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Lattice dynamics and anomalous bonding in rhombohedral As: First-principles supercell method

Shunli Shang,* Yi Wang, Hui Zhang, and Zi-Kui Liu
Department of Materials Science and Engineering, The Pennsylvania State University, 304 Steidle Building, University Park, Pennsylvania 16802, USA

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The pending understanding of lattice dynamics in rhombohedral (*A*7) arsenic has been resolved by the first-principles supercell method. An anomalous bonding with considerable stretching force constant is found between atoms spanning the alternately first and second nearest neighbors, which stabilizes the layered *A*7 structure by suppressing the appearance of imaginary phonon modes. This anomalous bonding, as a result of Peierls distortion, is traceable from the undistorted simple cubic lattice exhibiting giant Kohn anomaly at the R point due to Fermi-surface nesting along the Γ-R direction.

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Arsenic (As), a group-V elemental semimetal with electronic configuration of $4s^24p^3$, has a rhombohedral *A*7 structure, which can be derived from a simple cubic (SC) structure.[1,2] This *A*7 structure stems from the Peierls distortion in terms of the *p*-bonding mechanism[3]: the partially filled *p* band favors the alternation of short and long bonds in three almost orthogonal directions by opening a gap at the Fermi level to stabilize the distorted structure. Due to the presence of the Peierls distortion, arsenic possesses fascinating behaviors, for instance, (i) a semimetal to semiconductor transition occurs in the thin film[4] and the liquid state,[3] (ii) the structure of liquid arsenic is similar to its ground state *A*7 structure with a coordination number of 3,[3] and (iii) the *a* axis (in hexagonal setting) of arsenic has a negative thermal expansion.[5] Additionally, arsenic together with group-III elements widens the semiconductor family through forming the III-V compounds such as $B_{12}As_2$, GaAs, and InAs. However, the lattice dynamics of arsenic is still far from being fully understood in spite of its critical role in probing electron-phonon coupling, finite temperature thermodynamics, structure stability, and even the origin of melting as demonstrated in this work. To date, a successful prediction of phonon dispersions in rhombohedral arsenic is still pending. A ten-neighbor, 27-parameter Born–von Karman model gives only an overall description of the phonon dispersions but does not reproduce the fine structures of the optical modes, e.g., in the Γ-L direction.[6] Other attempts such as the third-order pseudopotential expansion method give even worse results, especially for the optical modes.[7] The unsuccessful understanding of phonon dispersions by empirical methods implies the presence of anomalous bondings in arsenic.

The present work aims to explore the existing problems of arsenic with rhombohedral *A*7 structure, such as the lattice dynamics and bonding nature, with the help of first-principles phonon calculations. To these ends, we calculate the force constants and phonon dispersions for arsenic with *A*7 and SC structures as a function of volume and the Fermi surface of the SC structure. Herein, the predictions for the SC structure are used to trace the origin of the Kohn anomaly[8,9] and, in turn, the Peierls distortion in arsenic (see the following discussions). In the present work, the first-principles calculations are performed by the projector-augmented wave method[10] together with the generalized gradient approximation[11] (GGA) as implemented in the VASP code.[12] The phonon calculations at several volumes are carried out by using the supercell approach[13] as implemented in the ATAT code.[14]

Figure 1 illustrates the rhombohedral *A*7 structure of arsenic represented by four distorted simple cubic lattices. The atoms linked by the first nearest bond lengths (heavy lines as shown in Fig. 1) form a layerlike structure perpendicular to the *c* direction in hexagonal setting, separated by the second nearest bond lengths (thin lines). Herein the bond length between the third nearest neighbors (3NN's) equals the lattice parameter *a* in hexagonal setting. The bond length of 6NN plus 9NN equals the lattice parameter *c*. Other bond lengths up to the 14NN at the equilibrium volume are also indicated in Fig. 1.

Figure 2 shows the predicted force constants of arsenic with *A*7 and SC structures at the measured and optimized

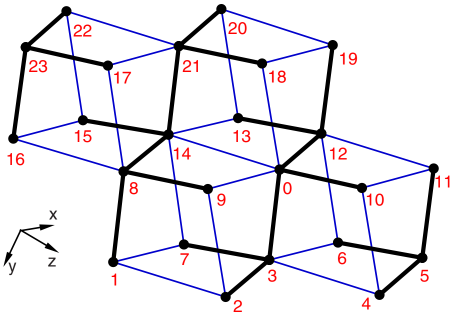

FIG. 1. (Color online) Crystal structure of arsenic with rhombohedral *A*7 structure represented by four distorted simple cubic (SC) lattices. The equilibrium bond lengths up to the 14th nearest neighbor can be identified as follows. The first nearest neighbor (1NN) is connected by the heavy solid lines and 2NN by the thin (blue) lines. 3NN, with its length equal to the lattice parameter *a* in hexagonal setting, is between the atoms 0-2, 0-7, 0-13, and 6-11, etc.; 4NN: 0-4, 0-6, 0-8, and 0-11; 5NN: 3-13, 7-12, 8-18, and 9-21; 6NN: 0-5, 3-8, and 14-23; 7NN: 0-1, 0-20, 3-11, and 4-12; 8NN: 0-15, 3-18, 9-12, and 11-13; 9NN: 0-17, 4-9, and 6-14; 10NN: 1-21, 3-19, 9-15, and 10-13; 11NN: 1-13, 10-21, and 5-13; 12NN: 7-18; 13NN: 9-20 and 2-13; and 14NN: 7-11 and 16-18. Note that the length of (6NN+9NN) equals the lattice parameter *c*, e.g., the in lines 5-0-17 and 6-14-23.

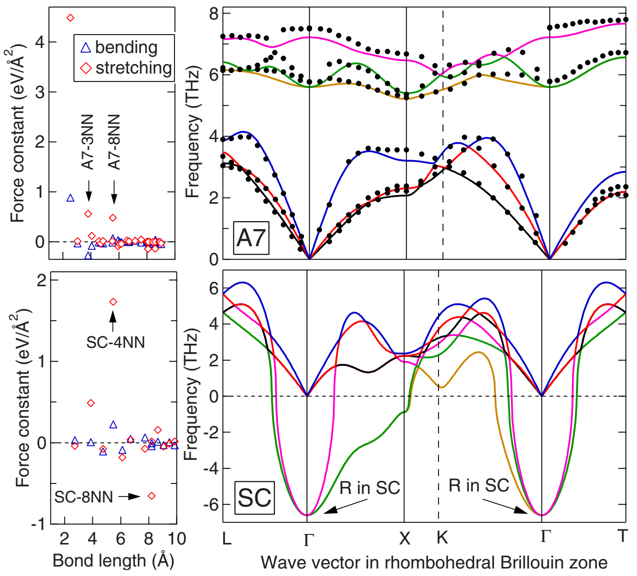

FIG. 2. (Color online) Comparison of force constants and phonon dispersions of arsenic between the $A7$ (top panels) and SC structure (bottom panels, the folded dispersions of two atoms per unit cell are shown along the same directions as in the $A7$ structure). The symbols show the measurements (Ref. 6). The 8NN in the $A7$ structure corresponds to the 4NN in the SC structure.

equilibrium volumes,[15] respectively, and the corresponding phonon dispersions represented in the rhombohedral Brillouin zone.[18] The predicted phonon dispersions of the $A7$ structure are in good agreement with the measurements by neutron scattering;[6] in particular, the measured fine structures of optical modes for the $A7$ structure are reproduced by the present work. By probing the force constants of the $A7$ structure as shown in Fig. 2, it is found that (i) the largest stretching force constant between the first nearest neighbors of the $A7$ structure ($A7$-1NN's) and the second largest stretching force constant between the $A7$-3NN's are all located in the intralayers, indicating the presence of strong bonding within each layer; (ii) the predicted stretching force constant between the $A7$-2NN's is close to zero, indicating the presence of weak bonding between interlayers; and (iii) a considerable positive stretching force constant is present between the $A7$-8NN's (spanning the alternately first and second nearest neighbors near linearly). The role of this anomalous force constant between the $A7$-8NN's is to glue the layers, which, in turn, stabilizes the $A7$ structure. It should be mentioned that the soft phonon mode (the lowest, most negative, imaginary phonon mode) would appear at the T point without this anomalous $A7$-8NN force constant (not shown). The presence of these anomalous bondings such as the ones between the $A7$-2NN's and the $A7$-8NN's makes the Born–von Karman model unsuccessful in reproducing the fine structures of phonon dispersions.

The origin of these anomalous bondings in the $A7$ structure is traceable from the undistorted SC structure. As shown in Fig. 2, the giant anomalous force constants are present in the SC structure, in particular, the largest SC-4NN stretching force constant (spanning two first nearest neighbors and corresponding to the one between the $A7$-8NN's). In addition, the stretching force constant between the SC-8NN's (spanning three first nearest neighbors) is a considerable negative value. In fact, the equilibrium SC structure is unstable, indicated by the soft phonon mode in the R point of the SC Brillouin zone (see Fig. 2); correspondingly, the near-zero force constants between the SC-3NN's are present along the bulk diagonal direction (corresponding to the c direction of the $A7$ structure). Therefore, the unstable SC structure tends to be distorted into the layered $A7$ structure along the bulk diagonal direction.

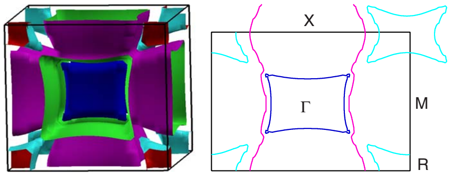

FIG. 3. (Color online) Fermi surface of arsenic with the SC structure. The right panel shows the (110) slice, i.e., the Γ-R-M-X plane. The nested features of the Fermi surface are clearly shown along the Γ-R direction with the length of wave vector of $\sim 2k_F$.

Appearance of the aforementioned anomalous bondings is due to the presence of Peierls distortion in arsenic.[3] In a sense, the precursor of the static Peierls distortion is the Kohn anomaly (dynamic distortion); both of them are due to partially filled bands especially for one dimensional atomic chains.[9] In the phonon dispersion curves, Kohn anomaly manifests as sudden dips in the phonon dispersions for a wave vector $q \sim 2k_F$, with k_F being the Fermi wave vector.[8,9] Figure 3 shows the Fermi surface of arsenic with SC structure.[20] Among the three kinds of Fermi surfaces, two of them are cubelike with lots of flat portions occurring mainly in the corner regions. The third one shows six-way cubic-pipe-like with flat portions occurring mainly in the joint regions. These flat portions indicate the presence of Fermi-surface nesting in the SC structure, i.e., a piece of a Fermi surface can be translated by a vector q and superimposed on another piece of the Fermi surface.[23] The (110) slice in Fig. 3 clearly shows the nested features of the Fermi surface along the $[\xi\xi\xi]$ wave vector direction with length of $\sim 2k_F$. The nested Fermi surface in the SC structure caused by the electron-phonon coupling results in a pounced softening (soft mode) of phonon dispersions, i.e., the giant Kohn anomalies, at the R point (corresponding to the Γ point in the folded rhombohedral Brillouin zone as shown in Fig. 2). It should be pointed out that the other high symmetrical points such as the X and M in the SC Brillouin zone also exhibit obvious Kohn anomalies (see Fig. 2, but not shown directly). The imaginary phonon modes in the SC structure disappear when SC is distorted into the $A7$ structure as shown in Fig. 2, whereas most of the features of phonon dispersions in the SC structure are retained in the $A7$ structure, in particular, the optical modes, for instance, at the Γ point as shown in Fig. 2. Actually the layered $A7$ structure of arsenic can be considered as a distorted quasi-one-dimensional structure along the c direction in hexagonal setting. This distorted quasi-one-dimensional structure is caused by the Peierls instability depending on the p-band mechanism, which is traceable to the Fermi-surface nesting mainly along the Γ-R direction and,

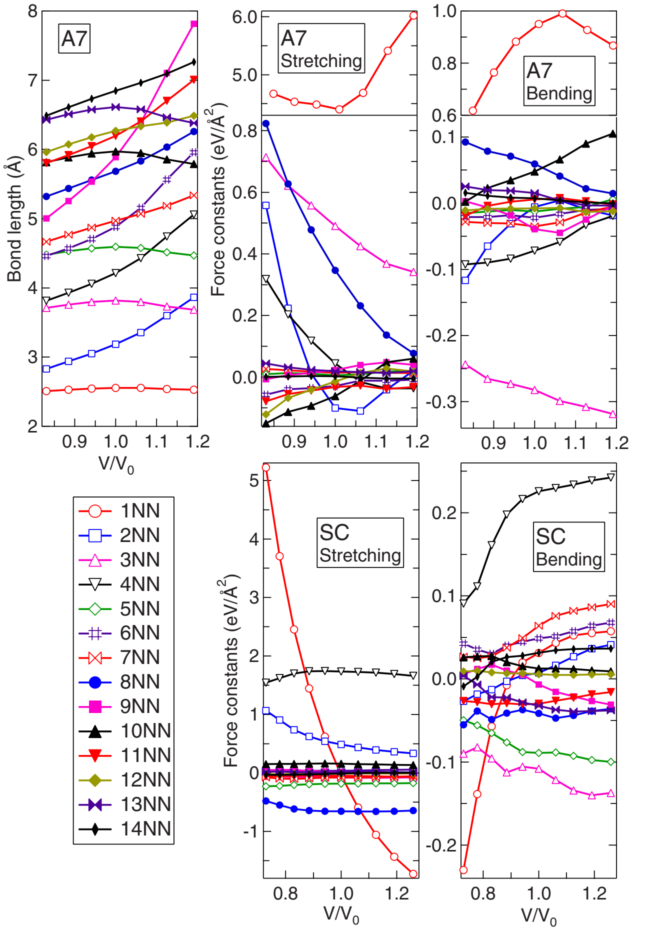

FIG. 4. (Color online) Calculated force constants and bond lengths of arsenic with the $A7$ and SC structures up to the 14th nearest neighbor as a function of volume.

correspondingly, the Kohn anomaly of phonon dispersion in the R point of the SC Brillouin zone.

The whole picture of the bonding nature in arsenic can be clearly represented by the variations of bond lengths and force constants as a function of volume. Figure 4 shows that the bond lengths of the $A7$ structure can be classified into two groups. One group is within the layer, such as the $A7$-1NN and $A7$-3NN, whose bond lengths increase with increasing volume when the volume is lower than the equilibrium one but decrease after the equilibrium volume is reached. The other group of bond lengths links (or crosses) different layers, such as the $A7$-2NN, $A7$-6NN, and $A7$-9NN, whose bond lengths increase with increasing volume. The variation of bond lengths with volume indicates further the layered feature of the $A7$ structure: the bonding trend within each layer and the separating trend between layers at larger volumes. Experimentally, the lattice parameter a of the $A7$ structure (in hexagonal setting) shows negative thermal expansion,[5] and the coordination number of arsenic remains 3 even in liquid,[3] indicating the strong layer formation ability in arsenic. Similar to the force constants as shown in Fig. 2, Fig. 4 also indicates that the larger force constants of the $A7$ structure are between (i) the $A7$-1NN's (the largest one within layer, its value even increases at larger volumes), (ii) the $A7$-3NN's (the second largest one within layer), and (iii) the $A7$-8NN's (the anomalous one to glue the layers). In the SC structure, the larger force constants are between the SC-1NN's, showing a quick decrease with increasing volume, and the SC-4NN's, remaining almost constant at larger volumes, which is the precursor of anomalous force constants between the $A7$-8NN's.

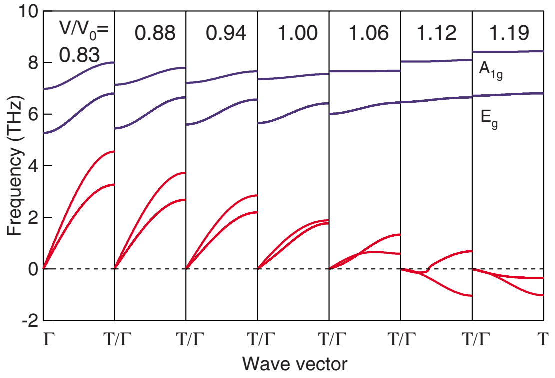

FIG. 5. (Color online) Calculated phonon dispersions of the $A7$ arsenic from Γ to T direction under different volumes.

Figure 5 shows the phonon dispersions of the $A7$ structure along the wave vector Γ-T as a function of volume. The soft mode appears at the T points when volumes $V/V_0 > 1.1$, indicating the mechanical instability at higher temperatures caused by the expansion of bond lengths along the c direction. This lattice instability gives a signal of phase transition (here, it is melting) at higher temperatures. The appearance of soft mode at the T point implies that the onset of melting is due to the cleavage of layers. According to the force constants as shown in Fig. 4, the melting of arsenic originates from the weakening of bonding between layers, especially the weakening of the $A7$-8NN bond. Figure 5 also shows that the predicted values of the optical modes E_g and A_{1g} at the Γ point decrease with decreasing volume (or increasing pressure), which is in good agreement with the Raman measurements as a function of pressure.[1] In addition, when $V/V_0 < 0.8$, the values of optical modes at the Γ point tend to equal the values of acoustic modes at the T points, indicating the occurrence of phase transition from $A7$ to SC structure at high pressures. These predictions also agree with the previous measurements and simulations.[1,2]

In summary, the pending description of lattice dynamics in arsenic with rhombohedral $A7$ structure has been resolved by using the first-principles supercell method. An anomalous bonding with a considerable positive force constant is found between the eighth nearest neighbors. This anomalous bonding stabilizes the layered $A7$ structure through gluing the layers and, in turn, suppressing the appearance of imaginary phonon modes. It is found that the anomalous bondings in the $A7$ structure, caused by the Peierls distortion, are traceable from the undistorted SC structure exhibiting giant Kohn anomaly and therefore the soft mode results at the R point due to the Fermi-surface nesting along the Γ-R direction. The appearance of the soft mode at the R point indicates the Peierls instability of the SC structure and, in turn, the $A7$ structure results. The present work also indicates that the soft phonon mode appears at the T points of the *A*7 structure at larger volumes ($V/V_0 > 1.1$) due to the weakening of bonding between layers, especially the bonding between the eighth nearest neighbors, implying the onset of melting triggered at higher temperatures due to the cleavage of layers.

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*Electronic address: sus26@psu.edu

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[15] In the VASP calculations, the energy cutoff of 260 eV is used for arsenic. The electronic structure calculations and the structure relaxations are performed on *k* meshes $23 \times 23 \times 23$ and $24 \times 24 \times 24$ for the *A*7 and SC structures, respectively. The equilibrium volumes 22.77 and 20.45 Å^3 per atom are obtained for the *A*7 and SC structures, respectively, predicted by the GGA (Ref. 11). The measured volume of 21.52 Å^3 per atom at room temperature (Ref. 16) for the *A*7 structure is used to calcucalte Fig. 2 in order to compare with the measured phonon dispersions (Ref. 6). It should be mentioned that the GGA predicts a softer *A*7 structure, while the local-density approximation (LDA) (Ref. 17) predicts a harder *A*7 structure (20.46 Å^3 per atom). Test calculations show that both the GGA and LDA give the same conclusions of phonon and bonding nature for arsenic.

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