Structure and Transport Properties in Itinerant Antiferromagnet 
RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ (RE = Ce, Sm)

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ABSTRACT: We report the crystal structure and physical properties of two Ni$_2$As$_2$-based compounds RE$_2$Ni$_x$As$_3$O$_2$ (RE = Ce, Sm). The former exhibits structural phase transition from tetragonal (space group I4/mmm, 139) to orthorhombic (space group Immm, 71) symmetry at 230 K, while the latter undergoes a charge-density-wave-like structural distortion with abrupt change of Ni–As bond length. Both compounds show antiferromagnetic transitions due to RE$^{3+}$ ions ordering at 4.4 and 3.4 K, accompanying with the large enhancement of Sommerfeld coefficients comparing to the nonmagnetic La analogue. Although the Cu substitution for Ni induces structural anomalies and suppression of structural transition like the behaviors in La/Pr/Nd analogues, the superconductivity is not observed in both Cu-doped RE$_2$Ni$_x$As$_3$O$_2$ (RE = Ce, Sm) above 0.25 K. Our structural refinements reveal that the lacking of superconductivity in RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ might relate to the anomalous increase of As height, $h_1$.

INTRODUCTION

Identifying the key structural unit and tuning its geometry are important in exploring superconductor and understanding the relationship between superconductivity (SC) and crystal structure. One known example is FeAs-based superconductors, in which the distorted degree of FeAs$_4$ tetrahedral empirically determines the highest superconducting critical temperature ($T_c$), magnetism, and correlation strength.$^{1-3}$ Replacing the La$_2$O$_3$ layer by Sm$_2$O$_3$ can effectively enhance the $T_c$ from 26 to 58.1 K by optimizing the FeAs$_4$ tetrahedral geometry.$^{4-7}$ Actually, the inherent mechanism is mainly tuning an indirect hybridization degree of Fe d$_{xy}$/d$_{yz}$ orbital and As p$_y$ orbital, which can make the regular shape of FeAs$_4$ tetrahedral (Fe–As–Fe angle: 109.5°, As height: 1.38 Å) have optimal electron-correlation strength and hopping exchanges.

Besides, the anionic cluster of (Ch$_2$)$_{25}$ (Ch = Se, Te) and (Pn)$_{16}$(Pn = P, As) can be viewed as novel carrier controlling unit$^{8-10}$ in which the main group elements are connected by covalent bond. Altering the bond length can change the total electron numbers and structural stability, which synergistically influences the carrier concentration and electron–phonon coupling strength. Previous experiments demonstrated that elongating the bond length of (Ch$_2$)$_{25}$ dimer could significantly enhance the $T_c$ and change the crystal structure. For example, in pyrite-type Ir$_x$Se$_{2-x}$, increasing Ir content can lengthen the bonds of Se–Se and simultaneously influence the $T_c$.$^{11,12}$ The maximal $T_c$ of 10 K can be reached as the weakest Se–Se bonding states and the structural instability emerges.$^{11}$ Similarly, the breaking of Te–Te bonds in AuTe$_2$ by chemical substitution and physical pressure could induce SC accompany with a phase transition.$^{13,14}$ Furthermore, As–As zigzag chain and As–As dimer are observed in Ca$_1$-$x$La$_x$Fe$_2$As$_2$,$^{15,16}$ and Pt–CaFe$_2$As$_2$,$^{17,18}$ respectively, which are critical to stabilize the crystal and SC.

Very recently, three series of RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ (RE = La, Pr, Nd) superconductors were discovered by us,$^{19}$ in which a Ni$_2$As$_2$ unit composed of antifluorite Ni$_2$As$_2$ layer and two As–As dimer is believed to be the critical ingredient for SC. It is found that Cu doping could enhance the $T_c$ to 2.5 K. It offers an opportunity to study the evolution of Ni$_2$As$_2$ unit and SC through tuning the geometry of Ni$_2$As$_2$ polyhedral and As
height. In this work, we report that the structure and properties of two analogous RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ (RE = Ce, Sm), which exhibit structural transition or charge-density-wave-like distortion under low temperatures. Through Cu doping, however, the SC is not observed as low as 0.25 K in all measured samples. Combing the crystallographic parameters in all five RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ compounds, the evolution of Ni$_x$As$_3$ unit has been systematically investigated, and the optimal geometry of Ni$_x$As$_3$ unit is identified.

**EXPERIMENTAL SECTION**

Polycrystalline samples of RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ ($x = 0.0–1.0$) were synthesized by solid-state reactions. The binary precursors CeAs/SmAs, Cu$_5$As and Ni$_3$As were presynthesized by reacting Ce/As filings, Cu, Ni, and As powders at 1000 K for 20 h. Then, the powders of Ce$_2$/Sm$_2$As$_3$, Cu$_5$As, Ni$_3$As, La$_2$O$_3$/Sm$_2$O$_3$, Ni and Cu were weighted as the stoichiometric ratio, ground and pelletted under a pressure of 15 MPa in an argon-filled glovebox. The pellets were loaded into an Al$_2$O$_3$ crucible and sealed into evacuated silica tube, which was heated up to 1250 K and kept for 40 h. The powder X-ray diffraction (PXRD) pattern was collected at room temperature using a Panalytical diffractometer (Cu K$_\alpha$ radiation) equipped a low-temperature option (10–300 K). Rietveld refinements were performed using Fullprof suites. The electrical resistivity ($\rho$), dc magnetic susceptibility ($\chi$), and heat capacity ($C_p$) were measured through the standard four-wire method, vibrating sample magnetometer and heat relaxation method at PPMS (Quantum Design), respectively. The resistance below 1.8 K was measured in an Oxford fridge equipped with a dilution refrigerator and a He-3 probe. Crystal orbital Hamilton population (COHP) analysis as implemented in the LOBSTER package gives information about the interatomic interaction, where a negative (positive) COHP value indicates bonding (antibonding) states.

**RESULTS AND DISCUSSION**

Figure 1a,b shows the Rietveld refinements of PXRD pattern of RE$_2$Ni$_x$As$_3$O$_2$ (RE = Ce, Sm) collected at 300 K, respectively. The calculated profiles are based on the initial model RE$_2$Cu$_5$As$_3$O$_2$. Two refinements converged to $R_p = 2.17%$ and $R_m = 3.00%$, $R_w = 1.99%$ and $R_p = 2.76%$, respectively, indicating the reliable structural determination. The lattice constants of Ce$_2$Ni$_x$As$_3$O$_2$ are $a = b = 4.0360(1)$ Å, $c = 22.3686(5)$ Å with space group Immm (No. 139), and those of Sm$_2$Ni$_x$As$_3$O$_2$ shrink to $a = b = 3.9738(1)$ Å, $c = 22.3053(6)$ Å due to the smaller ion radius of Sm$^{3+}$. The crystal structure of RE$_2$Ni$_x$As$_3$O$_2$ (RE = Ce, Sm) is drawn as inset of Figure 1a, which is consisted of fluorite-type RE$_2$O$_2$ layer and Ni$_3$As$_3$ unit. The Ni$_3$As$_3$ can be viewed as conjunction of two antifluorite Ni$_3$As$_3$ layers through Ni–Ni metallic bonds (2.60 Å). Here, the As(1)–As(2) distances along the c-axis (2.68 and 2.73 Å) locate the bonding regime of As–As covalent bonds, and the As(1)–As(2) bond length determines the thickness of Ni$_3$As$_3$ unit along c-axis.

The temperature-dependent electrical resistivity ($\rho$–$T$) of Ce$_2$Ni$_x$As$_3$O$_2$ is plotted in Figure 2a. It shows typical metallic behavior, where two resistivity kinks at $T_s = 230$ K and $T_M = 4.4$ K are observed. The former is associated with the structural phase transition like the observation in ref 19, and the latter is believed to be an antiferromagnetic transition of Ce$^{3+}$ ion. To check the structural phase transition, we measured the low-$T$ PXRD patterns of Ce$_2$Ni$_x$As$_3$O$_2$ from 300 to 10 K (see Figure S1). Figure 2b shows the Rietveld refinements of PXRD profile of Ce$_2$Ni$_x$As$_3$O$_2$ at 10 K, in which the structure symmetry lowers to Immm (No. 71) with $a_0 = 4.0315(1)$ Å, $b_0 = 4.0608(1)$ Å and $c = 22.1875(2)$ Å, exhibiting a rotation breaking ($C_2$–$C_2$). The inset of Figure 2b shows the schematic structure of Ni$_3$As$_3$ unit at 10 K. The Ni–Ni square plane changed into distorted Ni$_3$As polyhedral with two upshifted Ni(1) and two downshifted Ni(2). In Figure 2c, we found that the (105) and (200) peaks split into (015)/(105) and (020)/(200) peaks below 220 K. The resultant lattice constants are shown in Figure 2d. It can be seen that the symmetry breaking and the abrupt changes in c and volume (V) clearly evidence a structural phase transition as temperature going through 230 K.

The temperature-dependent magnetic susceptibility ($\chi$–$T$) of Ce$_2$Ni$_x$As$_3$O$_2$ is plotted at Figure 3a. The structural-transition induces a small drop in $1/\chi$ at 230 K. The data from 80 to 210 K can be well fitted by modified Curie–Weiss equation $1/\chi=(T-\theta)/C$, where $C$ is a materials-specific Curie constant and $\theta$ is Curie temperature. The estimated magnetic moment is $\sim 2.94$ $\mu_B$ and $\theta = 27$ K, indicating an AFM interaction due to RE$^{3+}$ ions ordering, which is often observed in the layered compounds with [RE$_2$O$_2$]$^{2+}$ layers. A little downward in $\chi(T)$ curve is found below $\sim 4.2$ K, which is a hint of AFM transition. In Figure 3b, we plotted the specific heat ($C_p$) of Ce$_2$Ni$_x$As$_3$O$_2$ from 270 to 2.0 K, in which a sharp peak shows up at 230 K, perfectly matching the temperature of phase transition. The sharp peak indicates that it is a first-order transition. Furthermore, fitting of low-temperature data using the equation $C_p/T = \gamma + \beta T^2 + \eta T^4$ gives Sommerfeld coefficient ($\gamma$) is 93.6 mJ/mol K$^2$, $\beta = 1.18$ mJ/mol K$^4$, and $\eta = 1.8 \times 10^{-3}$ mJ/mol K$^4$. The Debye temperature ($\Theta_D$) is estimated to be 270.2 K as the equation $\Theta_D = (12\pi^2 nR/S\rho)^{1/3}$. Meanwhile, we noted there is a large upturn of $C_p(0)$ of 0 K is about 15 J/(mol K), which comes from the strong interaction of Ce 4f electron spin rather than that of Ni$_x$.

Figure 1. Rietveld refinements of powder X-ray pattern of Ce$_2$Ni$_x$As$_3$O$_2$ (a) and Sm$_2$Ni$_x$As$_3$O$_2$ (b) collected at 300 K. The inset of (a) is crystal structure of RE$_2$Ni$_x$As$_3$O$_2$.
The \( \rho-T \) curve of \( \text{Sm}_2\text{Ni}_5\text{As}_3\text{O}_2 \) is shown in Figure 4a. Besides the metallic behavior, we observe a large jump of resistivity at \( T^* = 80 \) K and small increase at \( T_N = 4.05 \) K. The hysteresis of jump implies that it is a first-order transition. Meanwhile, the Hall coefficient \( (R_H) \), shown as inset of Figure 4a, changes from positive to negative below \( \sim 80 \) K, indicating that the Fermi surface is dominated by electrons after this transition. Similarly, the PXRD pattern at 10 K of \( \text{Sm}_2\text{Ni}_5\text{As}_3\text{O}_2 \) is refined to check the insight of resistivity jump (see Figure S2). Figure 4b is the Rietveld refinements profile of \( \text{Sm}_2\text{Ni}_5\text{As}_3\text{O}_2 \). In contrast to that of \( \text{Ce}_2\text{Ni}_5\text{As}_3\text{O}_2 \), this pattern is still well-refined by a tetragonal unit cell (space group: I4/\( \text{mmm} \)) without lowering rotation symmetry. The whole fitting converged to \( R_{wp} = 4.59\% \) and \( R_p = 3.04\% \). In Figure 4c, upon cooling, the lattice constant, \( a \), monotonously decreases, while \( c \) increases and tends to saturate below 150 K, showing a small kink at 80 K. This anomalous variation in lattice constants is totally different from what happened in the \( \text{RE}_2\text{TM}_5\text{As}_3\text{O}_2 \) (TM = Cu, Ni). Carefully examining the low-temperature structure, we found that an increase of \( c \), 0.05\%, is mainly attributed to the increase of As(1)−As(2) bond length (1.3\%), see Figure 4d. Actually, in the Ni5As3 unit, the two kinds of anion height (\( h_1 \) and \( h_2 \)) show inversed trend by cooling, i.e., the upper \( h_1 \) increases and the lower \( h_2 \) decreases (see Figure S3). It means that the value of coordination of \( z_{\text{Ni}(1)} \) will continuously decrease, what perfectly matches our Rietveld refinements as shown in Figure 4e,f. Furthermore, there is an abrupt drop of \( z_{\text{Ni}(1)} \) at 80 K, which is believed to be a kind of weak charge-density-wave-like transition as observation in \( \text{KNi}_2\text{S}_2 \).27

The temperature-dependent magnetic susceptibility (\( \chi-T \)) of \( \text{Sm}_2\text{Ni}_5\text{As}_3\text{O}_2 \) is plotted at Figure 5a. A clear AFM transition has been detected at \( T_N = 4.11 \) K, which confirms that the increase of \( \rho(T) \) is due to formation of magnetic ordering of Sm\(^{3+} \) ions. The 1/\( \chi \sim T \) data is fitted by modified Curie–Weiss equation, yielding magnetic moment (\( \mu_{\text{eff}} \)) is \( \sim 1.21 \mu_B \) and \( \theta = -15 \) K. The scale of \( \mu_{\text{eff}} \) is slight smaller than the theoretical value of free Sm\(^{3+} \) ions. In Figure 5b, we plotted the specific heat (\( C_p \)) of \( \text{Sm}_2\text{Ni}_5\text{As}_3\text{O}_2 \) from 120 to 2.0 K. We did not see any anomaly around \( T^* = 80 \) K. In the lower temperature
range, a well-defined peak has been observed at 3.37 K, which is consistent with the temperature of AFM ordering of Sm$^{3+}$ ions. Fitting the low-temperature data using equation, $C_p/T = \gamma + \beta T^2 + \eta T^4$, yields the Sommerfeld coefficient ($\gamma$) is 362.7 mJ/mol K$^2$, $\beta = 1.97$ mJ/mol K$^4$, and $\eta = 3.1 \times 10^{-4}$ mJ/mol K$^6$. Adding the contribution of $\eta T^4$ can better fit the data, implying that small anharmonic effect due to anisotropic bonding states may exist. The Debye temperature ($\Theta_D$) is estimated to be 228.3 K as the equation $\Theta_D = (12\pi^2 n R / 5 \beta)^{1/3}$, which is a little smaller than that of Ce$_2$Ni$_5$As$_3$O$_2$. These observations are like the behaviors of Kondo lattice reported in CeRuPO$_2$,$^{28,29}$ and RENiAsO$_2$, where the local criticality of 4f electrons mainly determine the intrinsic properties.

We prepared a series of Cu-doped RE$_2$Ni$_5$As$_3$O$_2$ samples to investigate the structure variation and superconductivity. The PXRD patterns and structural information is shown in Figures S4 and S5 and Table S1. Figure 6 presents the structural evolution of Cu-doped RE$_2$Ni$_5$As$_3$O$_2$ samples and the results are analogous to those of superconducting (La, Pr, Nd)$_x$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ ($x = 0.0-1.0$). The $a$-lattice increases, while the $c$-lattice slightly decreases as $x < 0.6$. Once $x > 0.6$, the $a$-lattice decreases, while the $c$-axis rapidly increases, see Figure 6a,b. Figure 6c displays that the minima of $c/a$ ratios show up at $x = 0.6$, where these minima are close to 5.45. Even though there are anomalies in lattice constants, the volumes of unit cell linearly increase by 3.6 and 4.2%, respectively, as shown in Figure 6d. Overall, the structural trend against Cu doping is similar to that of full solid solutions of La$_x$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$. However, the single-phase limits of solid solutions are 90 and 80% for Cu-doped Ce$_2$Ni$_5$As$_3$O$_2$ and Sm$_2$Ni$_5$As$_3$O$_2$, respectively.

Since the coordination environment of Ni and As is similar to that of FeAs-based superconductors, we summarize the Ni–As bond lengths, bond angles (Ni–As–Ni), and As height in the (Ni/Cu)$_x$As$_3$ unit of RE$_2$(Ni$_{1-x}$Cu$_x$)$_5$As$_3$O$_2$ (RE = Ce, Sm) compounds. The structure of (Ni/Cu)As plane in $ac$-plane is...
shown in the inset Figure 7a. The anion heights ($h_1$ and $h_2$) are not identical due to different Wyckoff position of As(1) and As(2), which are synergistically determined by the Ni−As bond length and angles 1 and 2, respectively. From Figure 7a, one can see that the Cu doping slightly changes the Ni(1)−As(1) bond length $x < 0.6$, while it abruptly elongates the Ni(1)−As(1) bond lengths once $x > 0.6$. For Sm$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_3$O$_2$, the Cu-doping mildly increase this bond length in whole doping range. For angle 1, see Figure 7b; the Cu-doping straightly increases the value, while the trend is inversed as $x > 0.6$. As for the anion height $h_1$, it first decreases as $x < 0.6$ and then drastically increases; see Figure 7c. However, $h_2$ monotonously increases in the whole range of Cu doping; see Figure S6. The distinct trends of $h_1$ and $h_2$ induce that the As(1)−As(2) distance initially increases and then rapidly increases once the $x$ is above 0.6, as shown in Figure 7d. As in previous reports, the As−As covalent bond length is around 2.7−2.9 Å. As $x > 0.8$, both As−As distances are above...
2.85 Å, leading to a rather weak bonding state. It means that the As–As bond gradually breaks against Cu doping. In La$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$, the As–As bond lengths are smaller than 2.80 Å, where the bonding states are stable. However, as the calculation of molecular COHP, the Fermi level is just below the antibonding states. The As–As bonding energy is 3.01 and 2.66 eV per bond for Ce$_2$Ni$_3$As$_4$O$_2$ and Sm$_2$Ni$_3$As$_4$O$_2$, respectively; see Figure S7. Doping Cu would naturally upshift the Fermi level to the antibonding states of As–As bond, destabilizing the structure.

Figure 8 is electrical resistivity of RE$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$ (RE = Ce, Sm) samples. Most samples show metallic behaviors, and the resistivity jump due to phase transition in RE$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$ is quickly suppressed by Cu doping. However, the low-temperature anomalies associated with AFM transition are still observed in Ce$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$. Unfortunately, we did not see any superconductivity above 0.25 K in all measured samples, contrasting the findings in La$_2$/Pr/ Nd$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$ samples.

As we know, in the FeAs-based superconductors, the optimal $h_1$ and Fe–As–Fe angle 1 are 1.38 Å and 109.5°, respectively. Lowering (elevating) the $h_1$ would increase (decrease) the orbital hybridization and drive the system to more itinerant (localized) states, leading to suppression of $T_c$.

In summary, detailed structure analyses reveal there is optimal (Ni/Cu)As$_4$ geometry with As height (1.15 Å) and angle 1 (120.9°) for SC in La$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$, which are far from the ideal values (1.38 Å and 109.5°) in FeAs-superconductors. Although the Cu substitution in antiferromagnetic (Ce/Sm)$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$ could realize the more regular (Ni/Cu)As$_4$ tetrahedral, the SC is absent. From this point of view, the findings in Cu-doped RE$_2$Ni$_3$As$_4$O$_2$ apparently do not obey those empirical rules in FeAs-based superconductors. It provides a new perspective to fully understand the TM-based oxypnictides superconductors.

### CONCLUSION

In summary, detailed structure analyses reveal there is optimal (Ni/Cu)As$_4$ geometry with As height (1.15 Å) and angle 1 (120.9°) for SC in La$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$, which are far from the ideal values (1.38 Å and 109.5°) in FeAs-superconductors. Although the Cu substitution in antiferromagnetic (Ce/Sm)$_2$(Ni$_{1-x}$Cu$_x$)$_3$As$_4$O$_2$ could realize the more regular (Ni/Cu)As$_4$ tetrahedral, the SC is absent. From this point of view, the findings in Cu-doped RE$_2$Ni$_3$As$_4$O$_2$ apparently do not obey those empirical rules in FeAs-based superconductors. It provides a new perspective to fully understand the TM-based oxypnictides superconductors.
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