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High-pressure crystal structures of TaAs from first-principles calculations

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ABSTRACT

In this work, we systematically studied the phase transition of TaAs under high pressures and reported three high-pressure structures *P*-6*m*2 (hexagonal, stable at 13–32 GPa), $P2_1/c$ (monoclinic, stable at 32–103 GPa) and *Pm*-3*m* (cubic, stable above 103 GPa), by using particle swarm optimization in combination with first principles electronic structure methodology. All predicted structures are dynamically stable, since there is no imaginary mode to be found in the whole Brillouin zone. At high pressures, the TaAs was found to become superconductor with the superconducting critical temperature of ~1 K at about 100 GPa.

1. Introduction

Weyl fermion was first predicted in 1929, it has not been observed in experiment. It possesses unique properties and can be used for quantum computers [1]. Recently, it could be understood that a Weyl fermion can emerge as a quasiparticle in certain crystals, Weyl fermion semimetals [1–16]. A Weyl semimetal is an unusual crystal where electrons behave as massless quasi-particle. Its electronic structure displays pairs of Weyl points connected by topological surface states, forming a unique arc-like Fermi surface.

Recently, TaAs was identified to be the topological semimetal by first-principles calculations, which greatly facilitates an exploration of Weyl physics in real materials [17–20]. However, the high-pressure research of TaAs is still scarce. At high pressure, the energy band gap of materials can overlap at sufficiently high pressure. Once these materials become good metal, they are possible to become good superconductors. A recent experimental work with Raman measurements [21] suggested two possible phase transitions, and its theoretical predictions also suggest two candidate crystal structures. However, to best of our knowledge, there is no detailed study on superconductivity and crystal structures at ultra-high pressure.

In this work, we have extensively explored the high-pressure phases of TaAs by using extensive structure searching in conjunction with first-principles calculations. A novel hexagonal structure of *P*-6*m*2 was found to be stable at 13 GPa. At higher pressure, a monoclinic $P2_1/c$ is more stable than *P*-6*m*2 at 32 GPa. At 103 GPa, the enthalpy of a cubic *Pm*-3*m* structure becomes more favorable. The enthalpy of all predicted structures is calculated to show that they are dynamically stable. Furthermore, the superconductivity is examined. The calculated superconducting critical temperature of TaAs reaches 1 K at about 100 GPa.

2. Methods

Our approach is based on a global minimization of free energy surfaces via PSO technique as implemented in CALYPSO (crystal structure AnaLYsis by particle swarm optimization) code [22,23], which was unbiased by any prior known structures. The approach has correctly predicted the crystal structures of a diverse variety of materials [24–29]. The underlying ab initio structure relaxation was performed using density-functional theory within projector augmented wave method as implemented in the Vienna Ab-inito Simulation Package code (VASP) [30–32]. The projector augmented wave (PAW) potentials [33] used here were derived using the generalized gradient approximation (GGA) [34] functional with valence electrons of $5d^36s^2$ and $4s^24p^3$ for Ta and As, respectively, suitable for the high-pressure study. A plane-wave

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kinetic energy cutoff of 800 eV and the use of Monkhorst–Pack *k*-points meshes of $12 \times 12 \times 12$, $6 \times 5 \times 6$, $16 \times 16 \times 16$, and for *P*-6*m*2, $P2_1/c$ and *Pm*-3*m* in the Brillouin zones produced enthalpy results well converged to below 1 meV/atom, respectively. The electron–phonon coupling properties were examined using linear response theory as implemented in Quantum Espresso package [35]. A MP grid of $16 \times 16 \times 16$ for *Pm*-3*m* was used to ensure *k*-point sampling convergence with Gaussians of width 0.03 Ry, which approximates the zero-width limits in the calculations of electron–phonon coupling constant parameter λ.

3. Results and discussion

To explore crystal structures of TaAs at high pressures, we have performed in the pressure range of 0–120 GPa with 1–4 f.u. per simulation cell. At ambient pressure, our structure predictions successfully reproduced the experimental $I4_1md$ structure. At higher pressure, our structural searches identified three high-pressure structures with *P*-6*m*2, $P2_1/c$ and *Pm*-3*m* space groups at different pressures, respectively. The structural parameters of these three phases are listed in Table 1. It is noteworthy that *P*-6*m*2, $P2_1/c$ phases are also predicted by recent theoretical work [21]. It is interesting to see that the coordination of Ta increased from 6 (*P*-6*m*2) to 7 ($P2_1/c$) and then to 8 (*Pm*-3*m*) as shown in Fig. 1. Moreover, it suggests that TaAs can adopt a dense cubic packing structure at sufficiently high pressure. The enthalpy $H=U+PV$ determined the stability of different phases at 0 K. As calculations suggested, the cubic phase possesses the smallest volume (24.47 Å^3/f.u.) compared to the *P*-6*m*2 (31.92 Å^3/f.u.) and $P2_1/c$ (29.01 Å^3/f.u.) phases.

Furthermore, we examined the enthalpies of the newly predicted stable phases which are plotted as a function of pressure in Fig. 2 to compare with the experimental $I4_1md$ structure. It clearly shows that this $I4_1md$ structure is the most stable phase up to 13 GPa, beyond which our hexagonal *P*-6*m*2 structure becomes most favorable up to 32 GPa. In the pressure range of 32–103 GPa, the monoclinic $P2_1/c$ structure becomes the most stable phase. At higher pressure (above 103 GPa), the enthalpy of cubic *Pm*-3*m* structure begins to become more favorable. In order to examine the dynamical stability, we calculated phonon dispersion curves for these three high-pressure structures using the supercell method as implanted in PHONOPY software package. No imaginary phonon frequencies are found in their low-enthalpy pressure range in the whole Brillouin zone (Fig. 3), indicating that they are dynamically stable phases.

Previous experiment and theory suggest TaAs is a weyl semimetal. There are "Weyl cones" and "Weyl nodes" to be found at around bulk or surface electronic band structures. The pressure is well known to alter chemical bonding environment and may significantly revise the electronic band structures. Therefore, it is important to explore the evolution of electronic structure for TaAs at high pressures. In Fig. 4(a)–(c), we have calculated electronic band structures of TaAs in the absence of spin–orbit coupling for *P*-6*m*2, $P2_1/c$ and *Pm*-3*m* structures at 20, 40 and 110 GPa, respectively. It is noteworthy that TaAs still has a band touch point along some direction (Fig. 4a and b) at high pressures. For instance, there is a semimetal point for *P*-6*m*2 phase along K–Γ direction and for $P2_1/c$ structure along Γ–Y direction. However, at higher pressure, TaAs becomes a good metal due to the strong overlap between

Table 1
Calculated lattice constants (Å), atomic positions and bond lengths for *P*-6*m*2, $P2_1/c$ and *Pm*-3*m* phases at ambient pressure.

Structure	*P*-6*m*2	$P2_1/c$	*Pm*-3*m*
Lattice constants (Å)	$a=3.409$ $c=3.488$	$a=6.141$, $b=4.896$ $c=6.221$, $\beta=130°$	$a=3.212$
Atom positions	Ta (0.667, 0.333, 0) As (0.333, 0.667, 0.5)	Ta (0.816, 0.144, 0.708) As (0.309, 0.354, 0.226)	Ta (0, 0, 0) As (0.5, 0.5, 0.5)
Bond lengths (Å)	Ta–As 2.629	Ta–As1 2.714 Ta–As2 2.717 Ta–As3 2.762 Ta–As4 2.647 Ta–As5 2.715 Ta–As7 2.646 Ta–As7 3.384	Ta–As 2.781

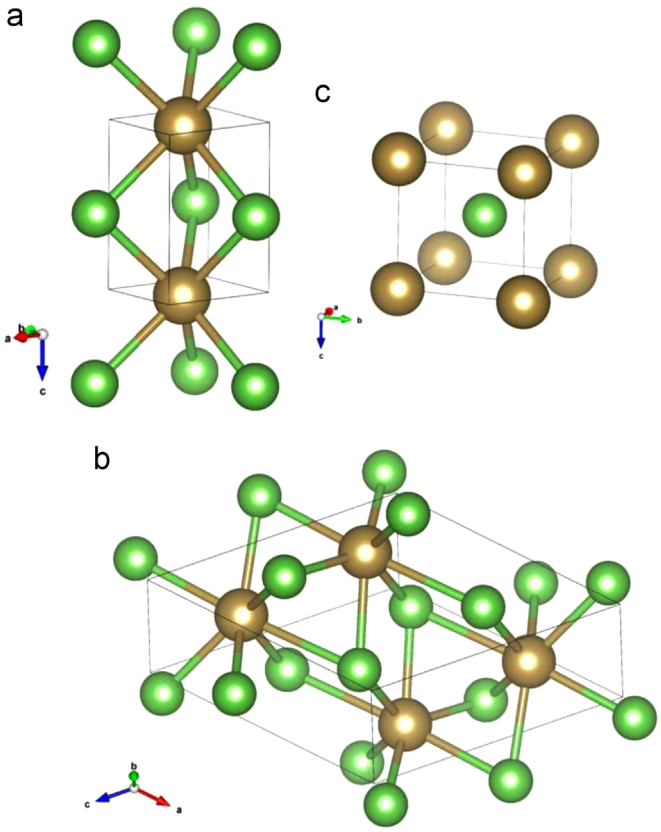

Fig. 1. (Color online) Predicted TaAs structures. (a) *P*-6*m*2, (b) $P2_1/c$ and (c) *Pm*-3*m* phase. The yellow brown and green spheres represent Ta and As atoms, respectively.

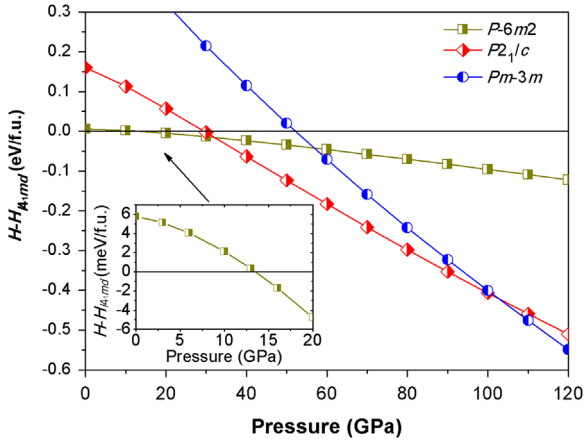

Fig. 2. (Color online) Calculated enthalpies per formula unit as functions of pressure between 0 and 120 GPa with respect to $I4_1md$ structure. Inset shows enthalpy versus pressure for *P*-6*m*2 structure relative to that of the $I4_1md$ structure.