

Total-energy calculations of the structural properties of the group-V element arsenic

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We report self-consistent density-functional calculations of the total energy of arsenic as a function of volume in the simple-cubic and the distorted α -arsenic ($A7$) structures. We find the stable structure to be the $A7$, with parameters which are close to experiment at zero pressure. The simple-cubic structure is found not to be a minimum in the total energy at any pressure because of an instability to $A7$ -symmetry phonon displacements of the atoms. For the stable structure the calculated electronic band structure is reported and shown to have the semimetallic character known for As.

INTRODUCTION

The typical structure of group-V elements in the α -arsenic or $A7$ structure. It is the common crystal phase of As, Sb, and Bi, and can be obtained in P under pressure.¹ The $A7$ structure may be derived from simple cubic (sc) by the application of two separate distortions, a rhombohedral shear and a relative displacement along the $[111]$ direction of the two fcc lattices into which a sc lattice can be resolved.^{1,2} The resulting lattice, which has trigonal symmetry and two atoms in the unit cell, is illustrated in Fig. 1 and described in the Appendix. Under these distortions the six nearest neighbors of each atom of the sc structure distort to become three nearest and three next-nearest neighbors. This can be understood in terms of chemical bonds, since the group-V elements preferentially form three bonds.^{1,2} Furthermore, the fact that the bond angles are close to 90° suggests that they are predominantly p -bonding orbitals.

In view of the relationship between the $A7$ and sc structures and the general tendency of solids at compressed volumes to form more symmetric structures with higher coordination, we might expect that with the application of pressure the distortion would decrease. This is indeed the case. Not only do the structural parameters of the $A7$ structures go towards their sc values under pressure,^{3,4} but in P (Refs. 5 and 6) and Sb (Ref. 7) a sc phase itself has been observed. To our knowledge there has been no observation of a sc phase in As.

There is a parallel between the structures of the group-V elements and the IV-VI compounds such as PbTe and SnTe.^{2,8} This family of materials can exist in the cubic NaCl structure, with a tendency for the two types of atoms in the unit cell can be displaced relative to each other, forming a trigonal structure which is ferroelectric. The $A7$ structures of the group-V elements may then be

generated exactly by making the two atoms in the unit cell identical. The group-V elements are simpler in that they have a center of inversion in both structures, but more complex in that they are semimetallic. We will consider only the group-V elements here and we point out that an *ab initio* investigation of the IV-VI compounds has recently been reported by Rabe and Joannopoulos.⁹

There have been several previous theoretical studies of

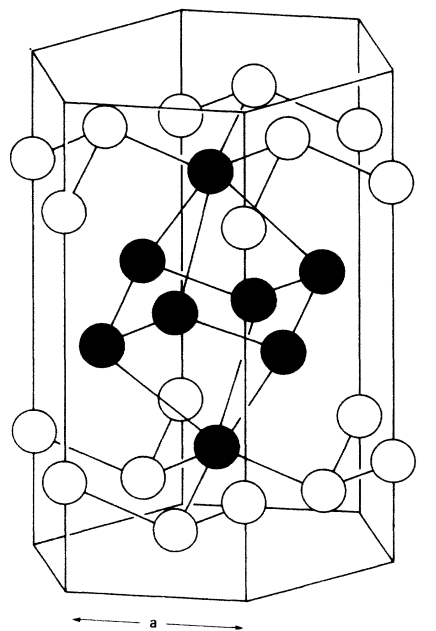


FIG. 1. $A7$ structure. The eight solid circles from a distorted primitive cube. The structure consists of pairs of planes stacked in the c direction.

the group-V elements.^{10–12} In particular, Weaire and Williams¹⁰ carried out an investigation of the structural energies using a second-order perturbation expansion for the total energy and the Lin-Falicov¹³ pseudopotential. They found an energy minimum at an *A7* structure close to the experimental one but also a slightly lower minimum at a simple rhombohedral structure. They concluded that the second-order “metallic” part of the bonding was important in stabilizing the *A7* structure, but that there are also important “covalent” contributions which are beyond second order in a perturbation expansion. Later work of Abe *et al.*¹¹ extended the calculations of Weaire and Williams to third order, which destroyed the good agreement with experiment obtained in the second-order calculation. Abe *et al.* considered that this situation was due to the use of the Lin-Falicov pseudopotential, which is truncated at large wave vectors, and in a later paper¹² they repeated the calculations employing a Topp-Hopfield pseudopotential¹⁴ which was not truncated. In these calculations a stable *A7* phase was not found in second-order calculations, but the inclusion of third-order corrections resulted in a stable *A7* phase in agreement with experiment. They concluded that the inclusion of covalent effects was vital in the stabilization of the *A7* structures of group-V elements.

In this paper we present an *ab initio* investigation of the stability and properties of the *A7* structure and the nature of the instabilities of sc for As. We utilize the methods which have recently been successful in calculating the structures and phase transitions of many group-IV elements and III-V and II-VI compounds, including their high-pressure metallic phases.¹⁵ The calculations are done using the same methods as in Refs. 16–18 to solve the self-consistent local-density equations for the electronic states. Of course, in this work the structural energies are calculated to all orders in the potentials, i.e., there is no perturbation expansion. We have chosen to carry out calculations for the element As, for which the experimentally established properties provide exacting tests of our results. The related group-V elements are not considered in detail here because less is known about P in the *A7* structure and the heavier elements Sb and Bi present the added complexity of the increasing importance of spin orbit and other relativistic effects. In future work we will report calculations for phosphorus as well as for nitrogen at extremely high pressure.¹⁹

LOCAL-DENSITY-FUNCTIONAL PSEUDOPOTENTIAL CALCULATIONS

We have performed self-consistent local-density-functional calculations on sc and *A7* arsenic, using the norm-conserving pseudopotential of Ref. 20, but without spin-orbit interactions. For the local-density approximation to the exchange and correlation (xc) energy of the homogeneous electron gas, we used the Ceperley-Alder form as parametrized by Perdew and Zunger.²¹ Within the local-density approximation to the exchange and correlation energy, the total energy E of a crystal is given by^{16,22}

$$E = \sum_{n,\mathbf{k}} \omega_{n,\mathbf{k}} \epsilon_{n,\mathbf{k}} - 4\pi\Omega \sum_{\mathbf{G} (\neq 0)} |\rho(\mathbf{G})|^2 / |\mathbf{G}|^2 - \Omega \sum_{\mathbf{G}} \rho^*(\mathbf{G}) [\mu_{xc}(\mathbf{G}) - \epsilon_{xc}(\mathbf{G})] + \gamma_{\text{Ewald}} + \alpha Z. \quad (1)$$

Here the eigenvalues of the local-density equations are denoted by $\epsilon_{n,\mathbf{k}}$, with weighting factors $\omega_{n,\mathbf{k}}$ described below, where n, \mathbf{k} are the band and wave-vector indices of the states, Ω is the cell volume, ρ is the electronic charge density, $\epsilon_{xc}(\mathbf{G})$ is the Fourier transform of the local-density functional $\epsilon_{xc}(\rho(r))$; $\mu_{xc}(\mathbf{G})$ is the Fourier transform of the xc contribution to the effective potential $\mu_{xc} = d(\rho\epsilon_{xc}(\rho))/d\rho$, γ_{Ewald} is the energy of the point ions in a uniform background, and the final term αZ is the non-Coulombic interaction of the ions with the average electronic charge density. The reciprocal-space form is appropriate for pseudopotentials sufficiently smooth that the wave functions and charge density can be expanded in plane waves. This is particularly advantageous for low-symmetry problems such as the *A7* structure because the basis functions are independent of the structure and the expressions for energy,^{16,22} as well as for forces^{16,22} and stresses,¹⁶ are given by simple universal forms.

The Schrödinger equation was solved at 17 points in the irreducible part of the *A7* Brillouin zone (BC) and the BZ integration was performed by the special-points method.²³ To deal with the Fermi surface we have used the Gaussian smearing technique of Fu and Ho.²⁴ In this scheme, states are smeared out into Gaussians and the Fermi level E_F is placed so that the correct amount of charge is present. The occupation $\omega_{n,\mathbf{k}}$ of a state is determined by the area of its Gaussian which is below E_F ,

$$\omega_{n,\mathbf{k}} = \frac{2}{\Delta\sqrt{\pi}} \int_{-\infty}^{E_F} dE \exp[-(E - \epsilon_{n,\mathbf{k}})^2/\Delta^2], \quad (2)$$

where Δ determines the width of the Gaussian. The total energy is insensitive to the value of Δ and a value of 0.25 eV was used. Our method differs slightly from the original version of Fu and Ho who calculated the charge density using the weighting factor of Eq. (2) but then calculated the total band energy E_{band} by integrating over a smeared density of states:

$$E_{\text{band}} = \sum_{n,\mathbf{k}} \frac{2}{\Delta\sqrt{\pi}} \int_{-\infty}^{E_F} dE E \exp[-(E - \epsilon_{n,\mathbf{k}})^2/\Delta^2]. \quad (3)$$

Taking the variation with respect to the wave functions of the total energy calculated using this form does not result in the Schrödinger equation that is actually solved. Furthermore, the forces and stress that we calculate are the derivatives of the total energy calculated using Eqs. (1) and (2) and not the band energy of Eq. (3).

We have calculated of total energy, the forces on the ions, and the stress for each crystal structure. The use of stress and force is extremely helpful in finding the minimum-energy structure of a complex crystal.^{17,18} Since the forces are the derivatives of the total energy with respect to the atomic positions in the unit cell and the stress is the derivative with respect to strains (i.e., the volume and shape of the unit cell), we calculate the total

energy and its first derivatives with respect to *all* the parameters that determine the crystal structure. The calculation of forces and stress greatly facilitates the determination of the equilibrium structure of crystals such as the *A7* (in which there are two free parameters at fixed volume). If we consider a crystal with N structural parameters and we assume that the energy as a function of the parameters is parabolic near the minimum, then we must calculate the total energy for $N^2/2 + 3N/2 + 1$ structures to determine the parameters at the minimum. On the other hand, if we calculate all derivatives of the energy with respect to these N parameters, we require only $(N + 3)/2$ calculations. Thus, at each volume of the *A7* crystal we perform three preliminary calculations on structures close to the minimum in energy in order to calculate the parameters of the minimum-energy structure. Furthermore, we find that the energy minimum may be located with greater accuracy using the analytic derivatives of the total energy.

In our calculations the wave functions and potential are described by a finite number of plane waves. The truncated basis set introduces errors into the calculation, which we wish to make as small as possible. If we include all waves up to some fixed-energy cutoff in the basis set for calculations at two different cell volumes, then approximately the same truncation of the pseudopotential and a similar resolution of wave functions occur at each volume so that much of the basis-set truncation error will cancel when we compare the two calculations. However, the size of the basis set changes when the volume is altered and we found that this caused unphysically large charge flow between states close to the Fermi level of sc As when the volume was altered. This problem was overcome by keeping the number of plane waves constant for different volume, consequently introducing a larger but smoothly varying volume-dependent error. We then adopted a correction procedure to reduce this error. Two calculations were performed on sc As at volumes of 18.5 and 21 Å³ per atom, sampling a large number (35) of k points in the irreducible part of the BZ and using a very large basis set including plane waves up to 24 Ry in energy. From these calculations we obtain corrections to the total energy and pressure to linear order in the volume which may be applied to calculations performed with smaller basis sets.

For the calculations on the sc structure we used a constant-size basis set fixed by a calculation at a volume of 20 Å³ per atom treating plane waves up to 8 Ry in energy exactly and further waves up to 14 Ry in second-order perturbation theory. For the three preliminary calculations at each volume on the *A7* structure used to determine the minimum-energy structure at that volume, we used a basis set of plane waves up to 8 Ry in energy which were treated exactly, and further waves up to 12 Ry in energy treated in second-order perturbation theory. The calculations on the predicted minimum energy *A7* structure were performed with the same basis-set energy cutoffs as the sc structure at that volume. The same volume-dependent corrections were then applied to both the sc and minimum-energy *A7* calculations. We feel that this procedure is justified, as the *A7* structures considered were reasonably small distortions of sc.

TOTAL ENERGY AND STABILITY OF THE *A7* AND sc STRUCTURES

The total energies of the sc and calculated minimum-energy *A7* structures are plotted in Fig. 2. We find that at zero pressure the *A7* phase is ~ 0.12 eV per atom lower than the simple cubic. Thus, the *A7* phase is the more stable at zero pressure. This is already a crucial result and shows the accuracy of the calculations, since the total energies involve cancellations between large numbers, which are sensitive to the detailed way the integrals are carried out for the occupied states below the Fermi energy. This is especially difficult for the comparison of the metallic sc and the semimetallic *A7* phases.

An important contribution to the total energy is the Coulomb energy of the ions and the surrounding electron gas. In order to understand this complex quantity we further divide it into a large term consisting of the electrostatic energy of point charges of $+5e$ in a uniform background of negative charge preserving charge neutrality and a smaller term due to the inhomogeneity of the electron gas. The former term, known as the Ewald energy, is "universal," whereas the latter term must come from full calculations of the electronic structure of the crystal such as those described in this paper. The Ewald energy of the experimental *A7* As structure is 2.3 eV per atom higher than a sc structure of the same volume. The occurrence of the *A7* phase can be understood in terms of a Peierl's instability associated with the displacement of the atoms of the sc lattice together in pairs along the [111] direction which opens up a gap at the Fermi level and lowers the band contribution to the total energy. In fact, the transition is from metallic to semimetallic as the *A7* phases of As, Sb, and Bi all have small valence-conduction-band overlaps.

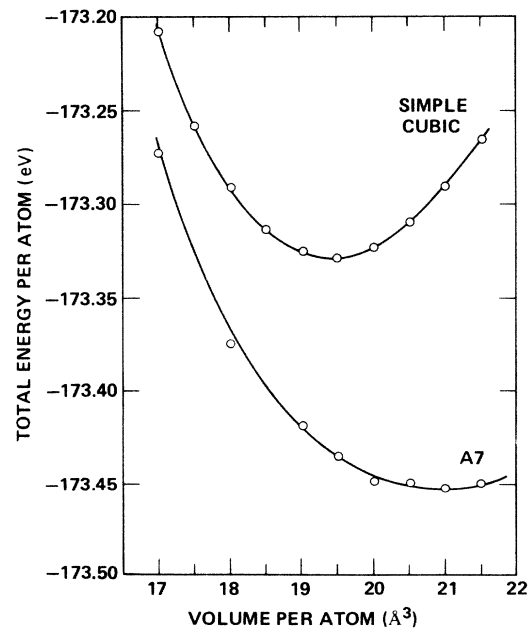


FIG. 2. Total energy of the sc and *A7* phases of As. The points indicate calculated energies and the solid lines are fits to Murnaghan's equation of state.

We have tested the stability of the sc structure against the zone-center optic-phonon displacement which gives an $A7$ structure and against the simple rhombohedral shears which correspond to stretching and compressing the primitive cube along the $[111]$ direction. If one considers only the electrostatic Ewald contribution to the total energy, the sc structure is unstable to simple rhombohedral distortions which take sc towards fcc or bcc. However, it is stable with respect to the $A7$ -symmetry phonon displacement. The present stability tests were performed by carrying out the full self-consistent calculations for the forces on the atoms and the stresses¹⁶ when small atomic displacements and strains of the unit cell were applied. At all volumes we found that the sc phase was unstable with respect to the phonon displacement, i.e., the electronic contributions to the forces overcome the Ewald terms to destabilize the cubic structure. However, the sc phase was found to be stable against both positive and negative rhombohedral shears at all volumes down to the smallest volume for which calculations were performed of 10 \AA^3 per atom. At some even smaller volume we expect the sc phase to become unstable to rhombohedral shears because at sufficiently small volumes the Ewald term must dominate the electronic structure terms. The stability towards rhombohedral shears contradicts earlier total-energy calculations.^{10,11,12} The second-order perturbation calculations of Weaire and Williams¹⁰ and of Abe *et al.*¹¹ showed instabilities of sc As to rhombohedral shears, while the third-order perturbation calculations of Morita *et al.*¹² gave an instability to negative rhombohedral shears at a volume of $\sim 18 \text{ \AA}^3$ per atom.

It has been reported that at pressures $> 120\text{--}150$ kbars, As transforms to a phase which is superconducting and has a tetragonal structure with many atoms in the unit cell.²⁵ Because of the existence of other As phases at pressures where we still find sc As to be unstable to the $A7$ distortion, we conclude that sc As will not exist as a stable intermediate phase between the $A7$ and superconducting tetragonal phases.

The total energies were fitted to Murnaghan's equation of states.²⁶ For the sc structure we found a good fit which was not significantly altered by including data points far from the zero-pressure volume, giving a bulk modulus $B = 1.04$ Mbar, the pressure derivative of the bulk modulus $dB/dP = 4.4$ and a zero-pressure volume $V_0 = 19.4 \text{ \AA}^3$ per atom. Fitting the total energies of the $A7$ structure to Murnaghan's equation of state gave parameters which depended significantly on how many data points were included in the fit. However, by fitting the calculated pressures of structures close to the zero-pressure volume or the derivative of Murnaghan's equation of state, we obtained reliable values of the bulk modulus and zero-pressure volume. We find $B = 0.43$ Mbar compared to the experimental value of 0.394 Mbar,²¹ and $V_0 = 20.95 \text{ \AA}^3$ per atom compared to the experimental value⁴ of 21.3 \AA^3 .

PROPERTIES OF THE $A7$ PHASE

The predicted structural parameters for the experimental zero-pressure volume of 21.3 \AA^3 per atom can be ob-

tained by linear interpolation between the calculated values of 21 and 21.5 \AA^3 . We find $u = 0.230$ and $\epsilon = 0.056$ to be compared with the experimental values of $u = 0.2276$ and $\epsilon = 0.08194$.¹ The internal parameter u agrees well with experiment but ϵ is 30% too small. The calculations have shown that ϵ is very sensitive to the details of the semimetallic Fermi surface, whereas u is not. We conclude that (i) the distortion u is determined by the overall bonding involving all the electrons, not primarily those at the Fermi surface, (ii) the predicted values of u are given accurately by the calculations described in the previous section, (iii) the strain ϵ is greatly affected by the Fermi surface and vice versa, and (iv) the predicted values of ϵ may not be accurately determined because of the large amount of computer time that would be required to eliminate all numerical uncertainties.

In Fig. 3 the shear of the unit cell ϵ and internal parameter u are plotted for the calculated equilibrium $A7$ structures for different volumes. As the volume decreases the structure goes towards sc but is still considerably distorted from it at the lowest volume for which calculations were performed of 17 \AA^3 per atom. The trends in the calculated values of the pressure dependence of the structural parameters agree reasonably well with the experimental results of Morosin and Schriber³ but in detail the numerical agreement is not good. Morosin and Schriber carried out x-ray diffraction experiments at ambient pressure and at 3.1 kbar. They obtained $d \ln(a)/dP = -1.1 \pm 0.4 \times 10^{-4}$

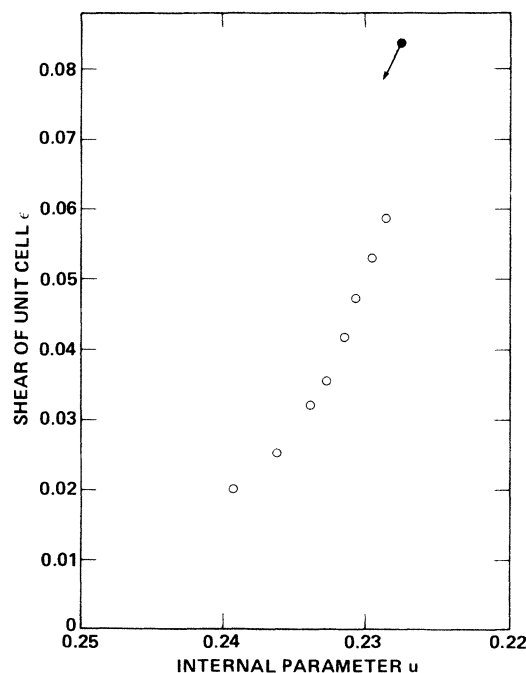


FIG. 3. Shear in the unit cell ϵ and internal parameter u for different volumes. The sc structure corresponds to $\epsilon = 0.0$ and $u = 0.25$. The volumes correspond to those of Fig. 2, with the largest volume having the greatest distortion from sc. The solid curve represents the experimental low-temperature structure (Ref. 1) and the arrow gives the trajectory in ϵ - u space of the structure with applied pressure (from the room-temperature measurements of Ref. 3).

kbar^{-1} , $d \ln(c)/dP = -23.9 \pm 0.9 \times 10^{-4} \text{ kbar}^{-1}$, and $d \ln(u)/dP = 12 \pm 2 \times 10^{-4} \text{ kbar}^{-1}$. Using the experimental value of the bulk modulus of As of 0.394 Mbar ,²⁷ we can convert these to dimensionless quantities: $d \ln(a)/d \ln(V) = +0.043 \pm 0.016$, $d \ln(c)/d \ln(V) = +0.942 \pm 0.036$, and $d \ln(u)/d \ln(V) = -0.473 \pm 0.079$. From our calculations we have $d \ln(a)/d \ln(V) = +0.21$, $d \ln(c)/d \ln(V) = +0.58$, and $d \ln(u)/d \ln(V) = -0.18$.

The internal motion of the atoms under compression is most clearly illustrated by the plot of the distance between the planes of the $A7$ structure in Fig. 4. The larger distance v between the pairs of planes decreases rapidly with increasing pressure, while the shorter distance w between members of a pair increases slightly. This is interpreted in terms of the different kinds of bonding in the $A7$ crystal. Strong covalent bonds exist between the members of a pair of planes, while the bonding between neighboring pairs is weak. Over the 21% volume change considered, the nearest-neighbor distance decreased by only 3% and the As-As bond angle changed from 97.3° to 93.9° . These small changes indicate strong bonding between the nearest neighbors. The weak bonds between pairs of planes are easily compressed; the separation v decreases by 20% over this volume range.

The phonon frequency of the zone-center Γ_1 optic mode (the mode associated with the sc to $A7$ distortion, i.e., the parameter u) was calculated for the theoretical equilibrium $A7$ structures and is shown in Fig. 5. The mode is already quite soft at the experimental zero-pressure volume with a frequency of $\sim 250 \text{ cm}^{-1}$. With increasing pressure the mode softens but within the calculated volume range it does not go to zero. The zero-

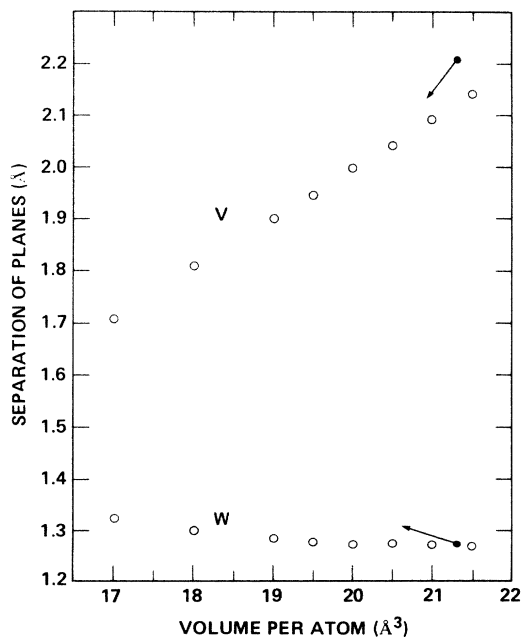


FIG. 4. Distance between pairs of planes v and between members of a pair w plotted against volume. The solid circles represent the experimental low-temperature structure and the arrows show the volume dependence of v and w from the room-temperature measurements of Ref. 3.

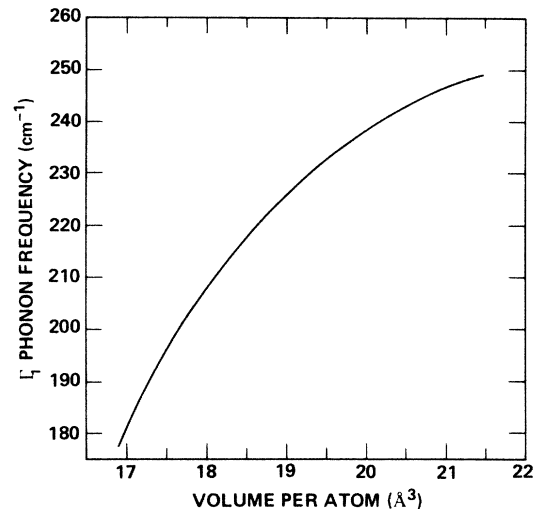


FIG. 5. Phonon frequency of the zone-center Γ_1 optic mode of the $A7$ structure as a function of volume.

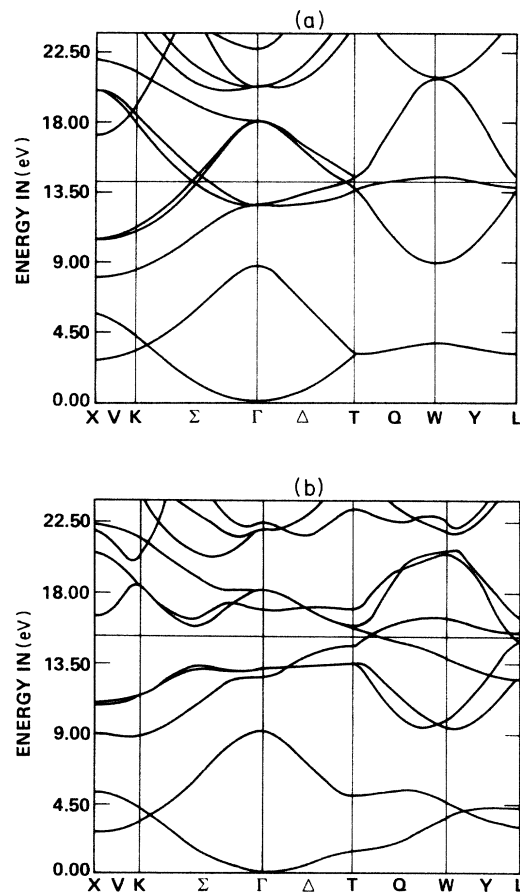


FIG. 6. Band structures of sc and $A7$ As. The symmetry points are labeled according to the notation of Cohen, Ref. 29. (a) sc at a volume $V=21.52 \text{ Å}^3$ per atom. (b) $A7$ As with the room-temperature experimental structure of $V=21.52 \text{ Å}^3$ per atom with $u=0.2271$ and $\epsilon=0.08823$. Note that the apparently equal energies of some bands are accident. In the distorted structure no true degeneracies exist at the L point.

pressure phonon frequency agrees well with the data of Richter *et al.*²⁸ who measured up to 7 kbars and found $\sim 254 \text{ cm}^{-1}$ at zero pressure.

We have also calculated the electronic bands in the local-density approximation for the experimental room-temperature *A7* structure and for sc As as the same volume, as shown in Figs. 6(a) and 6(b). Here we have used the symmetry notations of Ref. 29. Plane waves up to 10 Ry in energy were treated exactly and further waves up to 15 Ry were incorporated in second-order perturbation theory. The Schrödinger equation was solved at 44 special points in the irreducible part of the *A7* BZ to produce the self-consistent potential for the band-structure calculations. To facilitate comparison we have plotted the sc band structure folded into the BZ of an undistorted *A7* structure. Firstly, we note the low-lying *s* band whose contribution to the bonding is small. We see the dramatic effect of the doubling of the periodicity on the *A7* band structure. A gap opens at the Fermi level and only a small Fermi surface remains. There is a pocket of holes close to the *T* point and a pocket of electrons at the *L* point. In detail, the agreement with the pseudopotential calculations of Falicov and Golin³⁰ and the orthogonalized-plane-wave calculations of Golin³¹ is quite good. But we find only one band crossing the Fermi level near *L* and not two as in the calculations of Refs. 29 and 30. This present result is in agreement with a recent experimental study of Tokailin *et al.*³² using angle-resolved photoemission and with the empirical pseudopotential calculations reported in the same paper.

CONCLUSION

We have performed total-energy calculations on a family of structures of As. We find that the lowest-energy structure is an *A7* structure with internal parameters, equilibrium volume, and bulk modulus in good agreement with experiment. The correct trends in the pressure dependence of these parameters is given by our calculation, but in detail, numerical values are poor.

We find that sc As has a Peierl's instability to an *A7* distortion at all volumes for which calculations were performed. Under pressure the *A7* distortion is diminished, but a stable sc phase is not reached before a transition to another structure occurs.

APPENDIX: THE *A7* CRYSTAL STRUCTURE OF As

The *A7* structure can be viewed as a distortion of simple cubic. An *A7* structure can be obtained from sc by a strain of the unit cell along the [111] direction and a simultaneous displacement of the atoms of the basis towards each other in pairs along the same direction. The

distortion from simple cubic in As is large enough that the structure is layerlike.

The shape of the rhombohedral unit cell is commonly described in any one of three ways. We may define the rhombohedral angle α or the *c/a* ratio or the shear of the unit cell ϵ . The *c/a* ratio and rhombohedral angle α are related by

$$c/a = \sqrt{3} \frac{\cos \rho}{\sin \rho}, \quad (\text{A1})$$

where

$$\sin \rho = \frac{2}{\sqrt{3}} \sin \frac{\alpha}{2}. \quad (\text{A2})$$

The rhombohedral angle α and shear parameter ϵ are related by

$$\cos \alpha = \frac{1 + 2\epsilon}{2 + \epsilon^2}. \quad (\text{A3})$$

In this paper we use both the *c/a* ratio and the shear to describe the shape of the cell as dictated by simplicity or comparison with published work.

Defining translation vectors a_1 , a_2 , and a_3 are

$$\begin{aligned} a_1 &= (a/\sqrt{3}, 0, c/3), \\ a_2 &= (-a/2\sqrt{3} - a/2, c/3), \\ a_3 &= (-a/2\sqrt{3}, a/2, c/3), \end{aligned} \quad (\text{A4})$$

the positions of the two atoms of the basis are

$$\pm u(0, 0, c). \quad (\text{A5})$$

The sc structure is given by $u = 0.25$ and $c/a = \sqrt{6}$ or $\epsilon = 0$ or $\alpha = 60^\circ$. The low-temperature *A7* structure of As has¹ $u = 0.2276$, $c/a = 2.7774$, $\epsilon = 0.08194$, and $\alpha = 54.55^\circ$.

The volume V per atom is given by

$$V = a^2 c / 4\sqrt{3}. \quad (\text{A6})$$

At low temperature As has¹ $V = 21.3 \text{ \AA}^3$. The nearest-neighbor distance a_{nn} is given by

$$a_{nn} = a/\sqrt{3} [1 + \frac{1}{3}(6u - 1)^2 (c/a)^2]^{1/2}. \quad (\text{A7})$$

The structure consists of planes stacked in pairs along the direction of $a_1 + a_2 + a_3$. The nearest neighbors are in adjacent planes of a pair which are separated by a distance w :

$$w = (2u - \frac{1}{3})c. \quad (\text{A8})$$

The pairs of planes are separated by a larger distance v :

$$v = (\frac{2}{3} - 2u)c. \quad (\text{A9})$$

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