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Theoretical study of Raman modes in high-pressure phases of Si, Ge, and Sn

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Results of an *ab initio* investigation of the pressure-dependence of the Raman-active phonon modes in the β-Sn phase of Si, Ge, and Sn and the hexagonal-close-packed phase of Si are presented. The calculations are in very good agreement with experimental measurements. Both measurements and calculations show that the β-Sn–structure LO mode has a different pressure dependence for Ge than for Si. This difference between Si and Ge is discussed, and an explanation in terms of d electrons is given.

I. INTRODUCTION

In the last decade, the high-pressure behavior of the group-IV elements Si, Ge, and Sn has been the subject of many experimental[1–10] and theoretical[11–27] investigations. In particular, these elements undergo a series of pressure-induced first-order structural phase transitions, which are summarized in Fig. 1. A structural phase common to these elements is the metallic β-Sn phase. This is the stable low-pressure structure of Sn at room temperature.[28] Upon compression to 9.5 GPa, Sn transforms to a body-centered-tetragonal phase. Both Si and Ge exist in the diamond structure at low pressures and transform to the β-Sn structure at about 10 GPa. They both then transform to the simple hexagonal (sh) structure at about 15 GPa for Si and at 75 GPa for Ge. Upon further compression, Si transforms to an intermediate phase, denoted Si-VI, at about 38 GPa and to the hexagonal-close-packed (hcp) structure at about 42 GPa. No such transitions are observed in Ge.

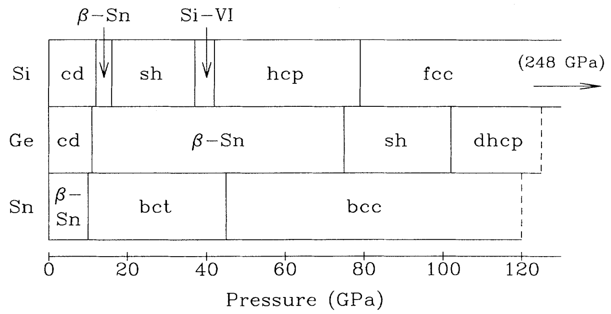

FIG. 1. A schematic summary of the experimentally observed room temperature structural phases of Si, Ge, and Sn as a function of pressure in GPa. The transition pressures are taken from Ref. 9 for Si, Ref. 4 for Ge, and Refs. 1 and 8 for Sn. The dashed lines correspond to the highest reported pressure for each element; for Si, the highest pressure achieved is 248 GPa and is not shown. The following abbreviations were not defined in the text: cubic diamond (cd), face-centered cubic (fcc), double-hcp (dhcp), and body-centered cubic (bcc).

Recently, Olijnyk[10] has used Raman spectroscopy to study the pressure dependence of the Raman-active phonon modes of Si, Ge, and Sn in the β-Sn structure and of Si in the Si-VI and hcp structures. For all three elements in the β-Sn phase, the frequency of the doubly degenerate TO Raman mode is found to increase with pressure over the range of stability, although with slightly decreasing mode-Grüneisen parameter. In contrast, the behavior of the LO Raman mode is found to change in going from Si to Ge to Sn. For Si, the LO mode is found to decrease with pressure, with an increasingly negative Grüneisen parameter, over the range of stability. This is attributed[10] to the onset of the β-Sn $\rightarrow$ sh transition and is addressed more fully below. For Ge, the LO mode is found to increase initially and then level off by 50 GPa. No measurements on Ge are presented for pressures between 50 GPa and the transition to the sh structure at 75 GPa, although it is speculated[10] that the mode will start to soften near the transition, as is seen for Si. Finally, the LO mode for Sn is found to increase over the whole range of stability, although more gradually than the TO mode, and with a more rapidly decreasing Grüneisen parameter. Two Raman modes are seen for Si-VI, the lower of which becomes the doubly degenerate TO Raman mode for hcp-Si. This mode is first seen at 33 GPa; it increases linearly with pressure (at least up to 47 GPa); and it is continuous across the Si-VI $\rightarrow$ hcp transition.

This paper reports on a first-principles investigation of the pressure-dependence of the Raman modes discussed above. Since the exact structure of Si-VI is not known, it is assumed to be the hcp structure, and the structural transition sequence is assumed to be sh $\rightarrow$ hcp instead of sh $\rightarrow$ Si-VI $\rightarrow$ hcp. These assumptions are acceptable for the purposes of the present study, since the lower frequency Si-VI Raman mode and the TO hcp Raman mode are closely related to each other and are both associated to the distortion back to the sh structure.[10] The higher frequency Si-VI Raman mode is not addressed in this study. The calculated results of phonon frequency vs pressure agree very well with the measurements of Ref. 10. Discussion will focus primarily on Si and Ge in the

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β-Sn structure, and the behavior of the LO Raman mode in particular. This feature of the data is the most challenging to understand because of the dissimilarity of the behavior of Si and Ge. An explanation of this disimilarity based on the presence of d electrons in the Ge core is provided. This paper is organized as follows. Section II discusses the methods used in the calculations and provides some computational details. A description of the structures and relevant phonon modes is contained in Sec. III. Section IV presents the computational results. Finally, in Sec. V the discrepancy between Si and Ge in the pressure-dependence of the β-Sn–structure LO Raman mode is discussed.

II. COMPUTATIONAL METHODS

Calculations are performed using the *ab initio* pseudopotential total-energy method.[29–31] Electron-ion interactions are evaluated in this method using nonlocal, norm-conserving pseudopotentials.[32] The Si, Ge, and Sn pseudopotentials used here have reference configurations $3s^{2.0}3p^{0.5}3d^{0.5}$, $4s^{2.0}4p^{0.5}4d^{0.5}$, and $5s^{2.0}5p^{0.5}5d^{0.5}$, respectively. The cutoff radii (in a.u.) for the s, p, and d potentials are equal to (1.12, 1.35, and 1.17), (1.17, 1.35, and 1.77), and (1.20, 1.50, and 2.55) for the three elements, respectively. Electronic exchange and correlation energies are calculated within the local-density approximation[33] (LDA) using a standard form for the exchange-correlation potential.[34] The only external inputs to the calculation are the atomic numbers and masses of the constituent atoms and the basic crystal structure. All relaxed structural parameters are calculated from first principles.

Wave functions and pseudopotentials are expanded in a plane-wave basis up to an energy cutoff of 35 Ry for Si and Ge and 30 Ry for Sn. The irreducible part of the Brillouin zone is sampled at 148 (279) special points[35] for the TO (LO) mode of the β-Sn structure and at 128 special points for the TO mode of the hcp structure. To overcome numerical instabilities associated with filling energy levels over a discretely sampled Brillouin zone, all energy levels are broadened into Gaussians with widths of about 0.7 mRy. Values of the computational parameters are chosen such that the calculated total energies are converged to within 1 mRy.

Phonon frequencies are calculated within the frozen phonon approximation. In this approach, the total energy is calculated for a crystalline system with a static phonon distortion of given amplitude imposed. Such calculations are done for several phonon amplitudes up to about 2% of the bond length. The total-energy vs amplitude data are then fitted, within the harmonic approximation, to a quadratic polynomial, and the phonon frequency is extracted from the coefficient of the leading term.

In these calculations, the unit-cell volume is a more natural choice for the independent variable than pressure. Therefore, to make contact with experiments, in which pressure is the more natural choice for the independent variable, an equation of state is required. For each system considered, the equation of state is obtained by first calculating the total energy at several unit-cell volumes and fitting these data to the Murnaghan equation of state.[36] A correction to account for the zero-point energy of the ions is then added (see below). Parameters of the fit to the Murnaghan equation are tabulated in Table I for each of the four systems considered here. For Si, Ge, and Sn in the β-Sn structure, these parameters are in good agreement with the previously calculated values of Refs. 14, 20, and 24, respectively. The agreement for Si with the calculated equation of state of Ref. 15 is only fair, due primarily to the smaller Brillouin zone sampling and energy cutoff used in the earlier calculation. Calculations for Ge and Sn in the β-Sn structure and for Si in the hcp structure agree well with experimental equations of state. No experimental equation of state for Si in the β-Sn structure has been published, to our knowledge, probably because the range of stability of this phase is so small. However, the calculations are consistent with the few measurements of volume vs pressure that exist.[2,3]

Since the pressure is obtained as the negative of the derivative of the total energy with respect to volume, at high pressures, the pressure is a sensitive function of volume, and the error can be significant. This often represents the largest error in the calculation. For Si in the β-Sn structure, the range of stability ($\sim$4 GPa) is of the same order as the error in the calculated pressure. Therefore, volumes whose pressures are calculated to lie within the range of stability may, in fact, lie outside of it. To account for this, calculations for Si in the β-Sn structure have been performed for a volume range larger than the range of stability.

The present computational method treats the ion cores classically, and the effect of the zero-point motion (ZPM) of the cores on the equation of state is approximated by a Debye model:

$$E_{\mathrm{ZPM}} = \frac{9}{8}\hbar\omega_D = \frac{9}{8}\hbar v_s q_D = \frac{9}{8}\hbar\sqrt{\frac{B}{\rho}}\,q_D, \qquad (1)$$

where ω_D is the Debye freqency, v_s is the speed of sound, B is the bulk modulus, ρ is the mass density, and q_D is the Debye wave vector. Volume-dependence of E_{ZPM} is contained in B, ρ, and q_D. The total energy is taken as the sum of the static-core total energy and the ap-

TABLE I. Best-fit parameters to the Murnaghan equation of state (Ref. 36) for Si, Ge, and Sn in the β-Sn structure and for Si in the hcp structure. The parameters are the equilibrium volume V_0 and the bulk modulus B_0 and its pressure derivative B_0' at this volume.

System	V_0 (a.u./atom)	B_0 (GPa)	B_0'
β-Sn			
Si	98.9	119	4.00
Ge	116.8	91	4.04
Sn	167.1	59	5.08
hcp			
Si	92.4	102	3.72

proximate zero-point-energy correction. Because of the increasing mass, the zero-point energy becomes less important in going from Si to Ge to Sn.

III. STRUCTURES AND PHONON MODES

The β-Sn structure (Fig. 2) is made up of two interpenetrating body-centered-tetragonal (bct) sublattices displaced from each other by the vector $[0, a/2, c/4]$. The relaxed values of c/a are fairly independent of volume, and are found to be about 0.545, 0.560, and 0.555 for Si, Ge, and Sn, respectively, in good agreement with experiments and previous calculations. The calculated phonon frequencies, however, are not very sensitive to c/a. Each atom in the β-Sn structure has four nearest neighbors by symmetry, but because of the value of c/a, the two second-nearest neighbors at $\pm[0, 0, c]$ are only slightly farther away. Thus, the atoms are effectively sixfold coordinated with a nearest-neighbor distance slightly larger than $a/2$. This represents an increase in coordination number from the fourfold coordination of the diamond structure. Increasing coordination number with pressure is a common feature of structural phase transitions and is attributed to the importance of the ion-ion Coulomb interaction at high pressure (small unit cell volume).

Both the LO and the doubly degenerate TO phonon modes at the center of the β-Sn Brillouin zone are Raman active. The TO mode corresponds to an opposing motion of the two interpenetrating bct sublattices in any direction perpendicular to the c axis. The LO mode corresponds to an opposing motion of the sublattices parallel to the c axis.

For Si in the hcp structure, the relaxed c/a ratio is found to be about 1.68, essentially independent of volume. This value is slightly higher than the ideal hcp c/a ratio (1.633) but is in very good agreement with experiments[2,5,7,9] and previous calculations.[12,15] The doubly degenerate TO phonon mode at the center of the hcp Brillouin zone is Raman active. This mode corresponds to an opposing motion of adjacent hexagonal planes in a direction perpendicular to the c axis.

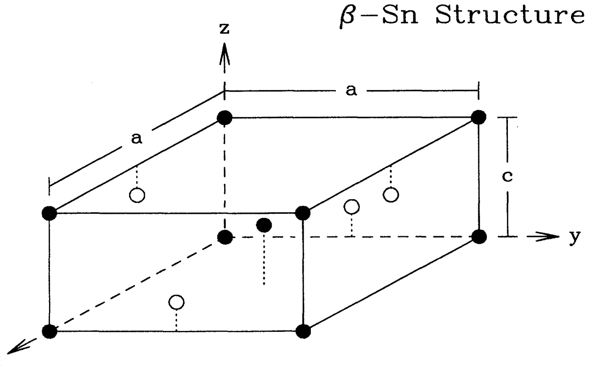

FIG. 2. A ball-and-stick model of the β-Sn conventional cell. Open circles correspond to one of the bct sublattices, and filled circles correspond to the other. The two sublattices are separated by the vector $[0, a/2, c/4]$. Dotted lines serve only to show atomic positions. The c/a ratio is roughly 0.55 for Si, Ge, and Sn in this structure.

Two of the Raman modes under consideration are associated with structural phase transitions. The β-Sn LO mode is related to the β-Sn → sh phase transition in that an LO-type displacement of the β-Sn lattice of amplitude $c/8$, accompanied by slight modifications of axial ratios, yields the sh lattice. The c-axis for the sh structure is parallel to the a-axis for the β-Sn structure. Similarly, the hcp TO mode is related to the sh → hcp transition. A distortion with amplitude $a/\sqrt{6}$ will bring the hexagonal layers into registry, and then a slight expansion of c/a brings about the stable sh structure.

IV. RESULTS

Figure 3 shows calculated phonon frequencies vs pressure for the LO and TO modes of Si, Ge, and Sn in the β-Sn structure and for the TO mode of Si in hcp. These theoretical results are compared to the experimental results of Ref. 10, and are shown to be in very good agreement. In particular, the observed change in the pressure-dependence of the β-Sn LO mode in going from Si to Ge to Sn is also exhibited by the calculations. Moreover, the speculation in Ref. 10 that the Ge LO mode will start to decrease with pressure beyond 50 GPa is not born out by the calculations, which show that this mode merely plateaus up to 80 GPa.

It is known that a displacive first-order structural phase transition is often accompanied by a softening of an associated phonon mode,[37] although the frequency of this mode need not vanish.[38] The β-Sn → sh and sh → hcp transitions are both displacive transitions of this kind, and they are associated with the β-Sn LO mode and the hcp TO mode, respectively, as mentioned in Sec. III. For Si, these modes both soften approaching their respective transition to the sh structure, as expected. However, for Ge, which also undergoes a β-Sn → sh transformation, the β-Sn LO mode does not soften near the transition pressure. In fact, the frequency increases initially with pressure and only levels off near the transition. This discrepancy is discussed in the next section.

The phonon frequency for a given mode is found to be highest in Si, next highest in Ge, and lowest in Sn (see Fig. 3). This ordering is anticipated, since in the harmonic approximation, phonon frequencies scale inversely as the square root of the mass. Furthermore, for the β-Sn structure TO mode the frequencies at a given pressure obey this scaling law almost exactly. This behavior is only approximated for the LO mode, since the pressure-dependence of this mode is different for the three elements.

In the β-Sn structure, the TO modes lie at higher frequencies than the LO modes because of the geometry of the structure. The bonds between the two bct sublattices are nearly perpendicular (angle $\sim 75°$) to the c axis. Therefore, for a given amplitude, the TO mode distorts the bonds more than the LO mode, resulting in a stiffer bond for the TO mode.

Figure 4 exhibits the calculated charge density contours in the (100) plane for Ge in the β-Sn structure at 13 GPa [Fig. 4(a)] and 60 GPa [Fig. 4(b)]. The region of the plane shown contains the two atoms of the basis plus two adjacent atoms along the c axis. The analogous contour plots for Si and Sn are qualitatively very similar to these, and thus have not been included. While the charge density is clearly highest between the two atoms of the basis, there is also a lot of charge between the two adjacent atoms along the c axis, indicating a secondary bond. This is not surprising considering that the interatomic distance along the c axis is only slightly larger than the nearest-neighbor distance.

The binding in the β-Sn phase is mainly metallic over the whole pressure range. This can be seen in the degree of uniformity of the charge density. Even at low pressure, the lowest value of the interstitial charge density in the (100) plane is about 5 electrons/cell, not much less than the average value of 8 electrons/cell. However, the peaking of the charge density in the bond region clearly indicates that there is still covalent character to the binding. Upon compression, the system becomes more metallic. This is seen in Fig. 4(b) by the transfer of charge from the bond regions to the interstitial region. The peak in the charge density decreases from 14.5 electrons/cell at 13 GPa to 14.0 electrons/cell at 60 GPa. Similarly, the charge density minimum in the interstitial region increases from 5.0 electrons/cell at 13 GPa to 5.6 electrons/cell at 60 GPa.

The decrease in bond charge with increasing pressure (decreasing volume) for Si, Ge, and Sn in the β-Sn structure is summarized in Fig. 5, which shows the calculated bond charge as a function of unit cell volume for the three elements. For the purpose of this study, the bond charge is defined as the amount of charge, in excess of a uniform background, contained in a symmetric ellipsoid whose major axis extends from one atom of the basis to the other, and whose minor axis is chosen to be half of the major axis. This definition is scale independent, and therefore, the choice of aspect ratio is somewhat arbi-

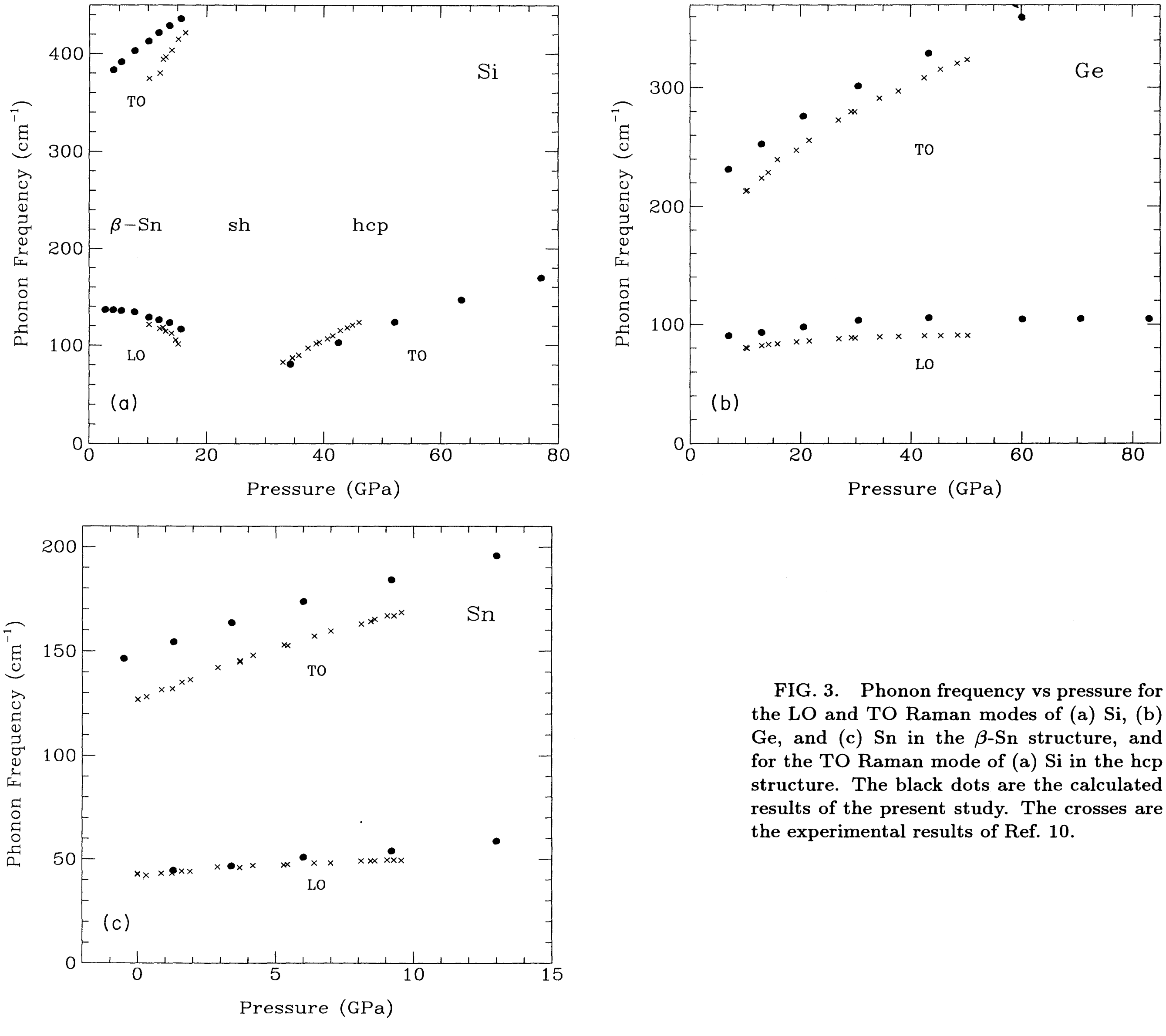

FIG. 3. Phonon frequency vs pressure for the LO and TO Raman modes of (a) Si, (b) Ge, and (c) Sn in the β-Sn structure, and for the TO Raman mode of (a) Si in the hcp structure. The black dots are the calculated results of the present study. The crosses are the experimental results of Ref. 10.

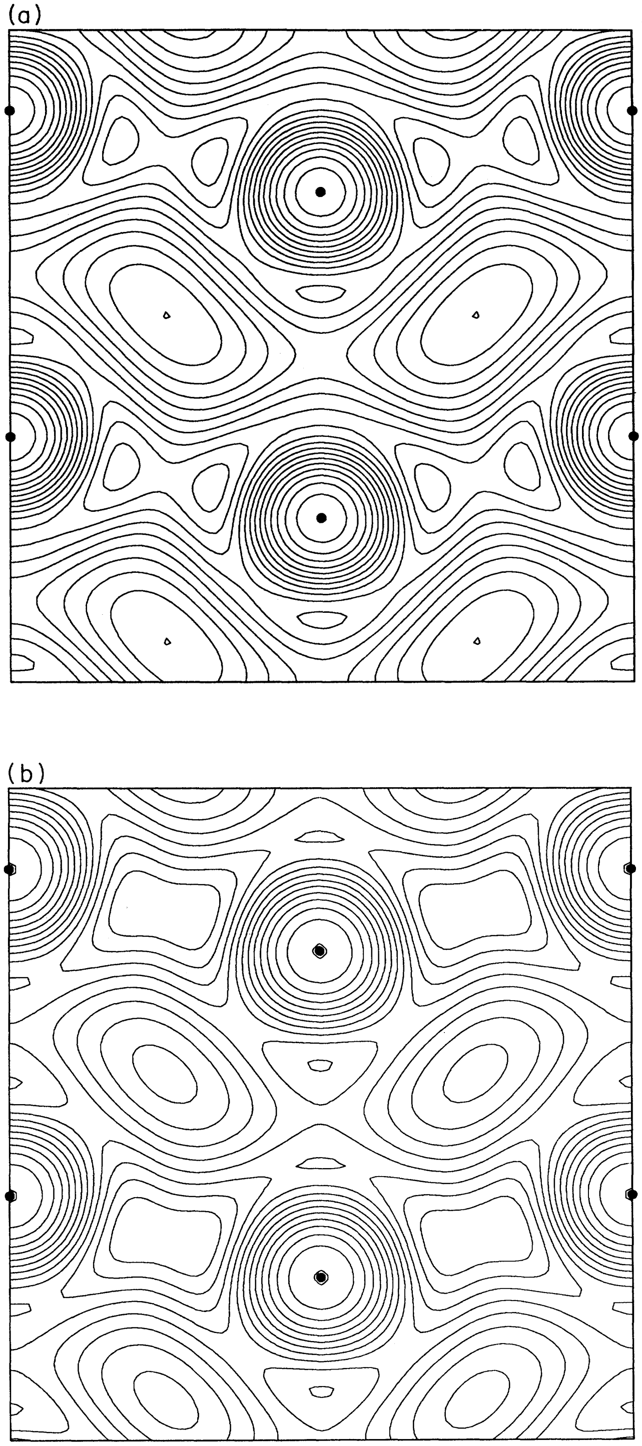

FIG. 4. Charge density contours in the (100) plane of the β-Sn structure for Ge at (a) 13 GPa and (b) 60 GPa. The maximum and minimum contours are (a) 14 and 2 electrons/cell, and (b) 13 and 1 electrons/cell, respectively, and the spacing between contours is 1 electron/cell. The black dots represent the locations of the atoms. The charge density peak goes from 14.5 electrons/cell in (a) to 14.0 electrons/cell in (b). The minimum in the interstitial region goes from 5.0 electrons/cell to 5.6 electrons/cell.

trary. The value used here was chosen to include in the ellipsoid all closed charge density level surfaces. For each element, the bond charge is found to vary linearly with volume. The curves for Si and Ge have approximately the same slope ($\sim$ 0.0084 electrons/a.u.), whereas the slope of the curve for Sn is about a third smaller. At a given cell volume, the bond charge is largest in Si and smallest in Sn, which is consistent with an increase in metallic character in going from Si to Ge to Sn. This trend is also seen for these elements in the diamond structure, and is attributed to the more effective screening of the nucleus by the core electrons with increasing atomic number.[39]

V. DISCUSSION

This section discusses the difference in the pressure-dependence of the LO mode for Si and Ge in the β-Sn structure, as described in Sec. IV. To understand this anomaly, it is useful to see how the different terms in the total energy contribute. The total energy can be written as[31]

$$E_{\text{tot}} = E_{\text{Ewald}} + E_{1-\text{el}} + E_{\text{Hartree}} + E_{\text{xc}} + E_{\alpha}, \qquad (2)$$

where E_{Ewald} is the ion-ion Coulomb energy, $E_{1-\text{el}}$ is the energy associated with single-electron effects such as kinetic energy and the electron-ion interaction, E_{Hartree} is the electron-electron Coulomb energy, E_{xc} is the sum of the exchange and correlation energies, and E_{α} is a term to account for the difference between the pseudopotential and a Coulomb potential. This last term depends only on volume and therefore does not contribute to the phonon frequency.

If each term in the total energy is fitted to a quadratic polynomial in the phonon amplitude u, then a component

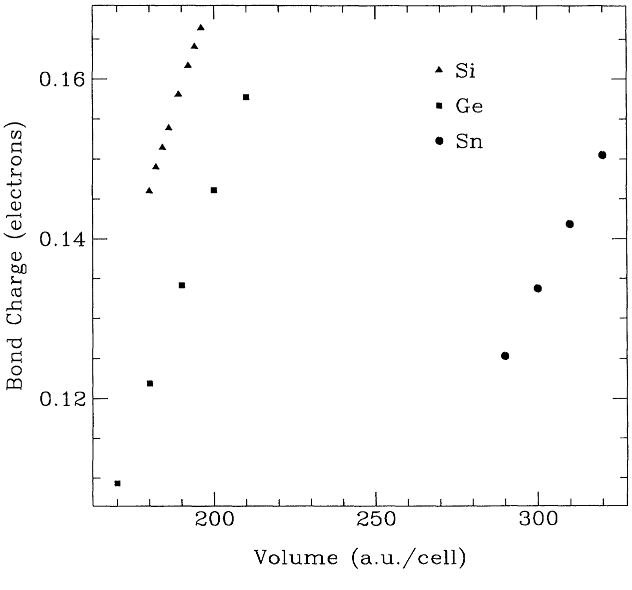

FIG. 5. Bond charge vs unit-cell volume for Si, Ge, and Sn in the β-Sn structure. The bond charge is defined as the amount of charge in excess of a uniform background contained in an ellipsoid. See text for details.

phonon frequency ω_i can be defined as follows:

$$E_i = A_i u^2 + B_i = \tfrac{1}{2} M \omega_i^2 u^2 + E_{0i}, \tag{3}$$

where A_i, B_i, and E_{0i} are constants, and M is the atomic mass. The term linear in phonon amplitude vanishes rigorously for each component of the total energy because the crystal is symmetric about $u = 0$ for this phonon mode. The total phonon frequency ω can be decomposed into the component phonon frequencies in the following way:

$$\omega^2 = \sum_i \omega_i^2. \tag{4}$$

In Fig. 6 we present the decomposition of ω^2 as a function of pressure for the LO mode of Si and Ge in the β-Sn structure. For both Si and Ge, the pressure-dependence of the phonon frequency comes mainly from the one-electron term, since the other terms are fairly independent of pressure. Thus, the discrepancy between Si and Ge should arise from single-particle effects. The primary difference between Si and Ge is that Ge has *d* electrons in its ion core. Therefore, the *d* component of the Ge pseudopotential is more repulsive than the Si *d* potential. This difference has been used effectively to explain why Ge is stable in the β-Sn structure over a much larger pressure range than Si.[20]

In Ref. 20 the *d* component of the valence electronic wave function is found to increase in going from the β-Sn structure to the sh structure. Furthermore, this component is found to increase with pressure for both phases. Since the sh structure is essentially the β-Sn structure with a large amplitude LO phonon distortion, the *d* component of the wave function for a smaller amplitude distortion should have a value somewhere between these two extremes. Thus, it is expected that an LO phonon distortion of the β-Sn structure produces an increase in the *d* character of the wave function.

This same conclusion is reached by examining the effect on the charge density produced by a small LO distortion. Figure 7 shows contours in the (100) plane of the *difference* in charge density between the distorted and undistorted crystal. Solid (dashed) lines represent positive (negative) contours and correspond to an increase (decrease) in charge density upon distortion. Heavy solid lines represent zero change in the charge density, and black dots denote atomic positions for the undistorted system. Contours shown range from −0.50 to 0.35 electrons/cell. The two lobes (one positive, one negative) surrounding each atom are primarily caused by a rigid shift of the charge density with the distortion and are not particularly relevant. The most physically relevant feature of Fig. 7 is the shift of charge density from the bond region (negative contours) to the interstitial region (positive contours). This is analogous to the effect of increasing pressure (see Fig. 4), and, since the *d* component increases with pressure,[20] it is consistent with the notion that the *d* character of the wave function increases with an LO distortion.

This behavior can be used to explain the initial increase with pressure (decreasing volume) of the β-Sn-structure LO mode of Ge. At smaller volumes the ion cores make up a larger fraction of the unit-cell volume. Since Ge has core *d* electrons, its pseudopotential is relatively repulsive to *d* symmetry valence electrons, which are, therefore, effectively blocked from the core region. Thus, as pressure increases, the valence *d* electrons in Ge are confined to a decreasing fraction of the volume, and are thus increasingly energetic. Since an LO phonon distortion of the β-Sn structure produces an increase in the *d* component of the wave function, the energy of the distorted system for Ge should increase with pressure

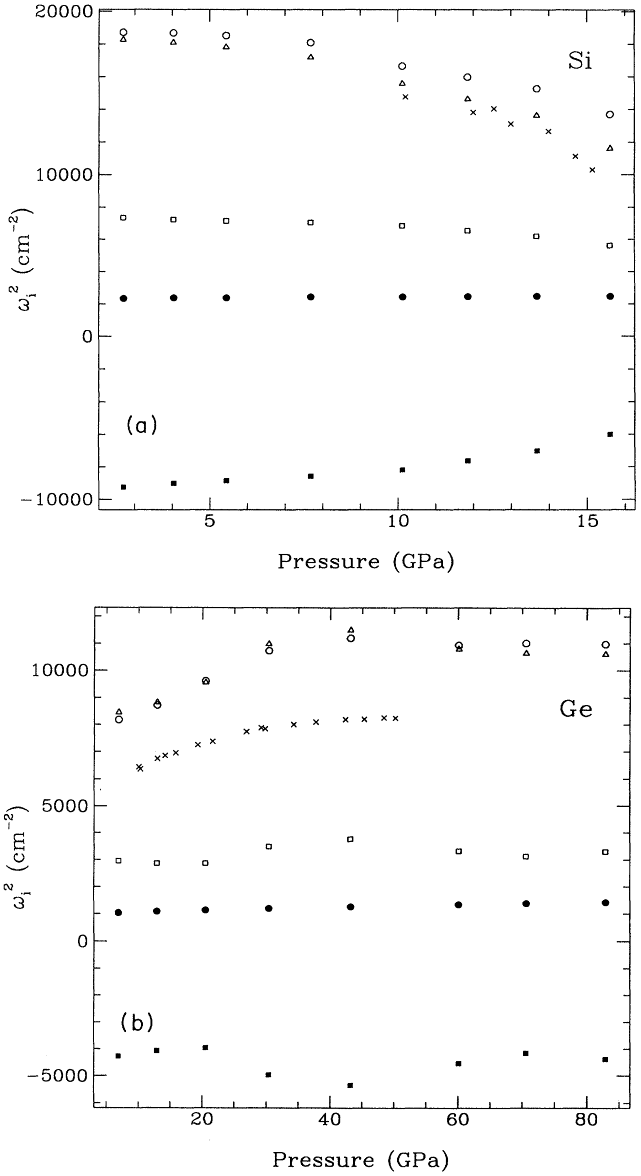

FIG. 6. Components of ω^2 vs pressure for the LO mode of (a) Si and (b) Ge in the β-Sn structure. The total ω^2 is given by an open circle, the one-electron component is given by an open triangle, the Hartree component is given by a filled square, the exchange and correlation component is given by an open square, the Ewald component is given by a filled circle, and the experimental results of Ref. 10 are given by crosses.

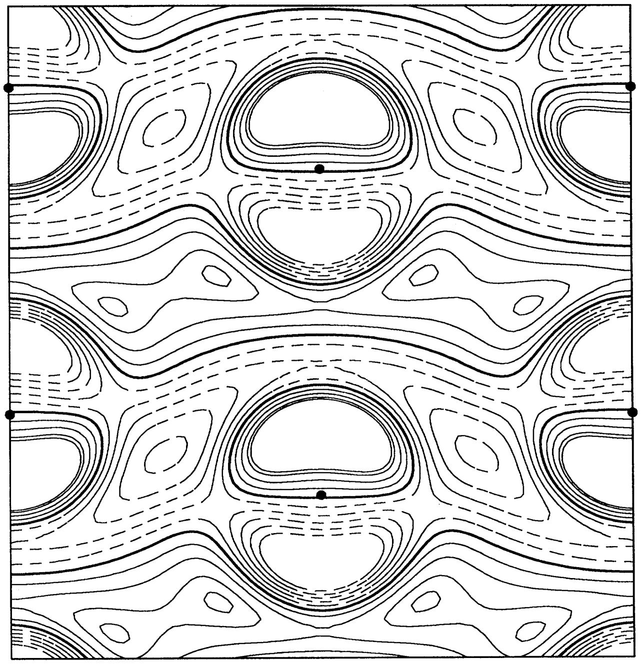

FIG. 7. The difference in charge density [in the (100) plane] between β-Sn–Ge at 60 GPa with and without a static LO distortion of amplitude 0.08 a.u. Solid (dashed) lines denote positive (negative) contours; heavy solid lines denote zero change in charge density. The maximum (minimum) contour shown is 0.35 (-0.50) electrons/cell. Black dots correspond to atomic positions of the undistorted system.

more rapidly than that of the undistorted system. Therefore, the curvature of the energy of Ge with respect to LO phonon amplitude increases as a function of pressure due to this "decreasing-volume-fraction" effect. In other words, the LO phonon frequency for Ge in the β-Sn structure should increase with pressure. Since Si has no *d* electrons in its core, this effect is less pronounced in Si.

It is also found in Ref. 20 that the increase in the *d* component of the wave function with pressure is slightly more rapid for the sh phase than for the β-Sn phase. Therefore, by similar reasoning as above, it is expected that, for an LO distortion of the β-Sn structure, the accompanying increase in the *d*-character of the wave function will increase slightly with pressure. Further evidence of this is obtained by examining contour plots like Fig. 7 for several different pressures. The shift in charge from the bond region to the interstitial region upon distortion, which was shown to signal an increase in *d* character, is found to be somewhat more pronounced at higher pressures. This is consistent with the above assertion that the distortion-induced increase in the *d* component of the wave function increases with pressure. Such behavior serves to enhance the "decreasing-volume-fraction" effect described in the preceding paragraph, and, therefore, also has a positive effect on increasing the phonon frequency with pressure.

The plateauing of the Ge LO mode near the transition pressure is caused by the competing effect of phonon mode softening due to the onset of a displacive structural transition.

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