Evidence of High-Temperature Superconductivity at 18 K in Nanosized Rhombohedral Bi Enhanced by Ni-Doping

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ABSTRACT: Superconductivity in bulk rhombohedral Bi has recently been detected to appear below 0.53 mK and 5.2 μT. Here, we unambiguously demonstrate that superconductivity in rhombohedral Bi can be greatly enhanced by incorporating Ni ions onto the Bi sites and reducing the size to the nanometer scale. The superconducting transition temperature $T_C$ of 12 nm rhombohedral Bi nanoparticles (NPs) reaches 4 K at ambient pressure. $T_C$ is significantly enhanced to reach 7, 12, and 18 K in 6, 8, and 10% Ni-doped Bi NPs, respectively, where superconductivity is found to coexist with ferromagnetism. Ni-doping causes a significant amount of electronic density shifts and spin suppliers for the developments of superconductivity and ferromagnetism.

1. INTRODUCTION

At ambient pressure, the pentavalent semimetal Bi ([Xe]-4f^{15}5d^{10}6s^{2}6p^{1}) crystallizes into a rhombohedral structure with a spatial symmetry belonging to the space group R3m. This crystalline structure gives rise to a Fermi surface that consists of ellipsoidal-shaped pockets, with a small Fermi surface area, hence a small density of states (DOS), and a low carrier density.1 An extremely low transition temperature for the superconductivity (SC) in rhombohedral Bi is hence expected. The search for SC in pure Bi has continued for decades, but experimental difficulties have been encountered because of the extremely low superconducting transition temperature $T_C$ and critical magnetic field $H_C$.2–4 SC in bulk rhombohedral Bi at ambient pressure has recently been detected to appear below $T_C = 0.53$ mK and $H_C = 5.2$ μT.6 This $T_C$ detected in a Bi single crystal at ambient pressure is 2.45 times lower than the 1.3 mK estimated7 according to the BCS formalism. Apparently, the SC in rhombohedral Bi cannot be fully understood by the BCS theory alone. It has also been found that the $T_C$ of Bi is largely enhanced when it crystallizes into a structure of higher crystalline symmetry. Three structural phases of Bi have been identified upon pressurizing up to 19 GPa. The rhombohedral phase that appears at the ambient pressure evolves into a monoclinic one at 2.55 GPa with a $T_C$ of 3.9 K, followed by a tetragonal one at 2.7 GPa with a $T_C$ of 7 K, and finally a body-centered cubic one at 8.1 GPa with a $T_C$ of 8.1 K.8–15 In addition, face-centered cubic (fcc) Bi can be grown on a thin Ni seed layer,15,16 in which SC and ferromagnetism (FM) are found to coexist below a $T_C$ of 4.2 K.16 SC has also been found in intermetallic compounds of Bi with magnetic atoms. Orthorhombic $\text{Bi}_3\text{Co}$17 and tetragonal $\text{Bi}_3\text{Fe}$18 become superconducting below 0.48 and 1.3 K (at 40 GPa), respectively. A type-II SC has been detected in orthorhombic $\text{Bi}_3\text{Ni}$ below 4.1 K.19–21 These enhancements of $T_C$ for Bi originate from the changes in the electronic band structures when the crystalline symmetry is altered. Similar to what has been observed in other compounds, the $T_C$ of Bi in the form of reduced dimensions can be significantly higher than that in its bulk form.4,22–25 The highest $T_C$ found thus far in rhombohedral Bi can reach 8.3 K and appears in granular Bi nanowires with rhombohedral grains that are 10 nm in diameter.22,23 It has also been demonstrated that the $T_C$ of In and Sn nanoparticles (NPs) can be significantly enhanced by the introduction of Ni NPs into the vicinity of the superconducting NPs.26–28

The goal of this study is to search for a doping component that enhances the SC in rhombohedral Bi. A small amount of doping component in the compound is a prerequisite for not altering the crystalline structure of the Bi. Partial replacement of Bi by Ni is a selection among others. The 8 d-electrons of Ni ([Ar]3d^{8}4s^{2}) can give rise to an enriched electron density together with an enlarged DOS near the Fermi level. The smaller ionic radius of Ni places less atomic strength in altering the crystalline structure of the host rhombohedral Bi lattice. The magnetic character of Ni may guide the magnetic flux to condense more near the Ni sites. In this report, we demonstrate that the $T_C$ and $H_C$ of rhombohedral Bi NPs can be greatly enhanced by the incorporation of Ni ions onto the NPs, and that SC coexists with FM. The $T_C$ of 12 nm rhombohedral Bi NPs reaches 4 K at ambient pressure. Surprisingly, a more than fourfold increase of $T_C$ to 18 K is found after the incorporation of 10% Ni into 11 nm Bi NPs. The isothermal magnetization $\chi (H)$ reveals a Langevin field profile and magnetic hysteresis is clearly revealed in the

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superconducting phase, showing the coexistence of SC and FM. Interestingly, the electronic charge distribution of the Bi$_{0.9}$Ni$_{0.1}$ NPs is quite different from that of the Bi NPs. The electronic charges in Bi$_{0.9}$Ni$_{0.1}$ have a more extended distribution, with a significant amount of electronic charges shift toward the interconnecting regions of the neighboring Bi ions. First-principles calculations show that the DOS, the carrier density, and the spin density near the Fermi surface increase significantly upon Ni-doping.

2. SAMPLE FABRICATION

Three sets of Ni-doped Bi NPs together with one set of Ni-free Bi NPs were fabricated employing the gas-condensation method, using a chamber equipped with two decoupled evaporation sources for separate evaporation of Bi or Ni. High-purity Bi spheres (∼0.3 g each, 99.999% pure and ∼2 mm in diameter) and Ni spheres (∼0.05 g each, 99.999% pure and ∼1 mm in diameter) were heated separately using current sources and were evaporated at a rate of 0.05 Å/s in an Ar atmosphere. The chemical composition of Ni in the resultant NPs was controlled by the selection of the heating current in the Ni electrode. The fabrication parameters are listed in Table 1. A nonmagnetic SS316 stainless steel plate placed 20 cm above the evaporation source and maintained at 77 K was used to collect the evaporated particles. After restoration to room temperature, the NPs were stripped off. The samples thus obtained were in powdered form and consisted of a macroscopic amount of individual NPs. There was no substrate or capping molecules on the NPs. The resultant powders were no longer silvery but dark black, indicating that the absorption intensities of the Bi and Ni lines are used to determine the Ni compositions between Bi and Ni in the compounds. The XPS spectra were taken using an enlarged y-axis scale for clarity of presentation of weak reflections.

Table 1. Parameters Used for Evaporation of the Four Sets of Bi$_n$Ni$_n$ NPs Fabricated

| chamber Ar pressure (Torr) | evaporation rate (Å/s) | Bi & Ni chemical composition |
|---------------------------|------------------------|----------------------------|
| sample 1                  | 0.1                    | 0.05                       |
| sample 2                  | 0.1                    | 0.05                       |
| sample 3                  | 0.1                    | 0.05                       |
| sample 4                  | 0.1                    | 0.05                       |

The XRD patterns reveal the same rhombohedral crystalline structure for the four sets of NPs, with the diffraction peaks of the Ni-doped NPs appearing at higher scattering angles (Figure 1a). The lattice constants of the Ni-doped Bi NPs are noticeably smaller than that of the Bi NPs, reflecting the smaller ionic size of Ni than that of Bi. No diffraction signals from the crystallized Bi$_3$Ni or Ni can be identified in the diffraction patterns (Figure 1a). Weak but visible diffraction intensities from incomplete cancellations of the rhombohedral (111) + (121), (112), (201), and (114) + (124) reflections appear in the diffraction patterns of the Bi$_{n}$Ni$_{n}$ NPs (Figure 1b), showing that the ions on the lattice sites are not all the same in these samples. This reflects the appearance of Ni ions on the lattice sites. XPS was used to demonstrate the existence of Ni ions in the compounds and determine the relative compositions between Bi and Ni in the compounds. The XPS spectra of Bi$_{n}$Ni$_{n}$ NPs reveal binding energies of 855.5 and 874 eV for the Ni 2p$_{3/2}$ and 2p$_{1/2}$ lines, respectively (Figure 2a). No Ni lines may be identified in the XPS spectra of the Bi NPs (Figure 2b). The binding energies for the Ni in Bi$_{n}$Ni$_{n}$ NPs are considerably higher than the binding energy of 852.8 and 870.2 eV obtained for the fcc Ni, revealing much stronger bonding of the Ni ions in Bi$_{n}$Ni$_{n}$ NPs to their neighboring ions than those in the pure fcc Ni. The spectral lines from the Bi ions are also revealed in the XPS spectra of the Bi$_{n}$Ni$_{n}$ NPs. The relative intensities of the Bi and Ni lines are used to determine the Ni compositions in the Bi$_{n}$Ni$_{n}$ NPs, giving rise to Ni compositions of 6, 8, and 10% for the three sets of Bi$_{n}$Ni$_{n}$ NPs.

3. SAMPLE CHARACTERIZATION

X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the samples. The XRD measurements for structural investigation were performed on a Bruker D8 ADVANCE diffractometer, employing the standard reflection geometry. The high-resolution transmission electron microscopy (HRTEM) images were taken using a JEOL JEM-2100, employing an acceleration voltage of 200 kV for a magnification of 3 × 10$^5$ times. The XPS spectra were taken on a Thermo Scientific K-Alpha+ XPS system, employing the standard setup with an Al Kα microfocused monochromator and a spot size of 400 μm.

Figure 1. (a) XRD patterns of the Bi (dashed line) and Bi$_{0.9}$Ni$_{0.1}$ (solid lines) NP assemblies taken at 300 K, revealing the same rhombohedral crystal symmetry for both NP assemblies, with a smaller unit cell for the Bi$_{0.9}$Ni$_{0.1}$ NPs. No crystalized Ni peak can be identified. (b) XRD pattern of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly plotted using an enlarged y-axis scale for clarity of presentation of weak reflections.
The difference between a size-dispersed particle assembly and the individual particle in the powder. The size distribution and mean particle diameter of the NP assemblies were determined by fitting the diffraction peaks to the diffraction profiles of finite sized particles, assuming log-normal size distributions for the assemblies. The curves in Figure 3 indicate the fitted patterns for the Bi$_{0.9}$Ni$_{0.1}$ (solid curve) and Bi (dashed curve) NP assemblies, with the size distributions shown in Figure 3, revealing mean particle diameters of 11(1) and 12(1) nm for the Bi$_{0.9}$Ni$_{0.1}$ and Bi NP assemblies, respectively. The mean particle diameters thus determined for the Bi$_{0.9}$Ni$_{0.1}$, Bi$_{0.92}$Ni$_{0.08}$, Bi$_{0.93}$Ni$_{0.07}$, and Bi$_{0.9}$N$_{0.1}$ NP assemblies are 12(1), 12(2), 11(2), and 11(1) nm, respectively. The strains accumulated in the NPs were investigated by a Scherrer plot, showing there is no significant stress in the NP assemblies. The average strain obtained from the XRD profiles was $3.2 \times 10^{-4}$ for the Bi$_{0.9}$Ni$_{0.1}$ NPs and $4.4 \times 10^{-4}$ for the Bi NPs. HRTEM images of the Bi$_{0.9}$Ni$_{0.1}$ NPs reveal the stacking of the wavy a-b layers along the c-axis direction to form Bi ellipses (Figure 3c,d). The layers revealed in the images correspond to the Bi(003) lattice planes because there are three wavy a-b layers in a unit cell. There are no identifiable traces of oxidation phases or core–shell structures in the TEM images but revealing elliptically shaped bare Bi particles, which is a direct result of an insufficient number of Ni atoms being provided during fabrication.

4. SUPERCONDUCTIVITY

The electric resistivity, magnetization, and ac magnetic susceptibility measurements were performed on a Physical Property Measurement System (PPMS), manufactured by Quantum Design, employing the standard setups. For magnetization andac magnetic susceptibility measurements, $\sim 60$ mg of the powdered sample was loosely packed into a thin
nonmagnetic cylindrical holder. Prior to loading, the sample was shaken at 50 Hz for 5 min using a Vortex-Genie mixer to avoid aggregation among the NPs. The mass density of the powdered sample packed in holder was ~5% of the bulk density, which indicates the ratio of the mass densities of the assembly to that of its bulk counterpart. This mass density for the NP assembly corresponds to an average interparticle separation from edge to edge of 1.1 times the particle diameter, thus the interparticle interaction would be insignificant. The holder, manufactured by Quantum Design, produced a smooth temperature curve with a background signal that was ~2% of the strength of the signal from the sample. The electric resistivity was measured on a solid piece sample of size ~4 × 3 × 0.7 mm$^3$, employing the standard four-probe setup operated in the constant current mode of $I = 0.1$ mA. The sample was obtained by cold-pressing the Bi$_{0.9}$Ni$_{0.1}$ NP powder flat using a mechanical pressure of 25 kg W/mm$^2$. The resultant sample was in the form of a solid piece, with a packing fraction that was 60% of the bulk density. At this point, the average separation from edge to edge between two neighboring particles is ~0.8 nm, which acts as resistive potential barriers for electrical conduction.

A drop to nearly zero resistance on cooling through 18 K is clearly revealed in the temperature dependence of electric resistance of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NP assembly, showing the transition to the superconducting state below $T_C = 18$ K (Figure 4a). The resistivity of this Bi$_{0.9}$Ni$_{0.1}$ NP compact is comparable to that observed in Bi single-crystal films.$^{31}$ The small residual resistivity (~20 $\mu\Omega$ cm) seen at low temperatures reflects the tunneling barriers in the NP assembly. This tunneling resistivity reflects mainly the work function for the electrons to leave the surface of an NP and entering the neighboring one because the average separation between two neighboring NPs is only 0.8 nm with which many NPs can be indeed in contact. Diamagnetic screenings that reveal a $T_C = 4$ K for the development of SC in the 12 nm Bi NPs are seen in the temperature dependence of magnetization (filled triangles in Figure 4b). Interestingly, the $T_C$ of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs reaches 18 K (open circles in Figure 4b). The $M(T)$ curve of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs may be described by Scalapino’s expression$^{32}$ (solid curve on data) for superconducting diamagnetic screening. Surprisingly, the incorporation of 10% Ni ions into the Bi NPs causes the superconducting $T_C$ to increase by 4.5 times. Meissner screening of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NP assembly is clearly revealed in the (M(T)) curve measured during zero-field cooling from 300 to 2 K (filled triangles in Figure 4c) followed by warming to 35 K after the application of a magnetic field $H_D$ of 50 Oe (open circles in Figure 4c). Magnetizations of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs remain zero within the noise level during zero-field cooling; diamagnetic responses appear with the application of a weak $H_D$ of 50 Oe. The $T_C$ of the Bi$_{0.9}$Ni$_{0.1}$ NPs increases with an increase in the Ni composition $x$ (Figure 4d). An attempt to fabricate rhombohedral Bi$_{0.9}$Ni$_{0.1}$ NPs with a higher Ni composition was not successful, producing instead orthorhombic Bi$_{0.9}$Ni$_{0.1}$ NPs with a $T_C$ of 4 K.

The application of a magnetic field $H_D$ suppresses the superconducting transition temperature $T_C$ to a lower temperature for both the Bi and Bi$_{0.9}$Ni$_{0.1}$ NP assemblies. Figure 5a show the isofield $M(T)$ taken at four representative $H_D$ where the solid lines indicate the results of fits to the Scalapino’s expression that allow the extractions of $T_C$. The variations of $T_C$ with $H_D$ can be described by $T_C(H_D) = T_C0[1 − C(2%$ the scale on the plot indicate the volume magnetization of the Bi$_{0.9}$Ni$_{0.1}$ NPs. A factor of 1.06 times higher for the scales is needed to indicate the volume magnetization of the Bi NPs. Diamagnetic signals that reflect the development of SC are clearly revealed below 4 and 18 K for the Bi and Bi$_{0.9}$Ni$_{0.1}$ NP assemblies, respectively. The solid line on the data points of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly indicates the results of the fit to Scalapino’s expression. (c) Temperature dependence of the magnetizations of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly, measured during zero-field cooling from 300 to 2 K (filled triangles), followed by warming to 35 K after the application of a magnetic field of 50 Oe at 2 K (open circles). (d) Variations of $T_C$ with the Ni composition $x$ in Bi$_{1−x}$Ni$_{x}$ NP assemblies, obtained from magnetization data.

Figure 4. (a) Temperature dependence of the electric resistivity of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NP assembly, measured in a constant current mode with $I = 0.1$ mA. A drop in resistivity on cooling below 18 K is clearly seen, revealing a transition into the superconducting state. (b) Thermal variation of the magnetization of the Bi (filled triangles) and Bi$_{0.9}$Ni$_{0.1}$ (open circles) NP assemblies, measured during warming process with $H_D = 50$ Oe after zero-field cooling to 2 K. The scales on the vertical axis on the right hand size of the plot indicate the volume magnetization of the Bi$_{0.9}$Ni$_{0.1}$ NPs. A factor of 1.06 times higher for the scales is needed to indicate the volume magnetization of the Bi NPs. Diamagnetic signals that reflect the development of SC are clearly revealed below 4 and 18 K for the Bi and Bi$_{0.9}$Ni$_{0.1}$ NP assemblies, respectively. The solid line on the data points of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly indicates the results of the fit to Scalapino’s expression. (c) Temperature dependence of the magnetizations of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly, measured during zero-field cooling from 300 to 2 K (filled triangles), followed by warming to 35 K after the application of a magnetic field of 50 Oe at 2 K (open circles). (d) Variations of $T_C$ with the Ni composition $x$ in Bi$_{1−x}$Ni$_{x}$ NP assemblies, obtained from magnetization data.
that affects the SC. For bulk systems, $\alpha = 2$ is expected, because the whole applied magnetic energy of $H^2/8\pi$ is affecting the SC. In NPs, only a portion of the applied magnetic energy will affect the SC because an appreciable amount of the magnetic field penetrates into the NPs. An $\alpha < 2$ may then be anticipated for NPs, as shown in Figure 5. A smaller value of $\alpha = 0.45$ is obtained for 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs than $\alpha = 0.62$ for 12 nm Bi NPs, reflecting the magnetic energy affecting the SC that is less for Bi$_{0.9}$Ni$_{0.1}$ NPs than for Bi NPs at an $H_c$.

5. FM IN SUPERCONDUCTING STATE

The values of $M$ for the Bi$_{0.9}$Ni$_{0.1}$ NPs in the normal state are ~3 times higher than those of the Bi NPs, showing the existence of a magnetic component in the Bi$_{0.9}$Ni$_{0.1}$ NPs. The field dependences of the isothermal $M(H)$ of the Bi$_{0.9}$Ni$_{0.1}$ NPs taken below $T_C$ can be described by a Langevin field profile plus a positive linear term (solid lines in Figure 6a). The positive linear term decreases with increasing temperature and is not visible at 20 K. An additional Lenz linear diamagnetic component is needed for the $M(H)$ curves taken at higher temperatures (Figure 6a). The observed Langevin $M(H)$ may be understood as the magnetic moments of the randomly oriented assembly of noninteracting Bi$_{0.9}$Ni$_{0.1}$ NPs that are being aligned by the $H_c$ which remains visible at 300 K. An average magnetic moment of 563(9) $\mu_B$ is obtained for each Bi$_{0.9}$Ni$_{0.1}$ NP at 20 K, which corresponds to an average magnetic moment of 0.03 $\mu_B$ for each Bi ion in the NP that remains visible at 300 K. The isofield $M(T)$ of the Bi$_{0.9}$Ni$_{0.1}$ NPs taken at 2 kOe departs from the Curie–Weiss profile below 17 K (Figure 6b). The transition at 17 K is not linked to SC because $T_C$ at 2 kOe drops to 5 K. These further increases in magnetization on cooling below 17 K are contributed from the magnetic moment of the Ni ions, which become thermally disordered above 17 K.

Magnetic hysteresis is clearly seen even at 2 K (Figure 6c). The appearance of the Langevin isothermal $M(H)$ and magnetic hysteresis below $T_C$ reveals the coexistence of SC and FM for the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs in the superconducting phase. SC persists up to $T_C = 18$ K, whereas FM remains at 300 K that is the highest temperature achieved in this study. It is known that metallic NPs can develop ferromagnetic moments. The saturation magnetization $M_s$ of the 12 nm Bi NPs reaches $6 \times 10^{-3}$ emu/g at 20 K, while that of the 11 nm Bi$_{0.9}$Ni$_{0.1}$ NPs can reach $3 \times 10^{-2}$ emu/g. The much larger $M_s$ for the Bi$_{0.9}$Ni$_{0.1}$ NPs shows that the Ni ions in the NPs do carry magnetic moments. However, the $M_s$ of the Bi$_{0.9}$Ni$_{0.1}$ NPs is much smaller ($\sim 10^3$ lower) than that of the fcc Ni in its bulk form. This is a direct result of the Ni ions in the Bi$_{0.9}$Ni$_{0.1}$ NPs being so far apart that the exchange interactions are significantly weaker.

6. ELECTRONIC CHARGE DENSITY

The introduction of Ni ions to the rhombohedral Bi lattice sites leads to a more intensive distribution of the outer electronic charge density (ECD) toward the interconnecting regions between neighboring ions, as a consequence of an outgoing shift of electrons from near the lattice sites. These changes in the charge distribution are better revealed in the difference ECD plots, where the ECD distribution of the Bi NP assembly is subtracted from that of the Bi$_{0.9}$Ni$_{0.1}$ NP assembly. Such difference ECD plots for the Bi$_{0.9}$Ni$_{0.1}$ NP assembly are
illustrated in Figure 7, where the atomic positions with negative values for the difference ECD represent the locations where the electronic charges are less in Bi\(_{0.9}\)Ni\(_{0.1}\) NPs, which have been redistributed to the positions with positive values. These ECD maps are obtained by employing the General Structure Analysis System (GSAS) program, starting with profile refinements of the XRD patterns, followed by calculation of the inverse Fourier transforms of the structure factors to extract the electron density distribution. The electron density contour map of a specific lattice plane is then obtained by slicing the electron density in the vicinity, including 0.025 Å below and above the plane.

Figure 6. (a) Isothermal \(M(H_a)\) curves of the Bi\(_{0.9}\)Ni\(_{0.1}\) NP assembly, measured in field-increasing loops at various representative temperatures. The solid lines indicate the results of the fit to a Langevin field profile plus a Lenz linear diamagnetic term. (b) Temperature dependence of \(1/M\) of the Bi\(_{0.9}\)Ni\(_{0.1}\) NP assembly, measured at \(H_a = 2\) kOe in a warming process after zero-field cooling to 2 K. The solid line indicates the result of a linear fit to the data about 20 K, revealing \(M(T)\) departs from the Curie−Weiss profile below 17 K. (c) Magnetization loops of the Bi\(_{0.9}\)Ni\(_{0.1}\) NP assembly at 2 K, revealing the appearance of magnetic hysteresis with a coercive field of 550 Oe and a remanence of \(1.6 \times 10^{-2}\) emu/g.

Figure 7. (a) Crystalline structure of rhombohedral Bi. The arrows indicate the positions in the crystallographic \(c\)-axis direction where the ECD is plotted. (b−e) Differences on the ECD between the Bi\(_{0.9}\)Ni\(_{0.1}\) and Bi NP assemblies in the (b) \(z = 0.234\), (c) \(z = 0.167\), (d) \(z = 0.333\), and (e) \(z = 0.284\) crystallographic planes, as inferred from the XRD data. The color bars are in units of e/Å\(^3\).

The crystalline structure of rhombohedral Bi may be viewed as composed of wavy Bi layers that are stacked along the crystallographic \(c\)-axis direction (Figure 7a). There is a significant increase in the number of electronic charges in the interconnecting region between two neighboring Bi ions within the layers, revealing a threefold symmetry for the additional ECD distribution in the Bi lattice plane (\(z = 0.234\)) of the wavy layer (Figure 7b). The regions with negative values in the difference ECD extend about half way toward its nearest neighbors, showing not only that the outer electrons but also the inner electrons become more extended distributed after Ni-doping. The additional electronic charges are more focused at specific locations in the inner regions of the wavy layers. A sixfold symmetry of the additional ECD is seen in the \(z = 0.167\) layer, as viewed from the center of the wavy hexagonal honeycomb web (Figure 7c). The changes in the ECD in the inner regions of the wavy layers can be as high as \(\pm 0.03\) e/Å\(^3\). Approaching the interlayer regions, it is interesting to see that the additional electronic charges appear more in the central region between two neighboring layers (Figure 7d) than closer to the layers (Figure 7e). A smaller number of electronic charges shifts to the interlayer region than to within the layers, as shown in Figure 8, where the contour surfaces for a difference ECD of \(+0.02\) e/Å\(^3\) are marked by light (light blue) shading while those for \(-0.02\) e/Å\(^3\) are marked by dark (vermillion) shading. Apparently, the change in the spatial distribution of the electronic charge from Ni-doping does not extend isotopically in all crystallographic directions, but rather a portion of electrons shift from specific regions to others. The redistribution involves not only spherically distributed 6s electrons but also includes directional 6p electrons and perhaps 5d electrons as well.
Interestingly, the DOS near Bi.42 is known to be crucial for the band structure calculation in bulk augmented wave representation, and a plane-wave basis set (VASP) as implemented in the Vienna ab initio simulation package as 14 times that of Bi8 (Figure 10a). This large increase of allowed for self-consistent calculation. Spin−ion is the structure that most closely resembles Bi0.9Ni0.1. This con replaces the Bi ions by Ni ions. The atomic energy was set to be 400 eV, and an error of less than 10−6 eV allowed for self-consistent calculation. Spin−orbit coupling was also considered in both the Bi8 and the Bi7Ni1 systems, which is known to be crucial for the band structure calculation in bulk Bi. Redistribution of the outer electronic charges resulting from the incorporation of Ni ions onto the vicinity of Bi ions is clearly revealed in the calculated ECD. Several features may be identified in the difference plots between the ECD of Bi8 and Bi7Ni1: (1) the appearance of a larger number of electronic charges in the outer regions of the Ni sites (Figure 9a), reflecting the fact that Ni ions possess more valence electrons than Bi ions; (2) the outer electronic charges appear to be focused more at specific positions but do not indicate a rhombohedral symmetry (Figure 9a,b), showing the occurrence of a shift in the electronic charge from Ni sites to neighboring Bi sites; (3) the appearance of a larger number of electronic charges in the interconnecting regions between two neighboring Bi ions (Figure 9a); and (4) a directional shift of the electronic charge away from Ni sites (Figure 9a,b).

The DFT calculations also show that Ni-doping gives rise to a large increase of the DOS near the Fermi energy EF. Interestingly, the DOS near EF for the Bi7Ni1 can be as much as 14 times that of Bi8 (Figure 10a). This large increase of DOS near the E F is mainly contributed from the d-orbitals of the Ni ions in Bi7Ni1, which generate a large number of electronic states within a narrow energy range near EF (Figure 10b). The electronic states contributed from the Bi ions, on the other hand, spread over a wide range in energy and with a much smaller DOS when is compared to that from the Ni ions (Figure 10c). The DOS near EF of Bi7Ni1 are mainly contributed from the Ni-d and Bi-p orbitals, which give rise to a large enhancement in the DOS near the EF. Clearly, the hybridization between the Ni-d and Bi-p orbitals in Bi7Ni1 distort the rhombohedral symmetry of the ECD distribution. A significant amount of electronic states renormalized from below the Fermi level to near and above upon incorporation of Ni ions onto the Bi sites (Figure 10d). In addition, a magnetic moment of 0.28 μB is obtained in the calculation for the Ni-d state in Bi7Ni1, with an orbital moment which is about 20% that of the spin moment. Table 2 lists the calculated spin and orbital moments along the three crystallographic axis directions. Apparently, the embedment of smaller Ni atoms onto the Bi crystalline matrix allows the 3d94s2 outer electrons of Ni to distribute toward the interconnecting regions between two neighboring ions and the electronic states of Ni-d orbitals give rise to additional DOS near the Fermi level.
8. CONCLUSIONS

In this report, we demonstrated that the $T_C$ and $H_C$ of rhombohedral Bi NPs can be greatly enhanced by the incorporation of Ni ions onto the NPs. A more than fourfold increase of $T_C$ to 18 K is found after the incorporation of 10% Ni into 11 nm Bi NPs. The isothermal magnetization reveals a Langevin field profile, and magnetic hysteresis is clearly revealed in the superconducting phase, showing the coexistence of SC and FM. Three key factors that enhance the SC in rhombohedral Bi NPs upon Ni-doping have been identified. Among them, the largest enhancement to the superconducting coupling strength is the enlarged DOS near the Fermi level contributed from the Ni-d orbitals. The DOS near Fermi level for the Bi-Ni$_1$ can be as much as 14 times that of the Bi. Second, the Ni ions serve to supply charges that deliver electronic charges to the interconnecting region between two neighboring Bi ions, which occurs because more valence electrons are available in Ni (3$d^8$4$s^2$) than in Bi (6$s^2$6$p^3$). Third, Ni-doping causes the lattice to shrink (by 0.3% at 300 K) which strengthens the lattice coupling between the Bi ions, resulting from a smaller ionic radius for Ni ion than for Bi ion. The enhancement from the stronger lattice coupling is relatively weak compared with that arising from changes in the electronic states. We remark finally that we found no evidence of the existence of magnetic coupling for SC in Ni-doped Bi NPs, as the superconducting transition temperature does shift to a lower temperature under the application of a magnetic field as weak as 50 Oe.

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