corresponding entropy correction.²⁷ Convergence tests have shown that a very good convergence with respect to the number of special k points has been achieved: for example, increasing the number of special k points in the case of the RS form of ZnS, with $a=5.0$ Å, to 28 ($6\times 6\times 6$ MP mesh) reduces the ground-state energy by less than 1 meV. This energy difference is not expected to alter the calculated structural parameters, and it has very small effect on the calculated values of the transition pressure, P_t , as will be shown in Sec. III B.

The used Zn and S pseudopotentials were generated using the Kerker scheme²⁸ in Klienman-Bylander form.²⁹ The Zn pseudopotentials used in the relaxed d electrons calculations was generated, with highly optimized $3d$ pseudopotential, as described in Ref. 17. In these calculations PW's up to a 55 Ry in energy were included.¹⁷ The Zn pseudopotential used in the NLCC calculations was generated from nonrelativistic atomic calculations, with the configuration $4s^{1.27}4p^{0.73}$ for the s and p pseudopotentials and the ionic configuration $4s^{0.50}4p^{0.25}4d^{0.25}$ for the d pseudopotential. The used core radii were 2.01, 2.01, and 3.4 a.u. for the s , p , and d pseudopotentials, respectively. In the NLCC calculations, we have used a 22.5 Ry energy cutoff, which is found to give a very good convergence. The S pseudopotential was generated as described in Ref. 30, without including the NLCC.

Both the ZB and the RS structures have only one structural parameter: the lattice parameter, a . The β -Sn form has two structural parameters: a and the c/a ratio. The cinnabar structure has four structural parameters: a , the c/a ratio, and two internal relaxation parameters, u and v , for the Zn and S ions, respectively.

The determination of the optimal c/a ratio, at a fixed value of a , for both the β -Sn and the cinnabar structures, was obtained using the constraint of isotropic stress. This was greatly simplified by making use of the linear variation of the stress components by small changes of the c/a ratio around its optimal value, and also by the linear variation of the c/a ratio with respect to a ; see below. The optimal values of the internal parameters, u and v , of the cinnabar structure, at fixed values of a and its optimal c/a ratio, were determined by minimizing the forces on both the Zn and S ions. The tolerance in the anisotropy of the stress components and the residual forces on the ions was 2.3 kbar and 10^{-5} dyn, respectively.

III. RESULTS AND DISCUSSION

A. The EOS's of the considered crystal structures

The EOS's of the ZB, the RS, the β -Sn, and the cinnabar structures of ZnS are obtained by calculating the total energy, E_{tot} , at five or six different volumes, and fitting the calculated values for each structure to the Murnaghan's EOS.³¹ The calculated EOS's obtained using both the relaxed d electrons and the NLCC calculations are shown in Fig. 1. For the

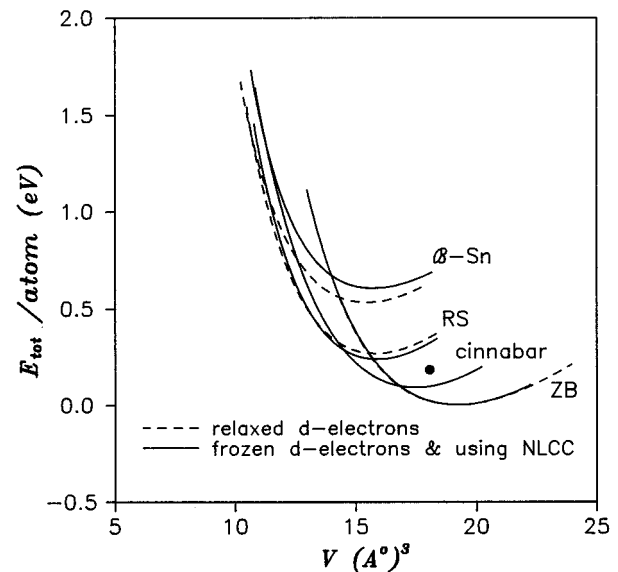


FIG. 1. The calculated EOS's of the ZB, the RS, the β -Sn, and the cinnabar structures of ZnS, using the relaxed d electrons (dashed curves) and the NLCC (solid curves) approaches. The EOS's in the case of the NLCC calculations are rigidly shifted such that the equilibrium total energy, $E_{\text{tot}}^{\text{eq}}$, and the equilibrium volume of the ZB structure match the corresponding values of the same structure obtained using the relaxed d electrons approach. Solid circle: E_{tot} of the cinnabar structure calculated using the relaxed d electrons approach at $a=3.8$ Å and its optimal values of c/a , u , and v (which are, in this case, 2.28, 0.46, and 0.49, respectively). The zero energy is taken to be equal to $E_{\text{tot}}^{\text{eq}}$ of the ZB structure.

cinnabar structure, only NLCC calculations were performed, because of the rather large computational effort required to calculate the EOS of this structure using relaxed d electrons approach. The calculated values of the structural parameters of the four considered structures are shown in Table I, compared with other available theoretical results and experimental data. The important features to note from Table I are as follows.

First, our results for both the ZB and the RS structures obtained using the relaxed d electrons approach are in very good agreement with the experimental data. For example, the discrepancy between our results for the ZB structure and the experimental data is 0.074%, 11%, and 9.6% for a , the bulk modulus, B , and its pressure derivative, B' , respectively.

Second, our calculated structural parameters using the NLCC approach are also in good agreement with the corresponding experimental data. For example, for the ZB structure the errors, in this case, were 2.4%, 11.07%, and 20% for a , B , and B' , respectively. These errors are much less than those in the similarly calculated values by Engel and Needs³² (4.2% and 38% for a and B , respectively). The main difference between the latter calculations and the present ones is that we have used a Zn pseudopotential obtained from non-relativistic atomic calculations. It has recently been noted by one of us³³ that the so generated pseudopotentials for group IIB elements give very good description of the structural properties of the II-VI compounds. This suggests that the relaxation of the semicore d electrons in these materials with respect to the superposition of the semicore atomic charge

TABLE I. Structural parameters of the ZB, the RS, the β -Sn, and the cinnabar structures of ZnS.

Structural parameter	ZB	RS	β -Sn	Cinnabar
a_0 (Å)	5.409, ^a 5.2803, ^b 5.394, ^f 5.413, ^c 4.715, ^g 5.410, ^d 5.186 ^h	5.02, ^a 4.95, ^b 5.06, ^c 5.21, ^e 5.094 ^f	4.769, ^a 4.738 ^b	3.761 ^b
B_0 (GPa)	83.2, ^a 83.3, ^b 75, ^c 76.9, ^d 75.9, ^e 82, ^f 145, ^g 106 ^h	104.4, ^a 107.6 ^b 103.6, ^c 83.1, ^e 100.1 ^f	93.8, ^a 86.7 ^b	92 ^b
B'_0	4.43, ^a 3.92, ^b 4, ^c 4.9, ^d 4.7, ^e 4.2 ^f	4.29, ^a 4.1, ^b 4, ^c 10, ^e 4.05 ^f	4.4, ^a 4.96, ^b	3.1 ^b
$(c/a)_0$			0.5683, ^a 0.5608 ^b	2.3363 ^b
u_0				0.455 ^b
v_0				0.48 ^b

^aPresent work, relaxed d electrons calculations.

^bPresent work, frozen d electrons and NLCC calculations.

^cReference 4, experimental data.

^dReference 34, experimental data.

^eReference 1, first-principles Hartree-Fock linear combination of atomic orbitals method.

^fReference 4, LMTO-LDA total energy calculations.

^gReference 32, PP-PW calculations, frozen core without including the NLCC.

^hReference 32, PP-PW calculations, frozen core and including the NLCC.

densities obtained from relativistic atomic calculations is larger and more important than that of the nonrelativistic atomic calculations.

Third, a comparison of the results for the β -Sn structure obtained using the above two approaches shows that the NLCC calculations also provide quite good structural properties for this structure of ZnS.

Fourth, the equilibrium structural parameters for both the β -Sn and the cinnabar structures of ZnS serve as predictions. To the best of our knowledge, there are no theoretical or experimental results available for these systems.

Fifth, our present calculations show that

$$(B_0)_{\text{ZB}} < (B_0)_{\text{cinnabar}} < (B_0)_{\text{RS}}.$$

This feature is consistent with the experimental results for HgTe reported in Ref. 10.

The variation of the optimal value of the c/a ratio with respect to a is shown in Fig. 2 for both the β -Sn and the cinnabar structures of ZnS. It has been found that (i) the c/a increases (decreases) linearly by increasing a for the β -Sn (cinnabar) structure. (ii) For the β -Sn structure, the optimal values of the c/a ratio obtained using the NLCC calculations are about 1.5% lower than the corresponding values obtained using the other approach; the variation of the c/a ratio with respect to a is almost identical for the two approaches. (iii) The variation of the c/a ratio of the cinnabar

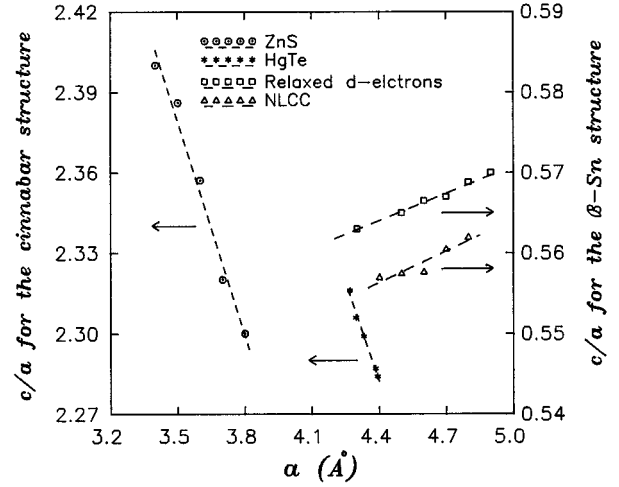


FIG. 2. The variation of the optimal value of the c/a ratio with respect to the lattice parameter, a , for the β -Sn structure as obtained from both the relaxed d electrons and the NLCC calculations, and for the cinnabar structure using the NLCC calculations. The results for cinnabar form of HgTe reported in Ref. 10 are also shown.

bar structure of ZnS is consistent with that of CdTe and HgTe reported in Refs. 5 and 10, respectively. Feature (i) indicates that the β -Sn structure is more susceptible for compression under high pressure along the c direction than the other axes; the opposite is true for the cinnabar structure.

Figure 3 depicts the variation of the optimal values of the internal structural parameters of the cinnabar structure of ZnS (u and v) with respect to a . The important features to note here are (i) the values of both u and v increase by increasing a , with a plateau around a_0 (between 3.5 and 3.7 Å for u , and between 3.6 to 3.8 Å for v) and (ii) the values of u and v in the considered range of a are very close to each other, which is consistent with the experimental results reported in Ref. 5 for CdTe (about 0.63 and 0.56 for u and v , respectively) and those reported for HgTe in Ref. 10 (about 0.64 and 0.56 for u and v , respectively). It is worth

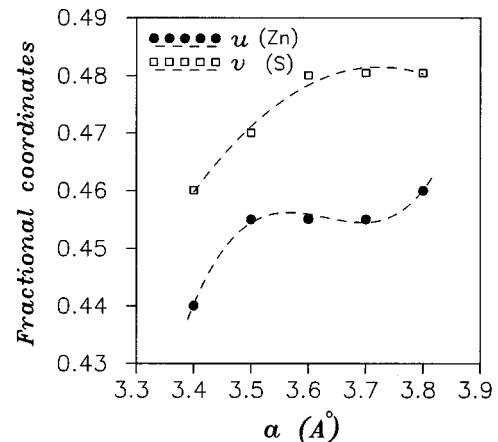


FIG. 3. The variation of the optimal values of the internal parameters u and v for the cinnabar structure of ZnS with respect to a .

TABLE II. The transition pressures (GPa) of ZnS, from the ZB to the cinnabar or the RS structures, and from the cinnabar to the RS structures. The other available theoretical and experimental results are also shown.

Phase transition	Present work		Other theoretical results	Experimental data
	Relaxed d electrons	NLCC		
ZB \rightarrow Cin		11.4		
Cin \rightarrow RS		14.5		
ZB \rightarrow RS	14.7	14.5	16.1, ^a 19.5 ^c	14.7–15.4, ^b 18.1, ^d 15.0–16.2 ^e

^aReference 1, first-principles Hartree-Fock linear combination of atomic orbitals method.

^bReference 34, experimental data.

^cReference 4, LMTO-LDA total energy calculations.

^dReference 35, experimental data.

^eReference 36, experimental data.

noting that in the case of the cinnabar structure of HgS the values of u and v are 0.72 and 0.48, respectively.^{12,13} Our calculated values are smaller than the above observed results for CdTe and HgTe by about 30% and 15% for both u and v , respectively, and the value of v is larger than the value of u in the present work. The origin of such discrepancies is not clear to us. However, they cannot be understood as shortcomings of the use of the NLCC calculations, since the relaxed d electrons calculations provided almost the same values for the two parameters (such calculations were performed only at one volume, see Fig. 1). Therefore, more calculations are required, especially for CdTe and HgTe compounds, to clarify this point—this work is now in due course.

B. Structural phase transformations

First we discuss the HP-SPT of ZnS from the ZB to the RS structures, which was found to be the first HP-SPT.^{1,4,8} We have found that such a transition takes place at 14.7 and 14.5 GPa, using the relaxed d electrons and the NLCC calculations, respectively. These results are found to change very little when 28 special k points are used in the calculations of the RS structure: a rigid downshift in energy of the EOS of the RS structure by 1 meV, see Sec. II, affects the calculated value of P_t by only 0.1 GPa. This shows that our results are well converged with respect to the number of special k points used. Our results for P_t are in very good agreement with the experimental results, which range between 14.7 to 18.1 GPa, and other theoretical values; see Table II. An important feature to note here is that the NLCC calculations provide a very accurate description of the above phase transformation.

The most remarkable feature to note from Fig. 1 is that the NLCC calculations reveal that for ZnS the cinnabar structure is an intermediate phase between the ZB and the RS structures. According to these calculations, the first HP-SPT takes place from the ZB to the cinnabar structure at about 11.4 GPa. The cinnabar structure remains stable up to about 14.5 GPa where it undergoes a HP-SPT to the RS structure. To assess the accuracy of these results, we have

calculated E_{tot} of the fully optimized structure of the cinnabar form at only one volume (also shown in Fig. 1) using the relaxed d electrons approach. This calculated value of E_{tot} and the very weak volume dependence of energy difference between the calculated two EOS's for each of the ZB, the RS, and the β -Sn structures (see Fig. 1), confirm our conclusion that the first HP-SPT of ZnS is from the ZB to the cinnabar structures. However, the stability range of the cinnabar structure is expected to be smaller than the one obtained from the NLCC calculations (3.1 GPa). It is worth noting here that the stability range of the cinnabar form of CdTe is also very small (about 0.8 GPa), and it was only observed as a single phase while decreasing the pressure.¹⁰ This is a very important finding, since it shows that the observation of the cinnabar structure as an intermediate phase between the ZB and the RS structures is not only limited to the Te- or Hg-based II-VI compounds, but it could be a common behavior for all of the II-VI compounds. Therefore, more experimental and theoretical investigations are needed to clarify this point.

It has been observed⁴ that the RS structure of ZnS remains stable up to about 27 GPa; then it transforms to as yet an unknown structure. Figure 1 shows that this unknown structure is not the β -Sn.

IV. CONCLUSIONS

In this study a first-principles pseudopotential technique and the local-density approximation are used to calculate the equations of state (EOS's) of the zinc-blende (ZB), the rock-salt (RS), the β -Sn, and the cinnabar structures of ZnS. From these EOS's the first and the second high-pressure structural phase transformations (HP-SPT's) have been investigated. Two approximations for treating the semicore $3d$ electrons of Zn were used: (i) as relaxed valence states, and (ii) as part of the frozen core and including the nonlinear exchange-correlation core corrections (NLCC). In the following we summarize our main results and conclusions.

(1) The calculated structural parameters for the ZB and the RS structures of ZnS, using both approximations for treating the semicore d electrons, are in good agreement with the available experimental data and all the electron calculations.

(2) For the β -Sn structure of ZnS, the calculated structural parameters using the above two approaches are very close to each other.

(3) For the cinnabar structure of ZnS, the u and v parameters are almost equal, and the c/a ratio decreases linearly with increasing a .

(4) The most important finding is that for ZnS the first HP-SPT takes place from the ZB to the cinnabar structures, unlike what has been previously thought (ZB to RS). The range of stability of the cinnabar structure is found to be very narrow, and it undergoes a SPT to the RS structure at about 15 GPa.

(5) The β -Sn structure of ZnS can be safely ruled out as a high pressure phase of this material.

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- ¹J. E. Jaffe, R. Pandey, and M. J. Seal, *Phys. Rev. B* **47**, 6299 (1993).
- ²R. J. Nelmes, M. I. McMahon, N. G. Wright, and D. R. Allan, *Phys. Rev. Lett.* **73**, 1805 (1994).
- ³B. A. Weinstein, *Solid State Commun.* **24**, 595 (1977).
- ⁴S. Ves, U. Schwarz, N. E. Christensen, K. Syassen, and M. Caradonna, *Phys. Rev. B* **42**, 9113 (1990), and references therein.
- ⁵M. I. McMahon, R. J. Nelmes, N. G. Wright, and D. R. Allan, *Phys. Rev. B* **48**, 16 246 (1993).
- ⁶W. Andreoni and K. Maschke, *Phys. Rev. B* **22**, 4816 (1980).
- ⁷A. San-Miguel, A. Polian, M. Gauthier, and J. P. Itiè, *Phys. Rev. B* **48**, 8683 (1993).
- ⁸G. R. Chelikowsky, *Phys. Rev. B* **35**, 1174 (1987).
- ⁹R. J. Nelmes, M. I. McMahon, N. G. Wright, and D. R. Allan, *Phys. Rev. B* **51**, 15 723 (1995).
- ¹⁰A. San-Miguel, N. G. Wright, M. I. McMahon, and R. J. Nelmes, *Phys. Rev. B* **51**, 8731 (1995).
- ¹¹V. Smelyansky and J. S. Tse, *Phys. Rev. B* **52**, 4658 (1995).
- ¹²R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963), Vol. 1.
- ¹³K. L. Aurivillius, *Acta Chem. Scan.* **4**, 1423 (1950).
- ¹⁴A. M. Rappe, K. M. Rabbe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).
- ¹⁵D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ¹⁶T. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁷J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, *Phys. Rev. B* **47**, 4174 (1993).
- ¹⁸R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ¹⁹M. P. Teter, M. C. Payne, and D. C. Allen, *Phys. Rev. B* **40**, 12 255 (1989).
- ²⁰A. Qteish, *Phys. Rev. B* **52**, 14 497 (1995).
- ²¹R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
- ²²G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- ²³D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²⁴J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ²⁵H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ²⁶C. L. Fu and K. M. Ho, *Phys. Rev. B* **28**, 5480 (1983).
- ²⁷C. Elsässer, M. Fähnle, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **49**, 13 975 (1994); A. de Vita, Ph.D. thesis, University of Keele, Keele, UK, 1993.
- ²⁸G. P. Kerker, *J. Phys. C* **13**, L189 (1980).
- ²⁹L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ³⁰A. Qteish and R. J. Needs, *Phys. Rev. B* **45**, 1317 (1992).
- ³¹F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1994).
- ³²G. E. Engel and R. J. Needs, *Phys. Rev. B* **41**, 7876 (1990).
- ³³A. Qteish (unpublished).
- ³⁴*Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung *et al.*, Landolt-Börnstein, New Series, Vol. 17b (Springer-Verlag, Berlin, 1982).
- ³⁵G. A. Samara and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 457 (1962).
- ³⁶G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975); S. C. Yu, I. L. Spain, and E. F. Skelton, *Solid State Commun.* **25**, 49 (1978); T. Yagi and S. Akimoto, *J. Appl. Phys.* **47**, 3350 (1976); A. Onodera and A. Ohtani, *ibid.* **51**, 2581 (1980).