Giant Phonon Softening and Enhancement of Superconductivity by Phosphorus Doping of BaNi$_2$As$_2$

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The effects of phosphorus doping on the structural and superconducting phase transitions of BaNi$_2$(As$_{1-x}$P$_x$)$_2$ were studied. The specific heat, resistivity, and magnetic susceptibility were measured. The results revealed an abrupt increase in the superconducting transition temperature ($T_c$) from 0.6 K in the triclinic phase (space group $P1\bar{1}$) with less phosphorus ($x \approx 0.067$) to 3.3 K in the tetragonal phase (space group $I4/mmm$) with more phosphorus ($x \approx 0.067$). Our data analysis suggests that a doping-induced softening related to an in-plane Ni and As(P) phonon mode is responsible for the enhanced superconductivity in the tetragonal phase.

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Superconductivity at high transition temperatures ($T_c$) is often associated with structural instabilities that are characterized by phonon softening and subsequent structural phase transitions. Enhancement in $T_c$ at a structural phase boundary has been observed in various systems including copper oxides [1,2], iron pnictides [3,4], A15 compounds [5], graphite intercalated compounds [6–9], and elements such as Li and Te under high pressure [10–16]. For example, the graphite intercalated compound CaC$_6$ exhibits a gradual increase in $T_c$ from 11.5 to 15.1 K under high pressure followed by a sudden decrease down to ~5 K at 8–10 GPa [8]. The temperature-dependent resistivity, together with first-principles calculations, suggests that the softening of in-plane Ca vibrations leads to the enhanced $T_c$ and the subsequent phase transition in CaC$_6$ under high pressure [7–9]. Tellurium (Te) exhibits a $T_c$ jump from 2.5 to 7.4 K at 32–35 GPa, which is related to the transition from the rhombohedral $\beta$-Po structure to the bcc phase [14]. First-principles calculations suggest that the remarkable increase in $T_c$ can be attributed to a phonon softening of the transverse mode in the bcc phase under high pressure [14–16]. Thus, the tuning of soft phonons appears to be important for maximizing $T_c$. However, the chemical tuning of soft phonons, which is essential for practical applications, has not yet been fully investigated.

BaNi$_2$As$_2$ crystallizes in a tetragonal ThCr$_2$Si$_2$-type structure (space group $I4/mmm$) [17–19]. This system exhibits a structural phase transition from a tetragonal to a triclinic phase (space group $P1$) at approximately 130 K, below which alternate Ni-Ni bonds (with distances of ~2.8 Å and ~3.1 Å) are formed in the Ni square lattice [18]. In this triclinic phase, superconductivity, considered to be of the conventional BCS type, emerges at 0.7 K [17,19–21]. Therefore, this system can be considered a nonmagnetic analogue of iron-based superconductors such as BaFe$_2$As$_2$. In this Letter, we report that $T_c$ abruptly increases from 0.7 to 3.3 K upon the phosphorus doping of BaNi$_2$As$_2$. The enhanced superconductivity is accompanied by the triclinic-to-tetragonal phase transition that is induced by phosphorus doping at $x = 0.067$ in BaNi$_2$(As$_{1-x}$P$_x$)$_2$. The specific heat and electrical resistivity suggest that doping-induced phonon softening, related to the in-plane Ni and As vibrations, is responsible for the enhanced superconductivity, demonstrating that the chemical tuning of soft phonons is an effective means to optimize superconductivity.

Single crystals of BaNi$_2$(As$_{1-x}$P$_x$)$_2$ were grown using a self-flux method. A mixture with a ratio of Ba: Ni: As: Ni: P = 1:4(1-x):4x:4x was placed in an alumina crucible, sealed in an evacuated quartz tube, heated at 700 °C for 3 h, slowly heated to 1150 °C, and cooled from 1150 to 1000 °C at a rate of 2 °C/h, followed by furnace cooling. Single crystals with a typical dimension of 1 × 1 × 0.1 mm$^3$ were mechanically isolated from the flux. The results of powder x-ray diffraction, performed using a Rigaku RINT-TTR III x-ray diffractometer with CuK$_\alpha$ radiation, showed that all specimens are in a single phase. Energy dispersive x-ray spectrometry (EDS) was used to determine the phosphorus content $x$. Samples with $x$ greater than 0.13 could hardly be obtained by either flux growth or the solid-state reaction, indicating that the solubility limit of P for As is at $x = 0.13$. The samples were treated in a glove box filled with dried Ar gas because they degraded in air within a few days. The magnetization $M$ was measured using a Quantum Design MPMS. The electrical resistivity $\rho_{ab}$ (parallel to the $ab$ plane) and specific heat $C$ were measured using a Quantum Design PPMS.

Figure 1 shows the temperature dependence of the electrical resistivity for BaNi$_2$(As$_{1-x}$P$_x$)$_2$. In a manner consistent with previous reports, pure BaNi$_2$As$_2$ exhibits a
transition at 130 K with a thermal hysteresis accompanying a sudden increase in resistivity upon cooling [17–19]. For 3.5% phosphorous doping, the transition is significantly suppressed to 90–100 K and the sudden resistivity increase changes into a sudden decrease upon cooling. The transition appears to be absent for 7.7% phosphorous doping. These results suggest the suppression of the triclinic phase at $x=0.07$ in BaNi$_2$(As$_{1-x}$P$_x$)$_2$.

We found that superconductivity emerges below 3.3 K as soon as the triclinic phase is suppressed with phosphorus doping, while it emerges below 0.7 K in the triclinic phase at $x<0.07$. This is demonstrated by the low-temperature magnetic susceptibility and resistivity data shown in Fig. 2. For $x=0.070$, the bulk superconductivity is evident from the full shielding diamagnetic signal and sharp resistivity transition at 3.33 K. The superconductivity persists until $x$ reaches the solubility limit at $x=0.13$, while $T_c$ decreases slightly to 3.24 K. The low-temperature specific-heat data, shown in Figs. 2(c) and 3, give further evidence of the enhanced superconductivity in the tetragonal phase. Pure BaNi$_2$As$_2$ exhibits a specific heat jump at 0.6 K, as reported previously [17–19]. The transition temperature increases slightly with phosphorus doping, but remains below 0.97 K as long as the system is in the triclinic phase. In the tetragonal phase with more than 7.7% phosphorous doping, the specific heat jump appears at an elevated temperature of 3.3 K, in a manner consistent with the magnetic and resistivity data.

The enhanced superconductivity at the structural phase boundary in phosphorus-doped BaNi$_2$As$_2$ is reminiscent of CaC$_6$ under high pressure [7–9] and tellurium at the $\beta$-Po bcc phase boundary under high pressure [11–16]. Mauri et al. proposed that the enhanced superconductivity in Te is due to the softening of transverse phonons along the $\Gamma\Sigma$ line in the bcc phase and the resultant enhancement of electron-phonon coupling under pressure [14]. In order to examine the role of soft phonons in the enhanced $T_c$ of phosphorus-doped BaNi$_2$As$_2$, the normal-state specific heat was examined at low temperatures. Figure 3 shows the specific heat divided by the temperature $C/T$ as a function of the squared temperature $T^2$. The normal-state data above $T_c$ can be well fitted by $C/T = \gamma + \beta T^2$, where $\gamma$ is an electronic specific-heat coefficient and $\beta$, the coefficient of phonon contributions from which the Debye frequency $\omega_D$ is estimated. As can be seen from Fig. 3, the slope of the $C/T$ vs $T^2$ lines is almost unchanged in the triclinic phase for less than 7% phosphorus doping. The slope increases suddenly for 7.7%
phosphorous doping, suggesting the occurrence of significant phonon softening when the triclinic-to-tetragonal phase transition occurs. The slope decreases upon further phosphorous doping in the tetragonal phase. Figure 4(c) shows the estimated Debye frequency $\omega_D$ as a function of the phosphorous content $x$. $\omega_D$ shows a significant reduction from 250 to 150 K at the structural phase boundary of $x = 0.07$.

In contrast to the strong dependence of both $\omega_D$ and $T_c$ on doping, the electronic specific-heat coefficient $\gamma$ ($\approx 14$ mJ/mol K$^2$) is almost independent of the phosphorous content $x$, as can be seen from the almost unchanged intercept of the $C/T$ axis in Fig. 3. Furthermore, the electronic density of states at the Fermi level $\approx 6$ eV$^{-1}$ per formula unit, as determined from the specific heat $\gamma$, is comparable to the band calculation value 3.57 eV$^{-1}$ for the tetragonal phase of pure BaNi$_2$As$_2$ [20]. These observations suggest that the structural phase transition, as well as the enhanced superconductivity in the tetragonal phase, is not electronic but phononic, specifically, enhanced electron-phonon coupling due to soft phonons, in origin [22]. Indeed, the normalized specific heat jump $\Delta C/\gamma T_c \approx 1.3$ for the triclinic phase at $x < 0.07$, determined from the data shown in Fig. 2(c), is comparable to the value of the weak coupling limit ($= 1.43$), while $\Delta C/\gamma T_c$ is enhanced in the tetragonal phase with a maximum value of 1.90 at $x = 0.077$, indicative of strong coupling superconductivity. $\Delta C/\gamma T_c$ is gradually decreased upon further doping to 1.78 and 1.60 for $x = 0.092$ and 0.104, respectively, as can be seen from Fig. 2(c) [23]. We estimate the logarithmic-averaged phonon frequency $\omega_{D}$ using the relationship for strong-coupling superconductors $\Delta C(T)/\gamma T_c = \omega_{D}^2[1 + (53/x^2) \ln(x/3)]$, where $x = \omega_{D}/T_c$ [24–26].

Figure 4(c) shows $\omega_{D}$, together with the Debye frequency $\omega_{D}$, as a function of the phosphorous content $x$. Both $\omega_{D}$ and $\omega_{D}$ exhibit significant softening as the system approaches the structural phase boundary from the tetragonal side, suggesting that the low-lying soft phonons, which are coupled strongly with acoustic modes, play an important role in the emergence of the strong-coupling superconductivity in the tetragonal phase. The in-plane Ni and As mode at $\sim 50$ cm$^{-1}$ (equivalent to 80 K) [20], which is thought to be quenched to form alternating Ni-As bonds in the triclinic phase, could be a soft mode, although further experimental confirmations of the same are required from inelastic neutron scattering and ultrasonic experiments.

**Figure 3** (color online). The specific heat divided by the temperature, $C/T$, as a function of $T^2$ for BaNi$_2$(As$_{1-x}$P$_x$)$_2$. The broken lines denote the fits by $C/T = \gamma + \beta T^2$, where $\gamma$ is the electronic specific heat coefficient and $\beta$ is a constant corresponding to the Debye phonon contributions.
Our results are summarized in the electronic phase diagram shown in Fig. 4(b). The triclinic phase transition temperature in pure BaNi$_2$As$_2$ is strongly suppressed with phosphorus doping. As a result, the superconducting transition temperature is enhanced from $T_c = 0.6$–$0.9$ K in the triclinic phase to $3.2$–$3.3$ K in the tetragonal phase. A similar stepwise shape of the superconducting phase boundary, where another structural phase boundary intersects, has been observed in tellurium under high pressure [14]. A similar mechanism may be active in the phosphorus-doped BaNi$_2$As$_2$. Phosphorous is isovalent with arsenic, but has a smaller ionic radius. Therefore, phosphorous doping serves to create chemical pressure. Indeed, lattice parameters $a$ and $c$ at $300$ K show monotonically dependence on the phosphorous content $x$, as shown in Fig. 4(a); thus, the unit cell volume decreases monotonically from $199.9$ Å$^3$ for pure BaNi$_2$As$_2$ to $198.1$ Å$^3$ for 13% phosphorus doping of BaNi$_2$(As$_{1-x}$P$_x$)$_2$. Soft phonons in the tetragonal phase, indicated by both $\omega_p$ and $\omega_{in}$, shown in Fig. 4(c), could enhance the electron-phonon coupling and thus the superconductivity [22]. When the phosphorous content $x$ is decreased from the tetragonal side, the soft phonon leads to a structural instability and eventually results in the triclinic phase transition and suppressed superconductivity. There exists a miscibility gap approximately at $x = 0.13$. It should be noted that superconductivity below $T_c = 3$ K appears when arsenic is completely replaced by phosphorus in BaNi$_2$P$_2$ [27].

To conclude, our experiments show that the enhancement of superconductivity associated with phonon softening and subsequent structural phase transition occurs because of the phosphorus doping of BaNi$_2$As$_2$. Specifically, the increase in $T_c$ from $0.6$ to $3.3$ K (approximately fivefold enhancement) is related to the giant phonon softening of approximately 50% at the triclinic-to-tetragonal phase transition induced by phosphorus doping. Our results demonstrate that the chemical tuning of soft phonons is practical and effective for optimizing superconductivity.

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the material parameters of BaNi$_2$As$_2$ are in the range where $\omega$ is larger than $(C/2M)^{1/2}$, and thus, the $\lambda$ term dominates the $\omega$ dependence of $T_c$. See W. L. McMillan, Phys. Rev. 167, 331 (1968).

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