

## Theoretical calculations of the thermomechanical properties of PbS

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The thermomechanical properties of PbS have been calculated by applying the self-consistent-field- $X\alpha$ -scattered-wave technique to a  $\text{Pb}_4\text{S}_4$  cubic cluster. The total energy for the cluster is calculated as a function of Pb-S separation and used to obtain equilibrium lattice constant, cohesive energy, equation of state, and bulk modulus for PbS. The results are in good agreement with the experimental data.

### I. INTRODUCTION

The early theoretical studies of the thermomechanical properties of solids have, in general, been highly approximate model calculations. With the development of new theoretical techniques and faster and larger computers, it has become possible to carry out accurate first-principles total-energy calculations. The previous studies of this type<sup>1-6</sup> have been limited to cubic elemental solids. Since these calculations, in general, have required a self-consistent calculation of the energy-band structure of the solid, they have involved considerable computational effort. In order to reduce the computational difficulties, it should be possible to take advantage of the generally local nature of the thermomechanical properties. The feasibility of this approach was already shown in the preliminary studies of PbS.<sup>7</sup> In this approach the solid is represented by a cluster of atoms. The total energy of the cluster is calculated using the self-consistent-field  $X\alpha$ -scattered-wave technique. It is seen that accurate results can be obtained using clusters of reasonable size. Moreover, in the case of close-packed materials, the muffin-tin potential model proves sufficient for the purpose of total-energy calculation.

### II. THEORETICAL TECHNIQUES

PbS is a member of the cubic lead chalcogenide family, possessing the rocksalt structure. The cluster used in this study is cubic with four lead and four sulfur atoms located at the corners and thus has the  $T_d$  symmetry. This  $\text{Pb}_4\text{S}_4$  cluster is the smallest cluster that reflects the cubic symmetry as well as the charge neutrality of the solid. The starting potential for the calculations is formed by superposition of atomic potentials obtained from self-consistent-field (SCF) Hartree-Fock-Slater calculations.<sup>8</sup> The space is then geometrically partitioned by placing touching spheres around the atoms in the cluster and then enclosing the atomic

spheres within a touching but not overlapping outer sphere. The potential is spherically averaged inside the atomic spheres and outside the outer sphere. The interstitial potential is obtained through volume averaging. This will be referred to from here on as a muffin-tin potential. The one-electron Schrödinger equation is solved for this potential using the SCF scattered-wave theory.<sup>9</sup> This technique has been successfully applied to molecules, clusters of atoms,<sup>9,10</sup> solid surfaces and chemisorption,<sup>11</sup> and localized states in solids.<sup>12-14</sup> The ground state total energy is then calculated using the  $X\alpha$  theory,<sup>15,16</sup> given by

$$E_{X\alpha} = \sum_{i=1}^n \int u_i^*(\vec{r}) [-\nabla^2 u_i(\vec{r})] d\vec{r} + \int \sum_{\alpha=1}^N \frac{-2Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \rho(\vec{r}) d\vec{r} + \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \frac{3}{4} \int \rho(\vec{r}) V_{X\alpha}(\vec{r}) d\vec{r} + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}}^N \frac{2Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|}, \quad (1)$$

where the terms represent electronic kinetic energy, electron-nuclear Coulomb interaction, electronic Coulomb interaction, the exchange-correlation potential, and nuclear-nuclear Coulomb interaction, respectively.  $Z_\alpha$  is the nuclear charge of  $\alpha$ th atoms at position  $\vec{R}_\alpha$  and  $\rho(\vec{r})$  is the electron density given by

$$\rho(\vec{r}) = \sum_i n_i u_i^*(\vec{r}) u_i(\vec{r}), \quad (2)$$

where  $u_i$  are electronic orbitals obtained from the solution of the one-electron Schrödinger equation.  $V_{X\alpha}$  is the local statistical exchange-correlation potential<sup>15,16</sup> given as

$$V_X = -6\alpha [(3/8\pi)\rho(\vec{r})]^{1/3}. \quad (3)$$

### III. CALCULATED RESULTS AND COMPARISON WITH EXPERIMENT

The calculations are carried out at seven Pb-S separations, corresponding to from  $-0.90$  to  $+1.25$  of the measured equilibrium lattice constant of the solid.<sup>17</sup> The radii of Pb and S spheres, for the case corresponding to the experimental lattice constant, are taken from the augmented-plane-wave energy-band calculations for PbS.<sup>18</sup> For the remaining six cases, the radii are scaled up or down by the same amount as the Pb-S separation. The radius of the outer sphere is chosen as  $\frac{1}{2}$ (cube body-diagonal) + radius of Pb sphere. One-fourth of the total energy of the cluster is fitted into a Morse curve,

$$\Delta E = b_1 \left( 1 - e^{-b_2(r-b_3)} \right)^2 + b_4, \quad (4)$$

$$E_{\text{total}} = E_1 + \Delta E,$$

using a nonlinear least-squares fitting procedure, with the obtained parameters given in Table I. Figure 1 shows the calculated total energy curve as a function of the Pb-S separation. The calculated lattice constant of  $6.408 \text{ \AA}$  is only 7.9% larger than the measured value of  $5.936 \text{ \AA}$ .<sup>17</sup> The cohesive energy  $b_1$  is the least accurate quantity resulting from the fit, due to the fact that total energies are calculated for Pb-S separation close to the equilibrium lattice constant. As a result, the energy for the infinitely separated atoms is not very accurate. Thus the theoretical cohesive energy of  $49.42 \text{ kcal/mol}$  is considerably lower than the measured value of  $135.5 \text{ kcal/mol}$ . The experimental cohesive energy is obtained as the sum of three quantities. The enthalpy of sublimation of PbS is measured to be  $55.7 \pm 1.6 \text{ kcal/mol}$ ,<sup>19</sup> using mass-spectrometric techniques. The dissociation enthalpy of PbS gaseous molecule into Pb and  $\frac{1}{2}\text{S}_2$  is determined to be  $28.8 \pm 2.6 \text{ kcal/mol}$  by the same technique.<sup>19</sup> Finally, the dissociation enthalpy of  $\frac{1}{2}\text{S}_2$  into a S atom is obtained through a Knudson torsion-effusion experiment to be  $101.7 \pm 2.9 \text{ kcal/mol}$ .<sup>20</sup> However, it should be kept in mind that the discrepancy between the calculated and measured cohesive energy, i.e.,  $0.275 \text{ Ry}$

TABLE I. Parameters of the nonlinear least-squares fit of the total energy for PbS to a Morse curve.

$b_1 = 0.1576$	Ry/mol cohesive energy
$b_2 = 0.6767$	(Bohr radius) <sup>-1</sup>
$b_3 = 6.0547$	Bohr radius. Equilibrium separation
$b_4 = -0.4829$	Ry/mol Minimum of $\Delta E$
$E_1 = -39844$	Ry/mol

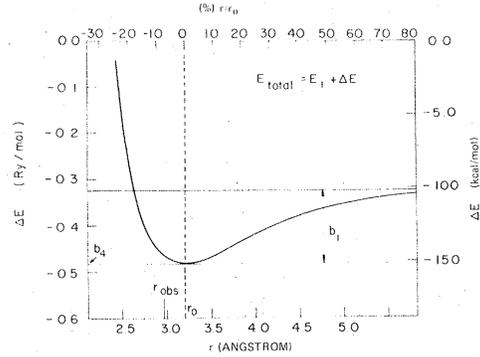


FIG. 1. Total-energy curve for PbS as a function of Pb-S separation  $r$ .  $\Delta E = -39844 \text{ Ry}$ .

amounts to  $(7 \times 10^{-4})\%$  of the total energy for the PbS molecule. This is quite reasonable for an *ab initio* calculation.

In the next step, the calculated total energy is used to obtain the equation of state using the relationship

$$P = -dE/dV. \quad (5)$$

Figure 2 shows the comparison of calculated and measured variation of pressure with volume. It is seen that the experimental data of Bridgman<sup>21</sup> and Wakabayashi *et al.*,<sup>22</sup> below 25 kbars, are in good agreement with the theoretical curve. At around this pressure PbS undergoes a phase transition from the cubic NaCl structure to a SnS-type structure,<sup>22</sup> and this is clearly shown by the break in the measured data at this pressure and the deviation of this data from the theoretical curve at higher pressures.

The bulk modulus is then calculated using the relationship,

$$B = -V \frac{dP}{dV} \quad (6)$$

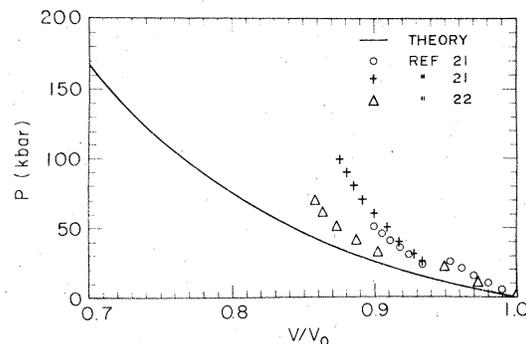


FIG. 2. Variation of pressure with volume for PbS.

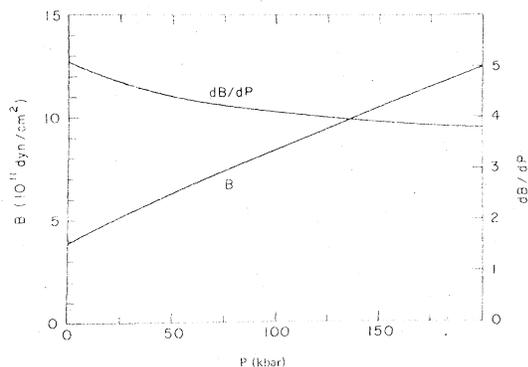


FIG. 3. Variations of the calculated bulk modulus and its pressure derivative with respect to pressure for PbS.

and the variations of  $B$  as well as  $dB/dP$  with pressure are shown in Fig. 3. The calculated zero-pressure bulk modulus of  $1.94 \times 10^{11}$  dyn/cm<sup>2</sup> is in good agreement with the experimental results of  $5.9 \times 10^{11}$ ,<sup>23</sup>  $6.22 \times 10^{11}$ ,<sup>24</sup> and  $5.29 \times 10^{11}$ ,<sup>25</sup> obtained from elastic-constant measurements.

#### IV. DISCUSSION

The comparison of the theoretical results with experimental data clearly shows that an eight-atom cluster is capable of furnishing reasonably accurate results for the thermomechanical properties of solid PbS, even with a muffin-tin potential model. This is due to the local nature of these properties in general, and the close-packed structure of PbS in particular. Larger clusters will undoubtedly improve the results for PbS; however, the large total-energy values, due to the massiveness of the atoms, will bring such calculations near the computational accuracy limit of the present computers. In the case of materials with anisotropic and open structures, additional correction will be required to the total energy.

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