Unexpected High Temperature Superconductivity in Titanium

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Abstract

Titanium metal is a prominent material that finds wide applications under extreme conditions, and its behaviors at synergetic high-pressure, low-temperature and high-magnetic-field conditions attract significant scientific research. Here we report discovery of superconductivity of titanium with an onset critical temperature of $T_{c_{onset}}$ above 26 K and zero-resistance $T_{c_{zero}}$ of 22 K at high pressures, which are record high values of $T_c$ hitherto achieved among elemental superconductors. The measured $T_c$ increases under pressure steadily across the $\omega$ phase, followed by a steep rise to about 20 K in the $\gamma$ phase around 100 GPa, reaching 26 K in the $\delta$ phase around 248 GPa, before descending slightly at further rising pressure of 310 GPa. The upper critical field of the 26 K superconducting phase is estimated to be 32 Tesla, which corresponds to a Ginzburg Landau (GL) coherent length of about 32 Å. First-principles calculations confirm experimental structural stability and transformation sequences and, more importantly, reveal intricate joint effects of enhanced carrier density and vibrational energy scale along with phonon softening that lead to strengthened electron-phonon coupling, thereby generating the unexpected high $T_c$ in titanium. Theoretical analysis also highlights major effects of non-hydrostatic pressure on $T_c$ under extreme compression.
Titanium (Ti) metal has long attracted tremendous scientific interest because of its special outer shell electron configuration of 3d²4s² that leads to uniquely combined properties of light weight, high strength and corrosion resistance. As an advanced structural elemental metal, Ti and its alloys have been widely applied in the field of aerospace[11], biomedicine[2] and under extreme conditions such as high-temperature and corrosive environment[3]. High pressure is powerful in modifying crystal structures which, in turn, may lead to new functionalities. At ambient pressure and room temperature, Ti crystalizes into a hexagonal close-packed (hcp) structure (Ti-α phase)[13]. Under applied pressure, Ti undergoes structural transitions in the sequence of Ti-α, Ti-ω, Ti-γ, Ti-δ and Ti-β phases, where Ti-ω phase is a hexagonal structure, Ti-γ and Ti-δ phases are orthorhombic and Ti-β phase is body-centered cubic[14-19]. The α-to-ω phase transition occurs around 8 GPa[5,6], and the Ti-ω phase is stable up to about 100 GPa, then transforms into Ti-γ phase[6,10], which further transforms into the Ti-δ phase at ~140 GPa[18], before cubic Ti-β phase stabilizes at 243 GPa[19].

Generally, compression of crystal lattice has different effects on the energies of the 4s and 3d bands and causes the 3d bands to be favorably occupied, leading to s-d electron transfer, which also impacts properties of transition metals, heavy alkali and alkali earth metals.[11,12]. Because of the narrow d-band characteristic, the s-d transfer would lead to a higher electron density of state (DOS) near the Fermi level, which is favorable to superconductivity (SC). The s-d transfer has been suggested to dominant the process of achieving Tc values up to ~20 K in select elemental metals under pressure[13-16]. Meanwhile, SC in Ti under pressure reported so far has a maximal Tc =3.5 K at 56 GPa[17]. Here, we report a dramatic pressure enhanced SC with Tc=26 K in Ti, which sets a new record of Tc among transition metals. Our theoretical studies based on first-principles calculations produce structural stability and transformation that are consistent with experimental results. Moreover, electronic and phonon calculations reveal intricate interplays of enhanced carrier density and characteristic vibrational energy scale along with softening of select optical phonon modes that produce notably strengthened electron-phonon coupling, leading to record high Tc values. Our study also highlights major effects of non-hydrostatic pressure that enhance Tc at high pressures, offering further insights into the underlying mechanisms responsible for the extraordinary structural and SC behaviors in highly compressed Ti metal.

Electrical resistance and Hall effect were measured by the four-probe method. The Van der Pauw method was used with an applied current of 100 μA. Diamond anvils with beveled anvils (30/300 μm) were used to produce high pressure up to 310 GPa. A plate of T301 stainless steel covered with c-BN powder was used as the gasket, and a hole of approximately 30 μm in diameter was drilled as the sample chamber. hBN powder was filled in the high-pressure chamber to act as pressure-transmitting medium. We used the ATHENA procedure to produce the specimen assembly[18]. Four triangular Pt foils with thickness of 0.5 μm as the inner electrode were deposited on the surface of the culet of the diamond anvil. Cross-shaped Ti specimens with side lengths of 10μm×10μm and thickness of 1 μm were stacked on the electrodes. Pressure was calibrated by the shift of the first order Raman edge frequency from the diamond cutlet. Diamond anvil cells were put into a MagLab system for transport measurements, which provide synergetic extreme environments with temperatures from 300 K to 1.5 K and magnetic fields up to 9 T[18-21].

In-situ high-pressure angle-dispersive X-ray diffraction data were collected at room temperature at GSECARS of Advanced Photon Source at the Argonne National Laboratory. The
x-ray with the wavelength $\lambda = 0.3344$ Å was focused down to a spot of ~3 μm in diameter on the sample. A symmetric diamond anvil cell with beveled anvil (50/300 μm) was used. Rhenium steel gasket was pre-pressed to a thickness of 20 μm, and a hole of diameter of 15 μm was drilled at the center to serve as sample chamber, which was then filled with Ti power mixed with Pt. Pressure was calibrated using the equitation of state of both Re and Pt.

To establish structural, electronic, phonon properties and determine electron-phonon coupling in Ti under pressure, we have performed calculations to determine the total energy, lattice dynamics and electron-phonon coupling (EPC) using the QUANTUM ESPRESSO code\textsuperscript{22}. Superconducting critical temperature $T_c$ has been evaluated based on the Eliashberg theory of superconductivity\textsuperscript{23,24}, using the following formula that McMillan derived\textsuperscript{25} and later modified by Allen and Dynes\textsuperscript{26},

$$T_c = \frac{\omega_{\text{log}}}{1.20} \exp[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}]$$

where $\omega_{\text{log}}$ is a logarithmically averaged characteristic phonon frequency, and $\mu^*$ is the Coulomb pseudopotential which describes the effective electron-electron repulsion\textsuperscript{27}. This equation is generally accurate for materials with EPC parameter $\lambda$ at 1.5 or less\textsuperscript{28-31}, which is mostly satisfied in the present study. The Coulomb pseudopotential $\mu^*$ is often treated as an adjustable parameter with values within a narrow range around 0.1 for most materials, making this formulism highly robust\textsuperscript{26-30}, and compares well with the latest \textit{ab initio} Eliashberg theory\textsuperscript{31}. In this work, $\mu^*$=0.13 provides a good description of the experimentally measured $T_c$ results, and this value is thus adopted for all the reported calculations.

Fig. 1a presents the experimentally measured temperature dependence of electrical resistance under high pressure up to 180 GPa for elemental metal Ti in experiment Run 1. The results show that Ti metal becomes superconductive with $T_c$ above 2 K at 18 GPa, which is enhanced slightly to ~3.5 K at 54 GPa, similar to the previously reported results\textsuperscript{17}. The value of $T_c$ increases at an enhanced pace from 54 to 99 GPa, then undergoes a steep rise from 10.2 K at 99 GPa to 20.3 K at 108 GPa, and $T_c$ is further enhanced to 22 K at 180 GPa. For experimental Run 2, higher pressures were applied with the highest pressure of 310 GPa. The resistance curves under pressure is shown in Fig. 1b. With further increasing pressure the $T_c$ reaches a maximum of 26 K at 248 GPa, as shown in Fig. 1c. The onset critical temperature ($T_c^{\text{onset}}$), the midpoint critical temperature ($T_c^{\text{mid}}$) and the zero-resistance critical temperature ($T_c^{\text{zero}}$) of superconducting transition are determined by the derivative of resistance with respect to temperature $dR/dT$ as shown in the inset of Fig. 1b. The transition width defined as the difference of $T_c^{\text{onset}}$ and $T_c^{\text{zero}}$ is about 4 K, indicating high quality homogeneous superconducting phase is achieved in the specimen. It is noted that $T_c$ stays almost constant over a wide pressure range up to at least 240 GPa that is the maximum pressure reached in our experiments. These results are consistently seen in different specimens (Fig. S1). At 108 GPa where $T_c$ has a jump up, the resistance exhibits a two-step superconducting transition behavior with the lower $T_c$ of ~11 K that is comparable to the $T_c$ value at 99 GPa, indicating a phase transition near 108 GPa, which is close to the pressure for the reported $\omega-\gamma$ phase transition \textsuperscript{6,10}. In the Ti-$\omega$ phase, $T_c$ rises smoothly with pressure below 56 GPa with a slope of 0.07 K/GPa; assuming this slope keeps unchanged, $T_c$ should reach 8.7 K before the $\omega-\gamma$ phase transition (at 128 GPa)\textsuperscript{17}. However, our results show that the slope $dT_c/dP$ increases significantly between 54-99 GPa, which leads to the much higher measured $T_c$ at 99 GPa.
To confirm the pressure driven SC phase of Ti metal, we have examined the effect of magnetic field on the SC transition behavior. Fig. 2a presents the electrical resistance measured at 248 GPa and under different magnetic fields. It is seen that the transition is gradually suppressed by the magnetic field. We have plotted onset Tc versus magnetic field in Fig. 2b, from which the upper critical field at zero temperature $\mu_0H_{c2}(0)$ can be estimated. The $\mu_0H_{c2}(T)$ date were fitted to the Ginzburg Landau (GL) function $\mu_0H_{c2}(T) = \mu_0H_{c2}(0)(1 - (T/T_c)^2)$, which gives a value of $\mu_0H_{c2}(0)=32$ T. At other pressures where Tc is above 20 K, the estimated upper critical field has also been obtained to be near 30 T. [Fig. S1(a-d)], which is larger than that of the most commonly used low-temperature NbTi superconductor ($\mu_0H_{c2}(T)=15$ T). Using the $\mu_0H_{c2}(T)$ value of 32 T, the GL coherence length was calculated to be $\xi=32$ Å via $\mu_0H_{c2}(0)=\Phi_0/2\pi\xi^2$, where $\Phi_0=2.067\times10^{-15}$ Web is the magnetic flux quantum.

Fig. 3(a,b) presents the measured Hall resistance at room temperature and different pressures. The Hall resistance is negative and decreases linearly with magnetic field, indicating that the dominant carriers are electrons. The carrier density $n$ as a function pressure estimated from the Hall resistance is presented in Fig. 3(c), with a value of about $2.5\times10^{22}/\text{cm}^3$ that is little changed in the low-pressure range. When pressure exceeds 108 GPa, $n$ increases dramatically and is enhanced by more than one order of magnitude to $3.1\times10^{22}/\text{cm}^3$ at 137 GPa. Further increasing pressure leads to reduced carrier density of $4.5\times10^{22}/\text{cm}^3$ at 144 GPa. The changes of the carrier density indicate phase transitions at pressures of about 108 GPa and 144 GPa, respectively. To see more clearly these phase transitions, the pressure dependence of resistance $R(P)$ at fixed temperature is plotted in Fig. 3(d). The $R(P)$ curve shows two peaks near the critical pressures, which corresponds to the $\omega-\gamma$ phase and $\gamma-\delta$ phase transitions reported by Y. Akahama$^{[9]}$ and Y. K. Vohra$^{[10]}$, respectively.

To study the phase transition, we have carried out the high-pressure X-ray diffraction experiments, as shown in Fig. S2. Combining the phase transition reported by previous works and our transport experiments, we plot the superconducting and structural phase diagram shown in Fig. 4. Up to 310 GPa, five different crystal structures, in the sequence of Ti-$\alpha$, Ti-$\omega$, Ti-$\gamma$, Ti-$\delta$ and Ti-$\beta$ are identified. The Ti-$\alpha$ phase ($P=0~9$ GPa) hosts SC with Tc below 2 K; the Ti-$\omega$ phase ($P=9~108$ GPa) sees a monotonously increasing Tc with pressure to 12 K at ~108 GPa; while in the high-pressure phases of Ti-$\gamma$ ($P=108~144$ GPa) and Ti-$\delta$ ($P=144~240$ GPa), Tc stays above 20 K with the maximum Tc =26 K occurring at the boundary of phases Ti-$\gamma$ and Ti-$\delta$.

Among all elemental solids, only a few have been reported to exhibit SC with Tc above 20 K at high pressures, including alkali metal Li (Tc= 16-20 K at 30-50 GPa)$^{[32, 33]}$, alkali-earth metal Ca (Tc~21 K)$^{[34]}$, rare-earth metals of Sc (Tc=19.6 K at ~107 GPa)$^{[14]}$ and Y (Tc=20 K at ~115 GPa)$^{[15]}$. The high Tc values of Li, which is the lightest element metal containing only simple 2s-electrons, is attributed to the enhancement of the electron-phonon coupling due to the phonon modes softening under high pressure$^{[35, 36]}$, while the role of Tc enhancements in Sc, and Y are mainly ascribed to pressure induced electron transfer from $s$ to $d$ shell. For transition metal V, Sc with Tc= 17.2 K was observed at 120 GPa$^{[16]}$, and it was suggested that this high Tc value is due to the synergy of pressure modified electronic density of states near the Fermi level N(E_f), electron-phonon coupling strength and Debye temperature$^{[37]}$.

We have examined the relative energetic stability of various phases of Ti metal from
systematic first-principles total energy calculations, and the results shown in Fig. S3(a) are consistent with the experimentally measured phase stability and transformation sequence under high pressure. Possible kinetic effects and non-hydrostatic pressure environments in the sample chamber may explain the scattering of the experimentally estimated phase boundaries and their quantitative discrepancies with theoretical results. Adopting the determined crystal structures of the Ti metal phases, we have calculated their electronic, phonon and electron-phonon coupling properties, which are used as input to determine the SC critical temperature $T_c$. The results are presented in Fig. S3(b), and the following phenomena are observed: (i) $T_c$ increases with rising pressure monotonically in the Ti-$\omega$ phase over its entire stability range; (ii) $T_c$ is significantly enhance upon the phase transition into the Ti-$\gamma$ phase over the relatively narrow pressure range where this transition occurs (note that the higher experimental transition pressure may be caused by kinetic effects or non-hydrostatic pressure); (iii) $T_c$ undergoes an even larger jump when the structure enters the Ti-$\delta$ phase (the higher transition pressure once again may be due to kinetic or non-hydrostatic pressure effects). These findings are in good agreement with the experimental observations. An in-depth analysis of the calculated results show that these interesting trends and results are driven by a combination of changes in the electronic density of states, characteristic phonon energy scale, and softening of select phonon branches (see Figs. S4 and S5 for the pressure evolution of these quantities), which are all sensitive to structural changes associated with the structural changes and transitions, leading to enhanced electron-phonon coupling and significant increases of $T_c$ at high pressures.

Interestingly, it is noted that the $T_c$ values of the Ti-$\delta$ phase obtained under hydrostatic pressure conditions are underestimated at high pressures, e.g., 180 and 220 GPa. Non-hydrostatic pressures, which commonly exist inside the sample chamber of diamond anvil cells and are especially prominent at very high pressures, may be a major driver for such behaviors. To verify this possibility, we have carried out further calculations by introducing a uniaxial compressive stress in addition to the previously indicated hydrostatic pressures, and the resulting $T_c$ values are indeed significantly moved toward to the values that are more consistent with the experimental data, in terms of the quantitative values and overall trend. These results show that non-hydrostatic pressure conditions promote changes in the structural, electronic and phonon properties that lead to significantly enhanced electron-phonon coupling and SC in Ti metal. It is expected that consideration of realistic experimental stress conditions may modify the $T_c$ values and potentially further improve the agreement between the theory and experiment at higher pressures.

This study unveils record-setting superconductivity among elemental solids in the high-pressure phases of Ti metal. This discovery raises intriguing new possibility of finding more materials that exhibit pressure-driven superconductivity with much higher $T_c$ values than previously believed achievable. The present results offer considerable impetus for further exploration and in-depth evaluation of wide-ranging material classes, from elemental solids to alloys, in search of hitherto unknown and unexplored superconductors that may lead to discoveries that could impact not only fundamental understanding of broader varieties of superconductors but, equally important, their practical implementation in greatly expanded and diverse applications.
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Fig. 1. (a) Temperature dependence of the electrical resistance of elemental metallic Ti (sample 1) measured under high pressures. The inset is an enlarged view of the resistance curve, showing the superconducting transition in detail. (b) The resistance curves for Ti sample 2. (c) The resistance curve measured at 248 GPa, where the derivative of the resistance with respect to temperature $dR/dT$ is plotted to clearly show the onset $T_c$. 
Fig. 2. (a) Temperature dependence of the electrical resistance of Ti metal measured under different magnetic fields at the fixed pressure of 248 GPa. (b) Upper critical field versus superconducting transition temperature of $T_c^\text{zero}$. The line is a fit obtained using the Ginzburg–Landau function.
Fig. 3. (a,b) Hall resistance as a function of magnetic field measured under different pressure. (c-e) Carrier density, resistance at fixed temperature, and onset $T_c$ versus pressure, respectively. The yellow and blue areas mark the anomaly of these data, indicating the critical pressures where the phase transitions occur.
Fig. 4. The superconducting and structural phase diagram for Ti metal.
Supplementary materials

Fig. S1 (a) The superconducting transitions measured under different magnetic fields at 154 GPa. (b) The upper critical field versus onset Tc and the Ginzburg–Landau fitting. (c,d) Same quantities with data taken at the pressure of 177 GPa.
Fig. S2. The in-situ high pressure X-ray diffraction patterns with the highest experimental pressure of 225 GPa, using the wavelength of 0.3344 Å.

Fig. S3. (a) The energy of various phases of Ti metal relative the value of Ti-β (bcc) obtained from first-principles calculations; (b) the superconducting critical transition temperature (Tc) of the indicated Ti phases in the pressure range of [20, 220] GPa, where the solid and open symbols represent the respective values obtained under hydrostatic and non-hydrostatic pressure conditions with the latter case containing a uniaxial compressive stress in additional to the indicated nominal hydrostatic pressure.
Fig. S4. Phonon dispersions of Ti-w phase (a-c) and Ti-d phase at selected pressure values and conditions, along with the corresponding spectral function $\alpha^2 F(\omega)$ and $\lambda(\omega)$ shown in (d, h) by the dashed lines in the same color as the solid lines in the phonon dispersion curves.

Fig. S5. Calculated electronic density of states at the Fermi level ($N_{\text{Ef}}$), logarithmically averaged characteristic phonon frequency ($\omega_{\text{log}}$) and electron-phonon coupling parameter ($\lambda$) at selected pressure values and conditions.