First-principles study of the robust superconducting state of NbTi alloys under ultrahigh pressures

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Abstract: A recent experiment reported that robust superconductivity appears in NbTi alloys under ultrahigh pressures with an almost constant superconducting $T_c$ of $\sim$19 K from 120 to 261.7 GPa [J. Guo et al., Adv. Mater. 31, 1807240 (2019)], which is very rare among the known superconductors. We investigate the origin of this novel superconducting behavior in NbTi alloys based on density functional theory and density functional perturbation theory calculations. Our results indicate that the pressure tends to transform NbTi alloys from a random phase to a uniformly ordered crystal phase, and the exotic robust superconductivity of NbTi alloys can still be understood in the framework of BCS theory. The Nb element in NbTi alloys plays a dominant role in the superconductivity at low pressure, while the NbTi crystal with an alternative and uniform Nb and Ti atomic arrangement may be responsible for the stable superconductivity under high pressures. The robust superconducting transition temperature of NbTi under ultrahigh pressure can be explained by a synergistic effect of the enhanced phonon frequency, the modestly reduced total electron-phonon coupling, and the pressure-dependent screened Coulomb repulsion.

I. INTRODUCTION

Pressure has played an important role in both synthesizing new superconductors and modulating the superconductivity of existing materials. For unconventional superconductors, the highest superconducting transition temperature $T_c$ of 164 K was achieved in the cuprate $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ under 31 GPa, in comparison, the highest $T_c$ of iron-based superconductors was observed in rare-earth iron oxyarsenides, while SmFeAsO$_{1-x}$F$_x$ was synthesized under 6 GPa. On the side of conventional superconductors, according to BCS theory, dense hydrogen was estimated to become a high-$T_c$ superconducting metal at high pressure half a century ago. Later, hydrides were prepared under ultrahigh pressures to avoid the difficulty in metallizing hydrogen. Several experimental breakthroughs have taken place in recent years: sulfur hydride shows a $T_c$ of 203 K at 155 GPa, and lanthanum superhydride possesses a record $T_c$ of $\sim 260$ K around 190 GPa, while the prominent isotope effect indicates their conventional character. Beyond those superconducting compounds consisting of metallic and nonmetallic elements, the superconducting alloys are also a large family of superconductors. Recently, robust superconductivity was observed in several superconducting alloys from ambient to ultrahigh pressures.

Among the alloy superconductors, NbTi alloys are a well-known commercial superconducting material with superior properties, such as high critical magnetic field $H_{c2}$, high critical current density $I_c$, an accessible superconducting transition temperature $T_c$, easy workability, etc. A fresh experiment reported the robust superconductivity in NbTi alloys under ultrahigh pressures, where $T_c$ of 19 K and $H_{c2}$ of 19 T set the corresponding records among all known transition-metal-alloy superconductors. Astonishingly, NbTi alloys remain at an almost constant $T_c$ of $\sim$19 K in a wide pressure range from 120 to 261.7 GPa and keep the bcc lattice structure under all measured pressures.

II. METHOD

The electronic structure, phonon dispersion, and EPC strength of the NbTi crystal under the pressure range from 0 to 250 GPa were studied with density func-
tional theory and density functional perturbation theory calculations as implemented in the QUANTUM ESPRESSO (QE) package. The interactions between electrons and nuclei were described by the norm-conserving pseudopotentials. The valence electron configurations were 4s²4p⁶4d⁴5s¹ for Nb and 3s²3p⁶3d²4s² for Ti. For the exchange-correlation functional, the generalized gradient approximation of Perdew-Burke-Ernzerhof type was adopted. The kinetic energy cutoff of the plane-wave basis was set to be 160 Ry. The Gaussian smearing method with a width of 0.004 Ry was employed for the Fermi surface broadening. In structural optimization, both lattice constants and internal atomic positions were fully relaxed until the forces on all atoms were smaller than 0.0002 Ry/bohr.

The superconducting $T_c$ of the NbTi crystal was calculated based on the EPC theory as implemented in the EPW package, which uses the maximally localized Wannier functions and interfaces with QE. We took the $6 \times 6 \times 6$ k mesh and $q$ mesh as coarse grids and interpolated to the $108 \times 108 \times 108$ k-mesh and $12 \times 12 \times 12$ q-mesh dense grids. The EPC constant $\lambda$ can be calculated either by the summation of the EPC constant $\lambda_{qv}$ in the full Brillouin zone for all phonon modes or by the integral of the Eliashberg spectral function $\alpha^2 F(\omega)$ as

$$\lambda = \sum_{qv} \lambda_{qv} = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega.$$  

(1)

The Eliashberg spectral function $\alpha^2 F(\omega)$ is defined as

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(\varepsilon_F)} \sum_{qv} \delta(\omega - \omega_{qv}) \frac{\gamma_{qv}}{\hbar\omega_{qv}}.$$  

(2)

where $N(\varepsilon_F)$ is the density of states (DOS) at the Fermi level $\varepsilon_F$, $\omega_{qv}$ is the frequency of the $\nu$th phonon mode at the wave vector $q$, and $\gamma_{qv}$ is the phonon linewidth.

The superconducting transition temperature $T_c$ can be estimated by substituting the EPC constant $\lambda$ into the McMillan-Allen-Dynes formula:

$$k_B T_c = \frac{\hbar \omega_{qv}}{2} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda(1 - 0.62\mu^*) - \mu^*} \right],$$  

(3)

where $\mu^*$ is an effective screened Coulomb repulsion constant. In general, $\mu^*$ is treated as a semiempirical parameter between 0.1 and 0.2. In our calculations, $\mu^*$ was set by two strategies for comparison: (1) a constant of 0.15 and (2) a pressure-dependent one $\mu^*(p)$ with $\mu^* = 0.26 N(\varepsilon_F)/[1 + N(\varepsilon_F)]$. $\omega_{qv}$ is the logarithmic average of the Eliashberg spectral function,

$$\omega_{qv} = \exp \left[ \frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right].$$  

(4)

III. RESULTS

According to a previous x-ray diffraction (XRD) experiment, the NbTi alloy retains a bcc structure under all measured pressures. In real NbTi alloys, the Nb and Ti atoms may distribute randomly in a bcc lattice. We thus considered two limits: one is the uniform “NbTi crystal” with the Nb and Ti atoms arranging alternately (as shown in the inset of Fig. 1(a)); the other is the pure Nb and Ti elemental crystals that also have a bcc structure but locate in different domains of materials. A real NbTi alloy is, to some degree, between these two extreme forms. Figure 1(a) shows the calculated lattice constants of the NbTi crystal (black dots), Nb elemental crystal (blue dots), and Ti elemental crystal (red dots) in comparison with the measured values of NbTi alloys in a previous XRD experiment (black circles) under pressure. The inset shows the structure of CsCl-type NbTi crystal. (b) Enthalpy differences $\Delta H$ between the NbTi crystal and the Nb and Ti elemental crystals: $\Delta H = H(\text{NbTi}) - [H(\text{Nb}) + H(\text{Ti})]$. Calculated (c) superconducting $T_c$, (d) total EPC $\lambda$, and (e) $\omega_{qv}$ of the NbTi crystal in the pressure range of 50 to 250 GPa. In (c), the red and blue circles represent the calculated $T_c$ of the NbTi crystal with $\mu^*$ set to 0.15 and 0.26, respectively. The open circles represent the calculated (red and blue) and experimental (black) superconducting $T_c$ of Nb elemental crystal at ambient pressure.
GPAs, lower than the one between graphite and diamond under pressure\(^{32}\). This suggests the high possibility of the occurrence of this transition (see Appendix A for more details). Therefore, employing NbTi crystal to simulate NbTi alloy under high pressure is reasonable.

To investigate the dynamical stability of NbTi crystal, we calculated its phonon dispersions under different pressures (Fig. 2). At 0 GPa, there is a large portion of imaginary frequencies across the Brillouin zone: the \(M\) point, the \(\Gamma\)-\(M\) path, the \(\Gamma\)-\(R\) path, the \(R\)-\(X\) path, and so on. This indicates that the uniform NbTi crystal is unstable at ambient pressure, which is also in accordance with the above enthalpy difference between the NbTi crystal and the Nb/Ti elemental crystals [Fig.1(b)]. The corresponding structural distortions of NbTi may be quite complex, implying the chaotic phase of NbTi alloys and random distributions of Nb/Ti atoms at 0 GPa. In fact, similar destabilization of the bcc phase at low pressure was also reported for Nb metals alloyed with Ti\(^{33}\). The phonon dispersions of the NbTi crystal in the pressure range from 50 to 250 GPa at an interval of 50 GPa are shown in Figs. 2(b) to 2(f). In these cases, almost all imaginary frequencies disappear except for some tiny ones around the \(\Gamma\) point, suggesting that the NbTi crystal is dynamically stable under high pressures, which agrees with the lower enthalpies of the NbTi crystal compared with Nb/Ti elemental crystals beyond 20 GPa [Fig. 1(b)]. With increasing pressure, the phonon modes around the \(M\) point show dramatic changes; meanwhile, the topmost phonon modes shift to higher frequencies due to the strengthened bonding between Nb and Ti atoms.

We further studied the superconducting properties of the NbTi crystal based on the EPC theory\(^{28}\) and calculated the superconducting transition temperature \(T_c\) according to the McMillan-Allen-Dynes formula [Eq. (3)]\(^{29,30}\). Here two strategies were adopted for the effective screened Coulomb repulsion constant \(\mu^*\). The first approach uses a constant \(\mu^*\) of 0.15 [red circles in Fig. 1(c)]. As can be seen, the superconductivity in the NbTi crystal is very robust against pressure. \(T_c\) increases from 21.6 K at 50 GPa to 24.5 K at 150 GPa and then remains above 20 K until 200 GPa, after which it begins to drop gradually. The second approach sets \(\mu^*\) as 0.26\(N(\varepsilon_F)/(1 + N(\varepsilon_F))\). Detailed values of \(N(\varepsilon_F)\) and \(\mu^*\) at different pressures are shown in Table I. With the pressure-dependent \(\mu^*\), the dropping of \(T_c\) after 150 GPa weakens, and \(T_c\) appears more robust under high pressure [blue circles in Fig. 1(c)]. To further confirm the reliability of our calculations, we also calculated the superconducting \(T_c\) of Nb elemental crystal. Its stable \(T_c\) at low pressures and rapid dropping at high pressures\(^{32}\) were also reproduced (see Fig. S1(a) in the Supplemental Material\(^{35}\)).

The pressure-dependent total EPC constant \(\lambda\) and logarithmic frequency \(\omega_{\log}\) of the NbTi crystal are summarized in Figs. 1(d) and 1(e), respectively. As the pressure increases, \(\lambda\) remains almost stable up to 150 GPa and then decreases gradually. Meanwhile, \(\omega_{\log}\) demonstrates a slow growth below 150 GPa and then increases with pressure. These can be understood via the variations of phonon dispersions. As can be seen in Fig. 2, the pressure hardens the phonon frequency on the whole. Nevertheless, the frequency of the lowest acoustic mode at the \(M\) point, i.e., the \(A_{2u}\) mode that provides the largest \(\lambda_{qv}\) [as indicated by the biggest red dots in Fig. 2(c)], shows a nonmonotonic variation: it first decreases and then increases with pressure. Between 50 and 150 GPa, the initial frequency decrease of the \(A_{2u}\) mode offsets the \(\lambda_{qv}\) which are proportional to the sizes of red dots on the phonon dispersions in Figs. 2(b)-2(f).

Table I. The calculated electronic density of states at the Fermi level \(N(\varepsilon_F)\) [in units of states/(eV atom)] and effective screened Coulomb repulsion constant \(\mu^*\) based on the relation: \(\mu^* = 0.26N(\varepsilon_F)/(1 + N(\varepsilon_F))\) under different pressures \(P\) (in GPa) for the NbTi crystal. The values at 0 GPa are from Nb elemental crystal.

| \(P\) (GPa) | 0     | 50    | 100   | 150   | 200   | 250   |
|----------|-------|-------|-------|-------|-------|-------|
| \(N(\varepsilon_F)\) | 1.49  | 1.42  | 1.20  | 1.02  | 0.94  | 0.72  |
| \(\mu^*\) | 0.155 | 0.153 | 0.142 | 0.131 | 0.126 | 0.108 |
Based on the BCS theory, electron than the Nb atom, the NbTi crystal has a lower one (bcc). Second, since the Ti atom has one less valence band splitting due to the lower symmetry of the crystal. Tc of Nb-based high-entropy alloys, it was reported that the superconductivity. In previous studies on Nb-based high-superconducting property. Actually, the observed superconducting Tc of 9.6 K in NbTi alloys at ambient pressure is very close to that of the Nb element (9.3 K) [Fig. 1(c)]. Under high pressure, the NbTi alloy gradually transforms to a uniform NbTi crystal phase [Fig. 1(b)], as verified by the consistent lattice constants between our calculations and the measured ones [Fig. 1(a)]. The homogeneous arrangement of Nb/Ti atoms in the NbTi crystal under high pressure promotes the electron transfer from Nb to Ti, which increases the density of states at the Fermi level (Fig. 3) and thus enhances the superconducting Tc. In the pressure range from 50 to 150 GPa, the A2u phonon mode at the M point with strong EPC has an abnormal softening (Fig. 2). This offsets partial influences of pressure on λ and ωlog [Figs. 1(d) and 1(e)], thus reducing the variation of Tc. At 150 GPa, the phonon softening at the M point becomes quite strong. Its relation to the electronic structure is discussed in Appendix B. Above 150 GPa, our calculated superconducting Tc shows a drop compared with the observed robust Tc until 261 GPa. This can be explained from two sides. On the one hand, NbTi alloys cannot completely transform to a single NbTi crystal. Although the ultra-high pressure energetically tends to make more Nb and Ti atoms arrange alternatively and uniformly, there is still a portion of atoms in the disordered distribution. As a result, there may be a hysteresis behavior for the evolution of superconductivity with pressure. On the other hand, the pressure-dependent μ* can bring more robust Tc than the constant μ* [Fig. 1(c)]. According to the classic relation μ* = 0.26N(εF)/[1 + N(εF)], μ* has a positive correlation with the DOS at the Fermi level. Compared with the value at 50 GPa, N(εF) is reduced by about 50% at 250 GPa (Table I), which leads to a smaller μ*. According to the McMillan-Allen-Dynes formula [Eq. (3)], the decreased λ [Fig. 1(d)], increased ωlog [Fig. 2(c)], and reduced μ* under high pressure will compensate each other and result in stable Tc of the NbTi crystal.

Our studies reveal that the pressure tends to transform NbTi alloys from a random phase to a uniformly ordered...
crystal phase (NbTi crystal). Therefore, we suggest that at ambient pressure the superconductivity mainly comes from the Nb elements in the alloy, while under high pressures it is mainly contributed by the NbTi crystal. The calculated superconducting $T_c$ of the uniform NbTi crystal with pressure-dependent $\mu^*$ can remain above 20 K until 250 GPa, where the softened phonon mode at the $M$ point with the largest electron-phonon coupling counteracts the partial influence of pressure. This gives a reasonable explanation for the observed robust superconductivity of NbTi alloys under high pressure and indicates that the EPC mechanism of BCS theory is still applicable to NbTi under extreme conditions. In addition to NbTi alloys, our studies may also apply to other alloy superconductors, which provides insight into tuning $T_c$ of superconducting alloys by controlling their atomic randomness in synthetic process.

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Appendix A: Transition barriers of NbTi alloys

To confirm the possibility of transformation from a disordered atomic arrangement to a uniform one in NbTi alloys, we propose a transition process exemplified by the one from a NbTi alloy with alternating Nb and Ti layers along the [110] direction [Fig. 4(a), space group $Cmmm$] to the uniform CsCl-type NbTi crystal [Fig. 4(c), space group $Pm – 3m$]. This process undergoes a metastable state with Nb and Ti bilayers arranged alternatively along the [112] direction (space group $P2_1/m$). Note that all three structures possess a bcc lattice but different atomic arrangements. The calculated transition barriers of the above transition process are shown in Fig. 4(d). At 100 GPa, the transition barriers are less than 0.2 eV/atom, which is lower than that between graphite and diamond under pressure (0.22 eV/atom)].

Figure 4. (Color online) (a)-(c) Proposed transition process exemplified by the one from a NbTi alloy with alternating Nb and Ti layers along the [110] direction (space group $Cmmm$) to the uniform CsCl-type NbTi crystal (space group $Pm – 3m$), which undergoes a metastable state with Nb and Ti bilayers arranged alternatively along the [112] direction (space group $P2_1/m$). (d) Calculated barriers of the above transition process.

Appendix B: Relation between electronic structure, phonon dispersion, and electron-phonon coupling

The strong electron-phonon coupling usually induces an abnormal phonon softening, as demonstrated in the calculated phonon dispersions of the NbTi crystal [Figs. 2(b)-2(f)]. Recalling the formula of the phonon
linewidth,
\[
\gamma_{qv} = 2\pi\omega_{qv}\sum_{knn'} \left| g_{k+qn',kn}^q \right|^2 \delta(\varepsilon_{kn} - \varepsilon_F)\delta(\varepsilon_{k+qn'} - \varepsilon_F),
\]
where \(g_{k+qn',kn}^q\) is the EPC matrix element and \(\sum_{knn'} \delta(\varepsilon_{kn} - \varepsilon_F)\delta(\varepsilon_{k+qn'} - \varepsilon_F)\) is the function of Fermi-surface nesting, perfect nesting of the Fermi surface along the \(\Gamma-M\) vector may give some information about the phonon softening around the \(M\) point. We thus calculated the Fermi surface of the NbTi crystal under 150 GPa [Fig. 5(a)], at which pressure NbTi has the most obvious phonon softening at the \(M\) point [Fig. 2(d)]. As shown in Fig. 5(a), the Fermi surfaces are very complex, and it is hard to make a direct connection with phonon softening. For better visualization, we further calculated the electronic susceptibility \(\chi\), whose real and imaginary parts are defined as:
\[
\chi'(q) = \sum_{nn'k} \frac{f(\varepsilon_{kn}) - f(\varepsilon_{k+qn'})}{\varepsilon_{kn} - \varepsilon_{k+qn'}},
\]
\[
\chi''(q) = \sum_{nn'k} \delta(\varepsilon_{kn} - \varepsilon_F)\delta(\varepsilon_{k+qn'} - \varepsilon_F),
\]
respectively. According to Figs. 5(b) and 5(c), neither \(\chi'\) nor \(\chi''\) shows a peak at the \(M\) point. These results indicate that the pure electronic structure of NbTi (Fig. 5) cannot directly reflect the variations of EPC and phonon softening (Fig. 2).
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