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Rhombohedral phase stability of the group-VA elements

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The structural stability of the rhombohedral and simple-cubic phases is studied for the group-VA elements. Using an *ab initio* pseudopotential total-energy method, the calculated phonon frequencies for the longitudinal acoustic mode at the corner of the simple-cubic Brillouin zone are found to soften. This suggests that all group-V elements are likely to form in the rhombohedral structure with respect to the simple cubic phase. At high pressures, the rhombohedral stability is diminished, causing a transition to the simple-cubic structure.

In analogy to the group–IV-VI compounds, the rhombohedral $A7$ phase (equivalent to the rhombohedral NaCl structure with one type of atom) is stable for the group-VA elements with respect to the simple-cubic (sc) structure (equivalent to the NaCl structure with one type of atom). At normal pressures, As, Sb, and Bi crystallize in the form of the $A7$ structure, while for black phosphorous (P) this phase is only stable at high pressures.[1] For nitrogen (N), although a theoretical calculation[2] predicted that either the $A7$ or the sc structure could be stable at high pressures, both structures have not been observed up to 1.3 Mbar.[3] The instability of the sc structure of the group-V elements is induced by small structural changes: a rhombohedral shear distortion along the body-diagonal axis and an internal displacement of one of two interpenetrating cubic lattices. With increasing pressure, the structural difference between the $A7$ and sc phases is reduced because of the delocalization of the covalent bonds. In fact, the $A7$-sc phase transition was found for P (Ref. 1) and Sb (Ref. 4) at 110 and 70 kbar, respectively.

Some earlier work[5] suggested qualitative explanations based on band theory for the stability of the rhombohedral structure for systems with five valence electrons. A Jahn-Teller type of symmetry breaking induces a transformation from semimetallic to insulating, or from metallic to semimetallic, by reducing the electron states at the Fermi level. Such a change of the electronic structure lowers the band-structure energy and thus stabilizes the distortion.

Here we report calculational results for the phonon frequencies at the point $R=\pi(1,1,1)/a$ of the sc Brillouin zone for the group-V elements N, P, As, and Sb. We concentrate on the longitudinal acoustic (LA) phonon mode at R because corresponding atomic displacements bring the sc structure into the internally displaced $A7$ structure. With these atomic motions, a rhombohedral shear along the [111] axis is a displacive transformation into the distorted $A7$ structure. The phonon frequencies are calculated as a function of pressure and used to investigate the structural stability of the $A7$ and sc phases. Furthermore, based on the structural properties, we discuss the superconducting behavior of the $A7$ phase at high pressures.[6] We also present results of calculations of the electron-phonon interactions for P and give some discussion of its abnormal superconducting behavior.[7]

The *ab initio* pseudopotential total-energy method[8] is used and the exchange-correlation potential is approximated by using the Wigner interpolation formula.[9] A plane-wave basis set with a kinetic energy cutoff of 55 and 11.5 Ry for N and the other elements, respectively, is used to expand the wave function. For the summation over the Brillouin zone, a uniform grid of 110 **k** points is chosen in the irreducible $A7$ Brillouin zone. A test of the Gaussian broadening scheme[10] for the electron states is found not to change the total-energy differences significantly in the calculations of the phonon frequencies. The phonon frequencies are calculated within the frozen phonon approximation.[8] Relativistic effects and spin-orbit couplings are not included.

A simple-cubic structure can be viewed[11] as a structure consisting of two interpenetrating face-centered-cubic lattices separated by $\frac{1}{2}\mathbf{d}$, where $\mathbf{d}$ is the body-diagonal vector of one of the fcc lattices. A rhombohedral structure is described by an internal displacive parameter u (≤ 0.25) and a rhombohedral shear angle $\alpha(\leq 60°)$, where the lattice separation is given by $2\tau=2u\mathbf{d}$ and α is the angle between the primitive translation vectors of the $A7$ structure. In the case of $u=0.25$ and $\alpha=60°$, the structure becomes the simple-cubic phase. At the Brillouin-zone point R, the longitudinal-acoustic-phonon mode is commensurate with a lattice having a periodicity of $\mathbf{d}$ along the body diagonal. For this phonon mode, every other atomic layer moves in an opposite direction with respect to its adjacent layers. This displacement resembles a one-dimensional Peierls-type distortion along the [111] axis, and the structure gradually changes into the $A7$ phase with $\alpha=60°$.

In Fig. 1, the changes of the total energies for simple-cubic P and Sb are plotted for different volumes as a function of the phonon displacement $\delta\mathbf{d}$, where $u=0.25-|\delta|$. For volumes of $0.72V_0$ (120 kbar) for P and V_0 (0 kbar) for Sb, where V_0 is the volume at normal pressures, the energy curves for the cubic structure have minima at $u=0.236$ and 0.237, respectively. When α is less than 60°, the u's for rhombohedral phase are found to be 0.233 and 0.235 for P($\alpha=57.21°$) and Sb($\alpha=57.35°$), respectively. These values for u and α are in good agreement with the measured values.[1,4,12] We note that a rhombohedral shear distortion does not affect significantly the shape of the energy curves, and the internal displacements' u's are similar for different values of α. Thus, in stabilizing the $A7$ structure, lattice displacements dominate compared to rhombohedral shears. This result agrees with a recent calculation for As (Ref. 13) and is also consistent with previous band-structure calculations.[5] The energies of the sc phase around $\delta=0$ increase

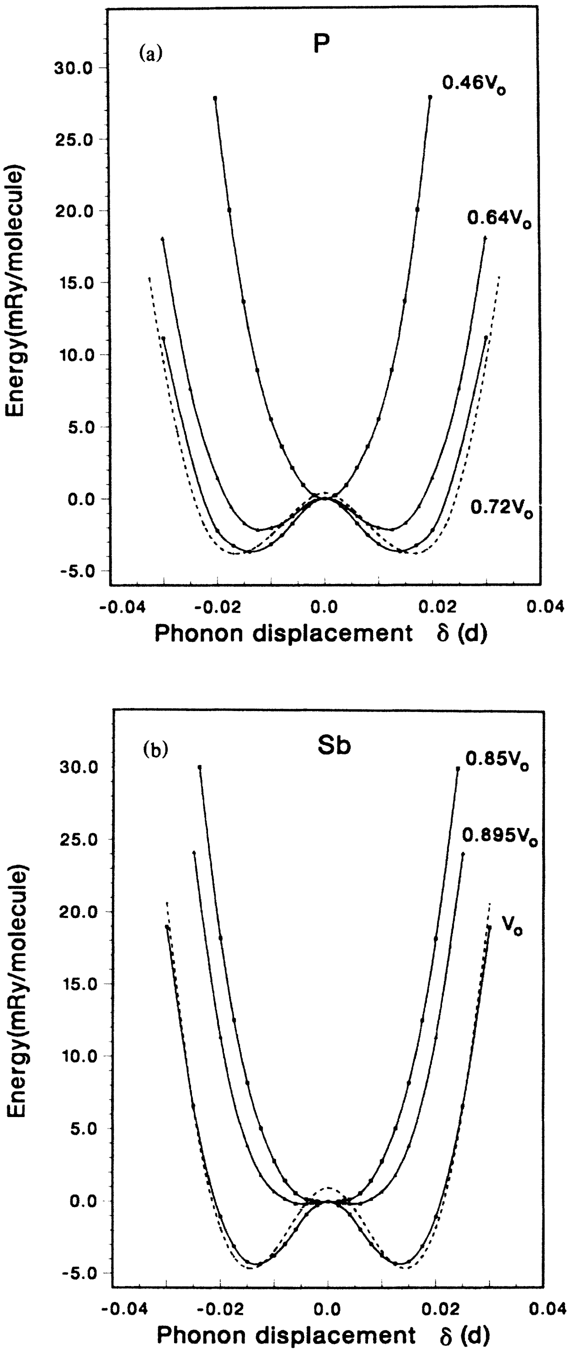

FIG. 1. Energies vs phonon displacements for (a) P and (b) Sb. Energies are calculated with respect to those of the sc structure. Dashed lines denote the energies for $A7$ P ($\alpha = 57.21°$ and $V = 0.72 V_0$) and Sb ($\alpha = 57.35°$ and $V = V_0$).

with shear while they decrease slightly for $\delta > \delta_0$, where δ_0 is a minimum position in Fig. 1.

Because of inversion symmetry, the energy curves are symmetric about $\delta = 0$. Hence, an expansion of the energy around $\delta = 0$ requires even powers of δ,

$$\Delta E_T = \kappa(\delta d)^2 + \eta(\delta d)^4 \ , \tag{1}$$

and the shape of the energy curves resembles the Landau expansion[14] of the free energy in powers of the order parameter for a second-order phase transition. Since the free energy is the sum of the total energy and the mechanical work (pressure × volume) at zero temperature, the energy curves in Fig. 1 do not represent the complete free energies. Experimentally, the $A7$-sc transitions for P and Sb were found to be of first order. However, because of the similarity between the $A7$ and sc structures and the small energy difference, the volume changes at the $A7$-sc transition are extremely small: 3.7 and 0.5% for P (Ref. 1) and Sb (Ref. 4), respectively. Therefore, the energy curves for various volumes give reasonable estimates of the $A7$-sc transition volumes.

With increasing pressure, the minimum positions of the energy curves move to $u = 0.25$, corresponding to the simple-cubic structure. This increase of u is caused mainly by a suppression of the covalent bonds under pressure; there is a tendency for both u and α to increase in going to heavier elements. Figure 2 shows the variations of the square of the frequencies given by

$$\omega^2 = \kappa/m \tag{2}$$

for several normalized volumes V/V_0, where m is an ionic mass. For N, the frequencies are found to be higher by an order of magnitude than those of the other three elements. Although the slope in Fig. 2 becomes larger in going from Sb to N, the Gruneisen parameter defined by $-d\ln|\omega|/d\ln V$ for imaginary frequencies, is highest for Sb, and the transition volume decreases in going to lighter elements. We find the LA phonon frequencies to be zero for volumes of 0.51, 0.72, and 0.86V_0 for P, As, and Sb, respectively. For further volume compressions, the energy increases with displacement and the sc structure becomes stable with

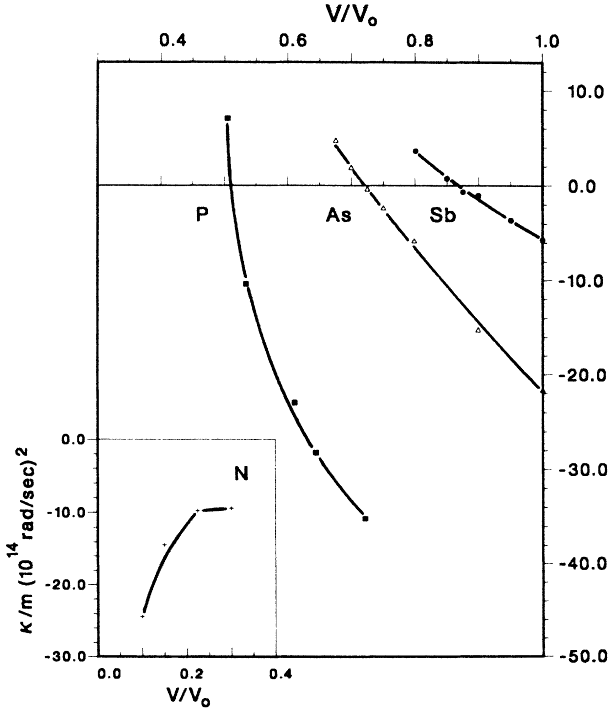

FIG. 2. Squares of the LA-phonon frequencies vs volumes normalized by the volumes at normal pressures. For N, a value for V_0 of 80 (bohr/atom)^3 is used (see Ref. 2). Lines are used as a guide.

respect to the $A7$ structure. Compared to the measured values of $(0.72\text{–}0.75)\,V_0$ for phosphorus[1] and $0.85\,V_0$ for antimony,[4] our calculated transition volume for Sb is in good agreement with experiment, while it is too small for P.

In a previous calculation[15] of the structural properties for P, it was found that the total energy of the $A7$ phase is underestimated compared to experimental data at room temperature. This calculation showed that a finite energy shift in the $A7$ structure could produce the measured transition volume. Since the phonon frequencies for the $A7$ structure of P are relatively higher compared to those for As and Sb,[16] the zero-point vibration energy for this phase is expected to be larger. In contrast, phonon frequencies for the sc structure of P are unstable near the point R, and they are lower than those of the $A7$ phase (see Table I). Hence, the Debye temperature is expected to be smaller for the sc phase. However, for heavier elements the zero-point energy correction is not too big because of the lower-phonon frequencies.

TABLE I. Calculated densities of states $[N(E_F)]$ at the Fermi level E_F, phonon frequencies $(\omega_{\mathbf{q}\nu})$, and electron-phonon couplings $(\lambda_{\mathbf{q}\nu})$ at the wave vector $\mathbf{q}$ and the phonon mode ν for sc P. Units of $\omega_{\mathbf{q}\nu}$ and $N(E_F)$ are 10^{13} rad/sec and electrons per rydberg per atom per spin, respectively. Details of calculations are in M. M. Dacorogna, M. L. Cohen, and P. K. Lam, Phys. Rev. Lett. 55, 837 (1985).

P (kbar)	$N(E_F)$	$\mathbf{q}$	Longitudinal $\omega_{\mathbf{q}\nu}$	Longitudinal $\lambda_{\mathbf{q}\nu}$	Transverse $\omega_{\mathbf{q}\nu}$	Transverse $\lambda_{\mathbf{q}\nu}$
120	2.09	$\pi(1,0,0)/a$	4.19	0.64	3.75	0.12
		$\pi(1,1,0)/a$	4.31	0.55	4.84	0.03
300	1.93	$\pi(1,0,0)/a$	5.16	0.46	3.89	0.12
		$\pi(1,1,0)/a$	5.35	0.39	5.28	0.02

For As, high-pressure modifications have been less clearly determined. Early, a superconducting tetragonal phase was found at 120–150 kbar.[17] A recent measurement of the superconducting transition temperature T_c suggested that a phase transition might occur at about 200 kbar.[6] In the present work, we find that the sc phase for As is unstable up to about 350 kbar (up to $0.72V_0$). Considering the existence of the tetragonal phase, the $A7$-sc phase transition will not be observed, and this agrees well with recent theoretical calculations.[13] For N, molecular phases were found to be more stable than both the $A7$ and sc phases up to 1.3 Mbar.[3] The present calculations indicate that the $A7$ phase is lower in energy than the sc phase for all pressures (up to $0.1V_0$). In this element, the $A7$ stability is more significant because of the strongly covalent bonds.

It is interesting to investigate the Hellmann-Feynman forces on the ions arising from ionic displacements. Because of a negative harmonic term in Eq. (1), the phonon frequency is imaginary. This instability of the LA phonon at R is similar to the soft optic mode at Γ in IV-VI compounds, i.e., GeTe and SnTe, because the point R is folded back into Γ in the fcc Brillouin zone. For small δ, the electronic contribution to the forces is larger than the ionic part. Since the internal displacement breaks the symmetry, the resulting decrease of the electron states at the Fermi level is larger for the group-V elements. This effect reduces the electron band energy and produces positive electronic forces on the displaced ions. In contrast, the symmetry breaking increases the Ewald energy and gives negative ionic forces. For the elements predominated by three p bonds, the electronic force dominates the ionic one. Then the force points in the direction of the displacements for $\delta < \delta_0$. If $\delta > \delta_0$, the change of the Ewald energy becomes greater than that of the band structure and hence the total energy increases. We find that for Si having sp^3 orbitals, the displacements increase the energy because of the larger ionic effect than the electronic contribution. Hence, the instability of the sc structure is closely related to the covalency of the bonds.

Except for nitrogen, all the group-V elements are found to be superconducting at high pressures.[6,7] For the $A7$ structure, superconducting transition temperatures were found to increase with increasing pressure P up to 7 K at 120 kbar, 2 K at 200 kbar, and 0.7 K at 85 kbar for $A7$ P, As, and Sb, respectively. A trend of decreasing T_c in going to heavier elements was also found in the β-Sn phase of the group-IV Si, Ge, and Sn.[18] In a series with the same structure in the periodic table, it was suggested[19] that the Debye temperature dominates in determining T_c. The optic-phonon frequency of the $A7$ phase at Γ increases in going from Sb to P: 4.64 (Sb), 7.62 (As), and 13.98 (P) THz.[16] Therefore, the T_c for $A7$ nitrogen is expected to be high.

A positive coefficient of dT_c/dP in the $A7$ structure is a common character in P, As, and Sb. From the present results of the structural properties, we expect that a pressure increase of T_c results from two major contributions. First, since the pressure decreases the covalency in the semimetallic phase, the $A7$ distortion associated with u and α is reduced and thus the electron density of states at the Fermi level increases because of the semimetallic-metallic transition. Another important effect is a rapid change of the $A7$ phonon spectrum. As indicated by the curvatures around the minima in Fig. 1, the optic-phonon frequency at Γ becomes softer with pressure because of the displacive $A7$-sc transition. Thus, soft modes enhance the electron-phonon couplings.

For sc P, recent experiments[7,20] showed abnormal superconducting behavior. In this phase, the present calculations indicate strong electron-phonon interactions because of a large electronic contribution to the forces and soft phonon modes around R. We find that the electron-phonon matrix element for this soft mode is high. Because the calculated phonon frequency at R is unstable, we cannot estimate an exact electron-phonon coupling. For other phonons at different points in the Brillouin zone, the electron-phonon interactions are also found to be strong, as shown in Table I. Furthermore, these electron-phonon couplings decrease with increasing pressure. This is consistent with the decreasing behavior of T_c at pressures from 120 to 170 kbar.[7] However, to determine whether the abnormal peak in T_c (10 K) observed at 230 kbar[7] is related to a phase transition into other structures, further theoretical work is necessary.

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