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Superconductivity in arsenic at high pressures

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We have investigated the pressure dependence of the superconducting transition temperature T_c of elemental arsenic up to 41 GPa both experimentally and theoretically. Our measurements indicate that a peak in T_c occurs at the rhombohedral–simple-cubic structural phase transition. A first-principles calculation provides a physical description consistent with the observed behavior of T_c under pressure.

I. INTRODUCTION

One of the most physically interesting pressure-induced structural transformations is the rhombohedral $A7$ (α-arsenic) to simple cubic (sc) transition in the group V elements phosphorus, arsenic, and antimony. At low pressure the $A7$ phase is stable. X-ray-diffraction experiments[1–5] show that pressure causes the low-symmetry rhombohedral unit cell to relax continuously toward the highly symmetric simple cubic phase. The $A7$ phase[6] is considered to be the result of a Peierls-like distortion of the sc phase at low pressure. This distortion results in a semimetal with a rather low electronic density of states at the Fermi level $[N(E_F)]$. Pressure stabilizes the sc phase and thus increases $N(E_F)$. Various theoretical studies[7–9] have been able to predict the occurrence of such subtle transformations by the onset of phonon softening.

Both the $A7$ and the sc phases of P, As, and Sb have been shown to be superconducting.[10–14] Because these transitions are nearly continuous (there are slight discontinuities in the lattice constants), it is expected that the superconducting transition temperatures (T_c) will be continuous with pressure as well. Work by Wittig, Bireckoven, and Weidlich[13] has shown that the T_c of Sb and P exhibit peak values of 5 K and 10 K, respectively, at the transition pressure. These peaks are ascribed to the softening of the phonon modes near the transition pressure, which has a positive effect on the electron-phonon coupling. This explanation is supported by *ab initio* total-energy calculations performed by Chang and Cohen,[8] which suggest the existence of soft phonons in the sc phase. Wittig[12(a)] also measured T_c of As under pressure. His data for As did not show a peak in T_c as in the case of P and Sb. However, a later work with Kawamura[12(b)] did mention that T_c in As reached a maximum value of 2.7 K at a pressure of ~24 GPa. Furthermore, these authors suggested phonon softening as the probable reason for the peak in T_c.

The vibrational properties of As in the $A7$ phase were studied as a function of pressure by Beister, Strössner, and Syassen[2] using Raman scattering. These authors found evidence of softening in the zone-center optical phonon at the $A7$-sc transition. The experimental results were found to be qualitatively in good agreement with the theoretical calculation of Needs, Martin, and Nielsen.[7] Although the experimental and theoretical results so far all suggest that phonon softening plays an important role in determining T_c, the importance of other factors such as $N(E_F)$ is still not clear.

In this contribution we report a detailed experimental and theoretical investigation of elemental As, which elucidates the roles of phonon softening and $N(E_F)$ in the pressure dependence of T_c in the neighborhood of the $A7$-sc transition. We measure both the normal-state resistance and T_c as a function of pressure up to 41 GPa. We establish the existence of a maximum value of $T_c \sim 2.4$ K similar to that reported by Kawamura and Wittig[12] but at 32 GPa. We also perform first-principles calculations of $N(E_F)$ and frozen-phonon calculations of the relevant phonon modes in both phases. Our results on $N(E_F)$ explain qualitatively the pressure dependence of the normal-state resistance and point to the importance of $N(E_F)$ in enhancing T_c. We find that phonon softening occurs as the transition pressure is approached from either side. Thus both an increasing $N(E_F)$ and phonon softening serve to increase T_c rapidly as As is pressurized toward the $A7$-sc transition. Above the transition further compression stiffens the phonons, while $N(E_F)$ remains relatively constant so that T_c decreases gradually.

Our investigation was further motivated by the recent report[15] of possible superconductivity in low-temperature grown, As-rich GaAs with T_c of approximately 10 K. This observation raised the question of whether excess As forced into the sc structure could be responsible for the superconductivity. Our findings indicate that this is unlikely, because the maximum T_c of sc As is less than 3 K.

This contribution is organized as follows. A description of the experimental technique immediately follows the introduction. In Sec. III we present the experimental results on T_c and normal-state resistance under pressure. Section IV describes the details and results of the first-principles calculations. In Sec. V we show that the experimental results can be qualitatively understood by the calculated behavior of $N(E_F)$ and the phonon spectrum under pressure. We conclude with a brief summary of our findings.

II. EXPERIMENTAL TECHNIQUE

The transport properties were measured inside a piston-type diamond anvil cell (DAC) using a four-probe resistance technique. This is a variation of the technique developed by Erskine, Yu, and Martinez.[16] Gold wires were contacted to the As sample by pressure and insulated from the metal gasket by Al_2O_3 powder. Use of $CaSO_4$ powder as a pressure medium resulted in an inhomogeneity of ±5%. Because thermal contraction of the DAC typically increased the pressure 15% above its room-temperature value, we monitored the pressure *in situ* by measuring the ruby fluorescence peak shift at liquid-He temperatures. The peak shift is converted into pressure using the conversion factor 0.274 GPa/Å. The experiments were done with nonbeveled diamonds with 400-μm culets. The resistance was measured using an ac current of 10 mA at 100 Hz with a lock-in amplifier. With low sample resistances of approximately 200 $\mu\Omega$ at 4 K, such a current did not appreciably warm the sample.

The samples tested were polycrystalline As samples of 99.99% purity purchased through the Johnson Matthey Aesar Group. Although the surfaces of the As pieces were covered with a black oxide, their interiors were shiny elemental As. We crushed the oxidized pieces into tiny fragments to expose the As and loaded one shiny piece into our DAC before it could visibly blacken (approximately 5 min). Typical fragment sizes were approximately $50 \times 50 \times 20$ μm^3. We did not visually notice any reaction of the As sample to the Au wires, $CaSO_4$, or ruby.

Temperatures down to 1.7 K were attained by pumping on a liquid-He bath with the DAC completely immersed in the liquid. When measuring T_c, we slowly decreased and increased the temperature by regulating a needle valve to vary the pumping speed. A hysteresis of less than 30 mK in the superconducting transition indicated that both the sample and the Si diode thermometer were adequately thermally grounded.

III. EXPERIMENTAL RESULTS

Figure 1 displays T_c of As as a function of pressure, measured for increasing pressure. The data were accumulated over several runs. The error bars in pressure indicate the ±5% in homogeneity; the vertical error bars correspond to the transition width.

Our results show a peak in T_c at approximately 32 GPa. With increasing pressure, T_c increases rapidly toward the peak value of 2.5 K. At pressures above 32 GPa, T_c decreases more slowly. The downward arrow on the plot indicates a pressure at which we did not observe any sign of a transition down to our lowest attainable temperature of 1.7 K. Although the data obtained by Wittig[12] agree qualitatively with our results for T_c below the peak, they observe a leveling of T_c at approximately 3 K at a pressure of 21 GPa. Furthermore, they observe the steep rise in T_c to occur at a pressure that is ~10 GPa less than what we observe. It is now established that the pressure measurements in Ref. 12 were underestimated by approximately 15%. This, however, does not fully account for the discrepancy. We will discuss this difference in further detail in a later section.

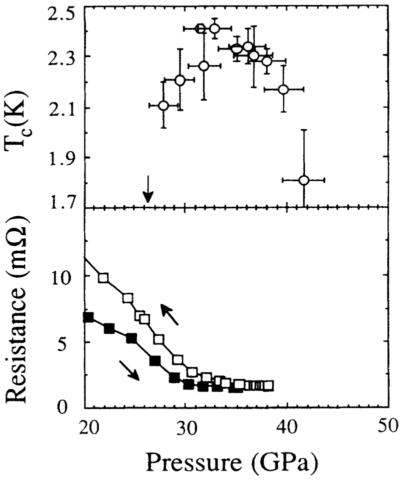

FIG. 1. The T_c and resistance at 300 K of As as a function of pressure. Horizontal error bars indicate the pressure inhomogeneity of ±5%, while vertical error bars represent the transition width. The T_c data were taken for increasing pressure only, while the resistance vs pressure curve was measured for both increasing and decreasing pressures. A downward arrow indicates a pressure at which we did not observe a transition above 1.7 K.

A closer look at the peak in T_c reveals that it is noticeably asymmetric. The rate of increase in T_c below the peak is larger than the rate of decrease of T_c above. Similar but more conspicuous behavior is observed in Sb across its $A7$-sc transition.[12] In the case of Sb, however, there is a discontinuity in the T_c presumably caused by the slight discontinuity in the lattice constants through the transition.

The behavior of the normal state resistance as a function of pressure is an indication of the trend in $N(E_F)$, since resistances of semimetals and metals are inversely proportional to $N(E_F)$. The resistance of As at 300 K is also shown in Fig. 1. We note that the resistance decreases at an almost constant rate until 32 GPa. Above 32 GPa the resistance becomes roughly independent of pressure. The observed decrease in resistance upon pressurization of the $A7$ phase may reflect an increasing $N(E_F)$, which becomes independent of pressure in the sc phase. This feature is reproducible upon decreasing the pressure, demonstrating the reversibility of the transition. There is, however, a slight difference upon reversing the stress that is attributable to deformation of the sample. The uncertainty in the geometric shape of the sample inside the DAC makes it difficult to determine the resistivity precisely. A rough estimate of the resistivity at high pressure (above 32 GPa) using the approximate dimensions of the sample stated in Sec. II gives a value of approximately 4×10^{-6} Ω cm, which is typical of a metal.

IV. CALCULATIONS

An understanding of the behavior of T_c under pressure requires an analysis of the physical properties that determine supercondutivity, namely, the electronic density of states at the Fermi level and the electron-phonon coupling. A theoretical investigation of the pressure dependence of these two properties can provide insight into the pressure dependence of T_c. In this section we present, for both structural phases, results of first-principles calculations of the $N(E_F)$ and the frequency of the phonon mode corresponding to the sc-$A7$ distortion, as functions of volume for both quantities. To make contact with the experimental measurements, in which the pressure is the independent variable, a calculation of the equation of state is provided and compared with experimental equations of state.

The calculations were performed using the *ab initio* pseudopotential total energy method.[17,18] The wave functions are expanded in a plane-wave basis up to a 17-Ry energy cutoff, and the electronic exchange and correlation energy is treated within the local-density approximation (LDA). Aside from the atomic number and mass of As, the only empirical inputs were the structural data for As in the $A7$ structure,[2] which depends, at each volume, on two parameters.[7] The use of these empirical structural data was necessitated by the prohibitive computational cost of relaxing both parameters at each volume.

The calculated equations of state for As in the sc and $A7$ structures are shown in Fig. 2. They were extracted from least-squares fits of total energy vs volume to a Murnaghan equation of state.[19] A Debye model was used to approximate the zero-point motion correction to the total energy. The experimental errors associated with the empirical structural parameters used in the calculation represent the largest limitation to the accuracy of the calculated equation of state for As in $A7$. With that taken into account, the calculated equations of state of As are in reasonably good agreement with the experimental equations of state of As (Refs. 2 and 3) (see Fig. 2).

According to band theory, As in the sc structure should be a metal with a fairly large $N(E_F)$. At low pressure, the metallic sc phase is unstable with respect to a Peierls-like distortion leading to the lower-symmetry $A7$ phase. In the $A7$ structure, As is semimetallic with a small $N(E_F)$. Figure 3 shows the calculated $N(E_F)$ vs volume for As in the sc and $A7$ structures. The error in the calculation is estimated to be 0.1 (states/Ry)/(spin/atom) and is attributed to an incomplete sampling of the Brillouin zone. When As in $A7$ is compressed toward the phase transition, $N(E_F)$ increases rapidly. Since pressure diminishes the Peierls-like distortion from sc, this concomitant increase in $N(E_F)$ is expected. When As in sc is compressed, $N(E_F)$ decreases very gradually. This behavior is consistent with a free-electron-like picture, in which $N(E_F) \sim V^{2/3}$.

If the sc structure is described as two identical, interpenetrating fcc sublattices, then one of the distortions that transforms sc to $A7$ corresponds to a relative displacement of the fcc sublattices along the [111] direction. The phonon mode corresponding to this displacement can be thought of either as the longitudinal-acoustic mode at the corner of the sc Brillouin zone or as the Γ_1-symmetry optic mode at the center of the $A7$ Brillouin zone. It is this mode that is of interest in relating the structural phase transition to the peak in the superconducting transition temperature.

Figure 4 presents the phonon frequency as a function of volume for both the sc and $A7$ sides of the phase transition. A comparison to a previous calculation[7] is also displayed. For both structural phases, the phonon frequency was extracted from a fit to an even polynomial of the total energy vs distortion from sc. In the sc case,

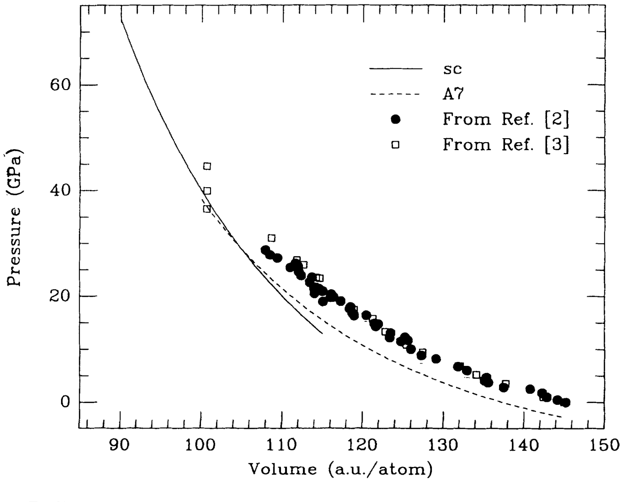

FIG. 2. Equations of state for arsenic. The solid line is the theoretical curve for the sc phase, the dashed line is the theoretical curve for the $A7$ phase, the blackened circles are the experimental measurements of Ref. 2, and the open squares are the experimental measurements of Ref. 3.

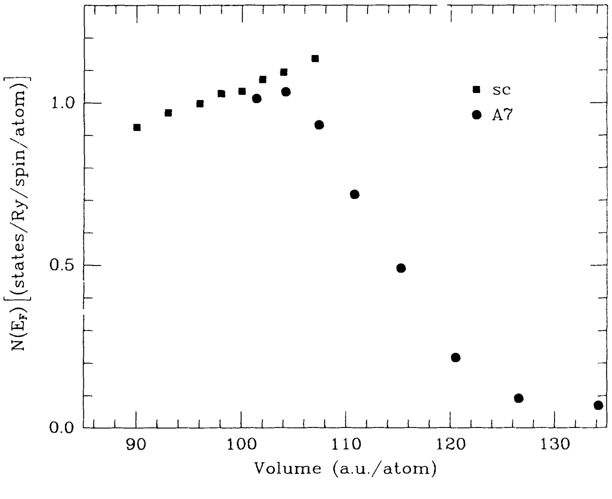

FIG. 3. Calculated electronic density of states at the Fermi level for arsenic as a function of volume per atom. Circles correspond to the $A7$ phase, and squares correspond to the sc phase. The error is approximately 0.1 states/(Ry spin atom).

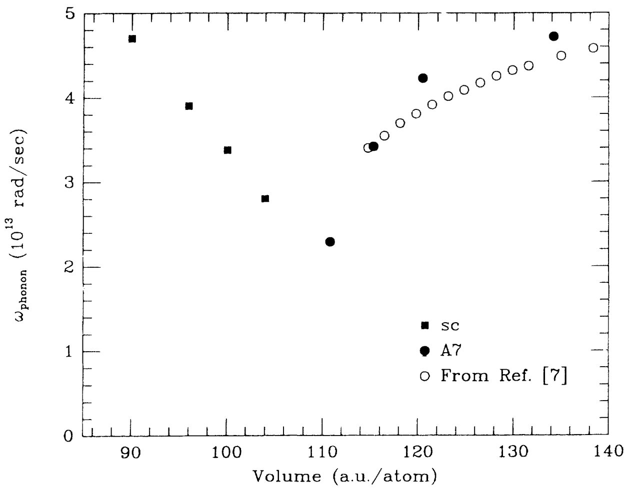

FIG. 4. Calculated frequency of phonon mode in arsenic that corresponds to sc-$A7$ distortion as a function of volume per atom. Circles correspond to the $A7$ phase, and squares correspond to the sc phase. The error is largest near the structural transition.

the polynomials were highly quartic single wells. Since the harmonic definition of phonon frequency fails in this case, the phonon frequency was defined as the energy difference between the ground and first excited states, as calculated by numerically solving the Schrödinger equation. It is reasonable to ignore higher excited states, because the relevant working temperatures (≤ 2.5 K) are much less than the vibrational energy level spacings (typically $\sim 200-300$ K). In the $A7$ case, the total energy vs displacement was usually well fitted by a sixth-order, double-well polynomial. At low pressure the double wells were quite deep. Upon compression toward the phase transition, the position of the well minimum and the depth of the well both decreased. The phonon frequency was calculated by expanding the polynomial to second order around the minimum. This works well at large volumes where the wells are deep but becomes less reliable at volumes near the transition where the wells become quite shallow.

The general trend of the phonon frequency is that as the structural transition is approached from either side, the mode, as expected, softens considerably. A comparison of the calculated phonon frequency for As with experimental values[2] shows good qualitative agreement overall, with good quantitative agreement at low compression.

V. DISCUSSION

Using the results of the theoretical calculation of the pressure dependence of both $N(E_F)$ and the phonon frequency, we can now understand the pressure dependence of the T_c of As.

We begin by examining the dependence of T_c on the average phonon frequency $\langle\omega\rangle$ and on $N(E_F)$ through an idealized McMillan equation:[20]

$$k_B T_c \simeq \hbar\langle\omega\rangle \exp\left(\frac{-1}{\lambda^* - \mu^*}\right), \tag{1}$$

where

$$\lambda^* = \frac{\lambda}{1+\lambda}$$

and (2)

$$\mu^* = \frac{\mu}{1+z\mu}\,, \quad z = \ln\left(\frac{E_F}{\hbar\langle\omega\rangle}\right).$$

The parameter λ is the electron-phonon coupling constant, which is proportional to $N(E_F)$ and inversely proportional to $\langle\omega^2\rangle$, and μ is the Coulomb repulsion pseudopotential, which is approximately proportional to $N(E_F)$. The logarithmic variation of T_c with respect to $\langle\omega\rangle$ and $N(E_F)$ is given by

$$d\ln(k_B T_c) = \left[1 - \frac{2\lambda^{*2}}{(\lambda^*-\mu^*)^2}\frac{1}{\lambda} - \frac{\mu^{*2}}{(\lambda^*-\mu^*)^2}\right] d\ln(\hbar\langle\omega\rangle) + \left[\frac{\lambda^{*2}}{(\lambda^*-\mu^*)^2}\frac{1}{\lambda} - \frac{\mu^{*2}}{(\lambda^*-\mu^*)^2}\frac{1}{\mu}\right] d\ln[\mathrm{N(E_F)}]. \tag{3}$$

If $\lambda \ll 1$, which is valid in the weak-coupling limit, and $\lambda^* > \mu^*$, which is the condition for superconductivity, then Eq. (3) implies that an increase in $\langle\omega\rangle$ decreases T_c, while an increase in $N(E_F)$ enhances T_c.

Our calculations indicate (Fig. 4) that the phonon frequency softens near the structural phase transition, in agreement with previous Raman-scattering results.[2] Because a lower average phonon frequency favors a higher transition temperature, the peak in T_c can then be explained by the minimum in phonon frequency at the phase transition. However, the rate of softening of the phonon frequency is, to the accuracy of our calculations, about the same on both sides of the transition, which cannot explain the slight asymmetry of the peak in T_c. The pressure dependence of $N(E_F)$ accounts for this asymmetry. Both the calculations (Fig. 3) and normal-state resistance measurements (Fig. 1) show that $N(E_F)$ increases strongly with pressure below the $A7$-sc transition and becomes independent of pressure above. Thus the increasing $N(E_F)$ and the decreasing phonon frequencies both contribute to the rapid enhancement of T_c as As is pressurized toward the $A7$-sc transition. Above the transition, further compression does not change $N(E_F)$ considerably, but does stiffen the phonon modes, so that T_c decreases gradually.

Our experimental results consistently place the $A7$-sc transition at 32 ± 1 GPa, in disagreement with Wittig's[12] data. Similar disagreements among earlier experimental investigations with regard to the $A7$-sc transition in As have been reported. In particular, the x-ray diffraction work of Beister, Stössner, and Syassen[2] pinpoint the transition at 24 GPa, while x-ray work by Kikegawa and Iwasaki[3] place the transition between 31 and 37 GPa.

The difficulty in establishing the $A7$-sc transition pressure also extends to the theoretical calculations. It is not possible to predict the $A7$-sc transition pressure and volumes by constructing a common tangent to the two energy vs volume curves, as is often possible for structural phase transitions. This is because the $A7$-sc transition is nearly continuous, and the energy vs volume curves do not cross but merge. Instead we suggest using another method to determine the transition pressure. Since the $A7$-sc transition is nearly continuous, we expect that the $N(E_F)$ and the phonon frequency will also be nearly continuous at the transition. These hypotheses are borne out by Fig. 1 of the present work and Fig. 8 of Ref. 2, respectively. Since $N(E_F)$ and the phonon frequencies vary appreciably with volume we can deduce the transition pressure from the volume, where $N(E_F)$ or the phonon frequencies of the two phases intersect. The calculated $N(E_F)$ for sc and $A7$ (Fig. 3) intersect at a volume of about 102 a.u./atom. According to the equation of state (Fig. 2), this corresponds to a pressure of about 36 GPa, which is in good agreement with the present experiment. An extrapolation of the calculated phonon frequency (Fig. 4) suggests a transition volume that is also consistent with the present experiment, however the large error in this calculation near the transition makes this prediction less reliable.

The fact that the total energy of both the $A7$ and sc phases are very nearly the same over a large pressure range causes the transition to be very sensitive to pressure inhomogeneity. For example, since the $A7$ phase is essentially a distorted sc phase, a uniaxial component in the stress may favor the $A7$ phase and thus suppress the transition until a higher average pressure is reached. The validity of such a hypothesis requires further investigation.

VI. CONCLUSIONS

We have measured the superconducting transition temperature and the normal-state resistance of elemental As as it is pressurized through the rhombohedral $A7$ to simple cubic structural phase transition. We observe an asymmetric peak in T_c at 32 GPa associated with this structural transition, and different pressure dependence in the normal state resistance above and below this transition. We perform first principles calculations of the pressure dependences of both $N(E_F)$ and the phonon frequency in both phases. The experimental results are qualitatively explained by the calculated behavior of $N(E_F)$ and the phonon frequencies as functions of volume.

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