Polymorphism and superconductivity in the V-Nb-Mo-Al-Ga high-entropy alloys

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ABSTRACT High-entropy alloys (HEAs) are the focus of current research for their diverse properties, including superconductivity and structural polymorphism. However, the polymorphic transition has been observed only in non-superconducting HEAs mostly under high pressure. Here we report the discovery of the superconductivity and temperature-driven polymorphism in (V0.5Nb0.5)3−xMoxAl0.5Ga0.5 (0.2 ≤ x ≤ 1.4) HEAs, which are of a single body-centered cubic (bcc) structure for x = 0.2 and a mixture of the bcc and A15 structures for higher x values. Upon annealing, the bcc structure undergoes a polymorphic transformation to the A15 one and all HEAs exhibit bulk superconductivity. For the sample with x = 0.2, the bcc polymorph is not superconducting down to 1.8 K, whereas the A15 polymorph has a superconducting transition temperature $T_c$ of 10.2 K and estimated zero-temperature upper critical field $B_{c2}(0)$ of 20.1 T, both of which are the highest among HEA superconductors. With increasing Mo content x, both $T_c$ and $B_{c2}(0)$ of the A15-type HEAs decrease, yet the large ratio of $B_{c2}(0)/T_c$ signifies a disorder-induced enhancement of the upper critical field over a wide x range. The decrease in $T_c$ is attributed to the decrease in both the electronic specific-heat coefficient and electron-phonon coupling strength. Furthermore, the valence electron count dependence of $T_c$, which is different from both the binary A15 and other structurally different HEA superconductors, suggests that $T_c$ may be increased further by reducing the number of valence electrons. Our results not only uncover HEA superconductors of a new structural type, but also provide the first example of polymorphism-dependent superconductivity in HEAs.

Keywords: polymorphism, superconductivity, V-Nb-Mo-Al-Ga high-entropy alloys

INTRODUCTION

In materials science, polymorphism refers to the property of a solid material to crystallize between at least two distinct structures. For superconductors, the presence of polymorphs is of considerable interest since it offers a unique opportunity to study how the spatial atomic arrangement affects the superconducting properties without changing the chemical composition, which may provide useful clues to the superconducting mechanism [1]. So far, the concurrence of structural polymorphism and superconductivity at ambient pressure has been observed only in ordered materials, such as pure elements [2], binary alloys [3,4], ternary rare/alkali-earth intermetallics [5,6], perovskite oxides [7], doped fullerides [1], transition metal dichalcogenides [8], and organic charge-transfer salts [9,10].

Recently, HEAs have received much attention due to their fascinating mechanical, thermal and physical properties [11–15]. These alloys are single solid-solution phases made up of five or more metal elements, whose concentrations are restricted between 5% and 35% atomic percent. Due to the extremely high chemical disorder, HEAs can be viewed as a metallic glass with an ordered lattice, and have been found mostly in high symmetry crystal structures, such as body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close pack (hcp). Among the large number of HEAs studied, a few members have been reported to show bulk type-II superconductivity [16]. These HEA superconductors are based on d transition metal elements, and can be categorized into four different structural types: bcc type [17], α-Mn type [18], CsCl type [19], and hcp type [20]. In particular,

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CsCl-type (ScZrNb)_{0.65}(RhPd)_{0.35} HEA has the highest $T_c$ of $\sim 9.3\,\text{K}$, [19] and the highest $B_{c2}(0)$ of $\sim 11.7\,\text{T}$ is achieved in the (TaNb)_{0.5}(ZrHfTi)_{0.5} HEA with a simple bcc structure [21]. Moreover, the bcc-type (TaNb)_{0.67} (HfZrTi)_{0.33} HEA shows robust zero-resistance superconductivity without structural transition at pressures up to 190 GPa, demonstrating the potential of HEAs for application under extreme conditions [22]. However, no polymorphs of these HEA superconductors have been reported so far. As a matter of fact, the polymorphic transitions are observed only in nonsuperconducting HEAs and mostly at very high pressure, though the different polymorphs can still exist after the pressure is relieved [23–25].

It is known that the formation energies of the bcc and A15 phases are very similar in some A,B-type compounds, where A is a group VB or VIB transition metal element such as V, Nb and Mo, and B is usually a IIIA main group element such as Al and Ga [3,26,27]. Consequently, a bcc-to-A15 polymorphic phase transition can be induced by thermal annealing. It is therefore of interest to study the HEAs based on the V-Nb-Mo-Al-Ga system, which, however, have not been explored to date. In this paper, we present a systematic study on the structural and physical properties of the (V_{0.5}Nb_{0.5})_{3−x}Mo_{x}Al_{0.5}Ga_{0.5} HEAs for $0.2 \leq x \leq 1.4$. It is shown that, the arc-melted (as-cast) HEA with $x = 0.2$ possesses a disordered bcc structure, which transforms to the A15 structure after annealing at 1600°C. Whereas the bcc polymorph remains normal down to 1.8 K, the A15 one turns out to be a bulk superconductor with a $T_c$ of 10.2 K and an orbitally-limited $B_{c2}(0)$ of 20.1 T. For $x \geq 0.4$, the as-cast HEAs contain a mixture of bcc and A15 polymorphs, and a similar bcc-to-A15 polymorphic transition is observed upon annealing. With increasing Mo content $x$, both $T_c$ and $B_{c2}(0)$ of the A15-type HEAs decrease, while the ratio of $B_{c2}(0)/T_c$ for $0.2 \leq x \leq 1.2$ is larger than or comparable to that of NbSn. The decrease in $T_c$ is concomitant with a decrease in both the density of states at the Fermi level [$N(E_F)$] and electron-phonon coupling strength, as expected in the Bardeen-Cooper-Schrieffer (BCS) theory. By comparing the valence electron account (VEC) dependence of $T_c$ for these A15-type HEAs, the binary A15 and other structurally different HEA superconductors, the immanent mechanism is revealed.

**EXPERIMENTAL SECTION**

The V-Nb-Mo-Al-Ga HEAs were prepared by arc melting high-purity V (99.9%), Nb (99.9%), Mo (99.9%), Al (99.9%) powders and Ga shots (99.9%) according to the stoichiometric ratio of $\text{V:Nb:Mo:Al:Ga} = (1.5−x)/2:(1.5−x)/2:x:0.5−0.5$ with $x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2$ and 1.4. In order to minimize the volatilization of Al and Ga during the arc melting process, the mixture prereacted at 1000°C for one week, and then was melted in an arc furnace under high-purity argon atmosphere. The melts were turned over and remelted several times to ensure homogeneity, followed by rapid cooling on a water-chilled copper plate. For annealing experiments, the as-cast ingots were thoroughly ground and pressed into pellets, which were loaded in alumina crucibles in an argon-filled glove box. The crucibles were then placed in Ta tubes, sealed in evacuated quartz tubes and heated at 1600°C under argon atmosphere in a muffle furnace for 12 h. After furnace cooling to 900°C, the quartz tubes were quenched into the cold water.

The phase purity of as-cast and annealed HEAs was checked by powder X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu Ka radiation at room temperature. The structural refinements were performed by using the JANA2006 program [28]. The chemical composition was measured with an energy-dispersive X-ray spectrometer (EDX, Model Octane Plus) affiliated to a Zeiss field emission scanning electron microscope. The spectra were collected on different locations of each sample for averaging. The electron diffraction was taken with a JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 kV. The electrical resistivity and specific heat were measured by the standard four-probe and the relaxation methods, respectively. The resistivity and specific heat measurements down to 1.8 K and up to 9 T were carried out by a Quantum Design PPMS-9 Dynacool. The direct current (dc) magnetization measurements down to 1.8 K were performed on a commercial SQUID magnetometer (MPMS3).

**RESULTS AND DISCUSSION**

The powder XRD patterns at room temperature for the series of as-cast and annealed (V_{0.5}Nb_{0.5})_{3−x}Mo_{x}Al_{0.5}Ga_{0.5} HEAs are shown in Fig. 1a and b, respectively. In Fig. 1a, for the as-cast HEA with $x = 0.2$, only several diffraction peaks appear and can be well indexed to the bcc structure with a lattice constant of 3.163 Å. At higher $x$ values, a number of additional peaks arise at 2θ angles corresponding to the A15-type structure, whose strongest peak overlaps with that of the bcc one. The peak intensity of the A15 structure tends to grow with increasing $x$, yet the coexistence of two phases persists up to $x = 1.4$, the highest Mo content investigated. Upon annealing at
At higher temperature much higher than 1600°C, the peaks of the bcc structure disappear but those belonging to the A15 structure remain. This reveals that the thermal treatment results in a bcc-to-A15 structural transformation. For $x \leq 0.6$, a small impurity peak is observed at $2\theta \approx 42^\circ$, probably coming from the Nb$_2$Al-type sigma phase. By using a least-squares method, the lattice constant of the A15 structure for both the as-cast and annealed HEAs was determined and plotted as a function of $x$.

According to the above results, the $(V_{0.5}Nb_{0.5})_3$–$Mo_{x}$–Al$_{0.5}$Ga$_{0.5}$ HEAs have two polymorphs at ambient pressure: one with the bcc structure and the other with the A15 structure. To gain more insight, we focus on the HEA with $x = 0.2$, where the two polymorphs are isolated from each other. Fig. 2a and b show the structural refinement profiles for the as-cast and annealed HEAs at this composition based on the $Im\bar{3}m$ and $Pm\bar{3}m$ space groups, respectively, and the refined results are listed in Table 1. In both cases, there is a good agreement between the observed and calculated XRD patterns, as indicated by the low $R_{wp}$ and $R_p$ values. In the bcc structure, there is only one crystallographic site for the five different atoms, whose occupancies are set by the respective atomic fraction. For the A15 structure, there are two distinct sites (0.25, 0, 0.5) and (0, 0, 0), while the atomic occupancy at each site remains unchanged. As a consequence, the one-dimensional chains consist of both transition metal and main group element atoms, in contrast to the binary A15 superconductors [29]. Fig. 2c and d show the electron diffraction patterns for the bcc and A15 polymorphs, respectively. In the former case, the pattern consists of a series of concentric rings, which match well with the crystal planes of the bcc structure with a small grain size. By contrast, for the A15 one, well defined spots from (100) planes can be observed, which also provides evidence for the growth in grain size during the annealing process. Overall, these results are very similar to those observed in binary A$_B$B-type compounds with the bcc and A15 polymorphs [26]. Nevertheless, it should be noted that, for example, annealing Nb$_3$Al at 800°C for several hours is sufficient to transform the bcc polymorph to the A15 one completely. This heat-treatment temperature is only half of that employed for the present HEAs. Actually, we have also performed annealing experiments at 1000°C, but found that the transformation is still not complete after more than one week. Hence it appears that, compared with binary compounds, the HEAs indeed have higher thermal stability. Furthermore, since the A15 polymorph can be regarded as a low-temperature phase and remains stable up to 1600°C, the polymorphic transition from the A15 to bcc structure should occur at a temperature much higher than 1600°C.

Recently, the effect of Al alloying on the bcc-type $(TaNb)_{0.65}(ZrHfTi)_{0.33}$ HEA superconductor has been investigated by von Rohr et al. [30]. The results show that the $[(TaNb)_{0.65}(ZrHfTi)_{0.33}]_1$–$x$Al$_x$ remains in a bcc struc-
ture up to $x = 0.3$, but changes to a sigma phase structure with increasing $x$ to 0.4, suggesting that the structure of this system is instable. Therefore, a polymorphic transition may occur for some $x$ value upon proper thermal treatment. It is worth noting that, even for the Al-free Ta-Nb-Zr-Hf-Ti HEAs, the bcc structure can be unstable against annealing, though no other polymorph has been observed [31]. This suggests that the occurrence of structure polymorphism in HEAs is closely related to their constituent elements.

Fig. 2e shows the temperature dependence of normalized resistivity below 50 K for the bcc and A15 polymorphs of the $(V_{0.5}Nb_{0.5})_{3-x}Mo_{x}Al_{0.5}Ga_{0.5}$ HEA with $x = 0.2$. A weak temperature dependence is observed in both cases, which is typical for HEAs [17,21]. Cooled below 10.3 K, the resistivity of the A15 polymorph drops sharply to zero, evidencing a superconducting transition. While a similar resistivity drop is seen at a slightly lower temperature for the bcc polymorph, no zero resistance is achieved down to 1.8 K. On the other hand, a large spe-

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**Table 1** Refined crystallographic data of the as-cast and annealed $(V_{0.5}Nb_{0.5})_{3-x}Mo_{x}Al_{0.5}Ga_{0.5}$ HEAs with $x = 0.2$

|          | As-cast       | Annealed      |
|----------|---------------|---------------|
| Structural type | bcc           | A15           |
| Space group   | $Im\bar{3}m$  | $Pm\bar{3}n$  |
| Lattice parameter | 3.163 Å      | 5.014 Å      |
| $R_{wp}$ factor | 6.8%         | 9.3%         |
| $R_p$ factor  | 5.3%          | 6.6%          |
| Atoms       | $x$ | $y$ | $z$ | Occ. | $x$ | $y$ | $z$ | Occ. |
| V1/Nb1/Mo1/Al1/Ga1 | 0 | 0 | 0 | 0.35/0.35/0.05/0.125/0.125 | 0 | 0 | 0 | 0.35/0.35/0.05/0.125/0.125 |
| V2/Nb2/Mo2/Al2/Ga2 | 0.25 | 0 | 0.5 | 0.35/0.35/0.05/0.125/0.125 |
sific heat $C_p$ jump appears for the A15 polymorph (see Fig. 2e), confirming the bulk nature of its superconductivity. Nevertheless, there is no anomaly in the $C_p$ data of the bcc counterpart. This suggests that the bulk bcc phase does not superconduct above 1.8 K and the observed resistive transition originates from a tiny amount of superconducting impurities. In addition, the $C_p$ data indicates that the electronic specific heat coefficient ($\gamma$) for the bcc polymorph is much smaller than that of the A15 one, which will be discussed further below. In the next part of the paper, we restrict our attention to the superconducting properties of the A15 polymorph in the annealed ($V_{0.5}Nb_{0.5}$)$_3$Mo$_x$Al$_{0.5}$Ga$_{0.5}$ HEAs.

Figure 3a–c show the temperature dependence of resistivity ($\rho$), magnetic susceptibility ($\chi$) and $C_p$ of these HEAs below 12 K, respectively. For each $x$ value, the superconducting transition was characterized by a sharp drop in $\rho$, a strong diamagnetic response and a clear $C_p$ jump. Here $T_c$, determined as the midpoint of the resistive transition, is found to decrease monotonically from 10.2 K to 3.2 K with increasing $x$ to 1.4. The onset temperature of the diamagnetic signal in the zero-field cooling $\chi_{ZFC}$ agrees well with the $T_c$ determined from the $\rho$ measurements. Moreover, the $\chi_{ZFC}$ data at 1.8 K for all HEAs correspond to a shielding fraction of more than 130% without correcting the demagnetization factor. This, together with the $C_p$ jump, clearly demonstrates bulk superconductivity in these HEAs. In the normal state, the $C_p$ data are well fitted by the Debye model $C_p/T = \gamma T + \beta T^2$, where $\beta$ is the phononic specific heat coefficient. Once $\beta$ is known, the Debye temperature $\Theta_D$ can be calculated by the formula $\Theta_D = (12\pi N R/5\beta)^{1/3}$, where $N$ is the number of atoms per unit cell and $R = 8.314$ J mol$^{-1}$ K$^{-1}$ is the molar gas constant. The analysis results are summarized in Table 2. For $x = 0.2$, $\gamma$ has a value of 30.9 mJ mol$^{-1}$ K$^{-2}$ and the normalized specific heat jumps $\Delta C_p/\gamma T_c$ is estimated to be 2.01, which is significantly larger than the BCS value of 1.43 [32]. Nevertheless, the jump can be reasonably reproduced by a modified BCS model with $\Delta_0/T_c = 2.07$, where $\Delta_0$ is the fully isotropic gap at 0 K (see Fig. S1, Supplementary information). This suggests that the superconducting state is still BCS-like [33]. With increasing $x$, the two quantities decrease and reduce to 16.5 mJ mol$^{-1}$ K$^{-2}$ and 1.33 at $x = 1.4$, respectively. On the other hand, with the knowledge of $T_c$ and $\Theta_D$, the electron-phonon coupling...
constant λ_{ep} can be calculated by the inverted McMillan formula [34],

\[ \lambda_{ep} = \frac{1.04 + \mu^* \ln(\gamma/0.45 \Theta_c)}{(1-0.62 \mu^*) \ln(\gamma/0.45 \Theta_c) - 1.04.} \]

where \( \mu^* \) is the Coulomb repulsion pseudopotential. Assuming that \( \mu^* = 0.13 \), \( \lambda_{ep} \) values are also found to decrease from 0.81 to 0.52 with increasing \( \pi \) from 0.2 to 1.4. Taken together, these results suggest that the annealed \((V_{0.5}Nb_{0.5})_3MoAl_{0.5}Ga_{0.5}\) HEAs are moderately coupled superconductors for \( 0.2 \leq \pi \leq 0.8 \) and weakly coupled superconductors for \( 1 \leq \pi \leq 1.4 \).

To obtain the \( B_{c2}(0) \) values for these HEAs, temperature-dependent \( \rho(T) \) was measured under various magnetic fields up to 9 T, an example of which for \( \pi = 0.2 \) is shown in Fig. 3d (for other \( \pi \) values see Fig. S2, Supplementary information). With increasing magnetic field, the resistive transition is slightly broadened and shifts toward lower temperatures as expected. The \( T_c \) value at different fields is determined based on the same criterion as that under zero field, and the resulting \( B_{c2}(T) \) phase diagrams are displayed in Fig. 3e. By using the Wathameter-Helfand-Hohenberg (WHH) theory [35], \( B_{c2} \) can be extrapolated to zero temperature, yielding \( B_{c2}(0) = 20.1, 17.7, 16.5, 14.2, 9.9, 7.6 \) and 4.8 T for \( \pi = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, \) and 1.4, respectively. The Ginzburg-Landau (GL) coherence length \( \xi_{GL} \) can be calculated as \( \xi_{GL} = (\Phi_0/2nB_{c2}(0))^{1/2} \), where \( \Phi_0 = 2.07 \times 10^{-15} \) Wb is the flux quantum. This gives a relatively short \( \xi_{GL} \) varying between 4.0 to 8.3 nm for these HEAs.

The examination of the correlation between the physical properties for these HEAs reveals the following salient features. First, as shown in Fig. 3f, the ratio of \( T_c/\Theta_0 \) increases as the increase of \( \pi \) and hence \( N(E_F) \), which is consistent with the BCS theory [32]. In this respect, the absence of superconductivity for the bcc polymorph of \( \pi = 0.2 \) is likely due to the low \( N(E_F) \) since its \( \pi \) value (12.9 mJ mol\(^{-1}\) K\(^{-2}\)) is only ~40% of that of the A15 one. Nevertheless, the possibility of a weakening of the electron-phonon coupling strength cannot be excluded. Second, when the logarithm of \( T_c \) is plotted as a function of the inverted electron-phonon coupling constant \(-1/\lambda_{ep}\) (see Fig. 3g), two different slopes are discernible, which contrasts with the case of Heusler superconductors [36]. Note that these two slopes correspond well with the weak \((1 \leq \pi \leq 1.4)\) and moderate \((0.2 \leq \pi \leq 0.8)\) electron-phonon coupling regimes found above, respectively. In addition, the data of the A15 superconductor \( Nb_3Sn \) falls on the extrapolation of the data in the moderate coupling regime. Nevertheless, the slope appears to be steeper for smaller \( \lambda_{ep} \), pointing to a more significant role of electron-phonon coupling on \( T_c \) in this regime. Third, as can be seen from Fig. 3h, \( B_{c2}(0)/T_c \) ratio of these HEAs is larger than or comparable to that of \( Nb_3Sn \), despite their much lower \( T_c \). Especially, the \( B_{c2}(0) \) value for \( \pi \leq 0.6 \) slightly exceeds the Pauli paramagnetic limit, \( B_{p}(0) = 1.86 T_c \). While this \( B_{c2} \) behavior has been observed in bcc-type \((Ta_{0.5}Nb_{0.5})_3(HfZr)_{0.6}Zr_{0.4}\) HEA [21], whose \( T_c \) and \( B_{c2}(0) \) values are only about half of those in the present case. In the dirty limit, we have \( B_{c2}(0) \propto \rho_p \gamma \propto -\rho_p \propto \rho_n \propto \sqrt{\rho_p} \propto \rho_n \). Since the \( \gamma \) values of A15-type HEAs are smaller than that of \( Nb_3Sn \) [38], their larger \( B_{c2}(0)/T_c \) is apparently attributed to an enhancement of \( \rho_n \) resulting from the strong disorder, similar to the ball-milled \( Nb_3Sn \) [39]. Also, it is worth noting that the \( B_{c2}(0)/T_c \) ratio tends to increase with the increase of \( T_c \), and that a \( B_{c2}(0) \) value of ~20 T is attainable for a \( T_c \) of 10.2 K. Provided that the \( T_c \) can be enhanced to ~15 K, the \( B_{c2}(0) \) of the A15-type HEAs might be above 30 T, which is higher than that of \( Nb_3Sn \) [40] and may be applied in high field superconducting magnets.

To provide hints for the \( T_c \) enhancement, we plot the \( T_c \)
terminating the constituent elements also play a nontrivial role in determining the upper critical field. Our results not only present a new type of HEA superconductors, but also provide the first example of how this disorder affects normal state resistivity and magnetoresistance, which requires high magnetic fields to suppress superconductivity completely. Third, it is prudent to note that the (V0.5Nb0.5)3Mo3Al5Ga3,5 HEAs exhibit the same polymorphism as the binary combinations of their constituent elements, such as Nb3Al, Mo3Al and V3Ga. Further studies are called for to assess the generality of this observation in other polymorphic HEAs.

CONCLUSIONS

In summary, we have discovered both superconductivity and temperature-driven polymorphism in the (V0.5Nb0.5)x−Mo3Al5Ga3,5 HEAs with x in the range of 0.2 to 1.4. The results show that the as-cast HEA has a single bcc structure for x = 0.2 and a mixture of the bcc and A15 structures for higher x values. Upon annealing, a bcc-to-A15 polymorphic transition takes place and all HEAs are found to exhibit bulk superconductivity. In particular, for x = 0.2, though the bcc polymorph is not superconducting down to 1.8 K, the A15 one has a Tc of 10.2 K and an estimated Bc2(0) of 20.1 T, both of which are the highest among HEA superconductors. With increasing Mo content x, Tc of these A15-type HEAs decreases monotonically, which is ascribed to the reduction in both electron phonon coupling strength and N(EF). Furthermore, the Tc also decreases with increasing el/a from 4.55 to 4.85. This is different from the binary A15 as well as other structurally different HEA superconductors, and suggests that Tc may be enhanced by reducing the number of valence electrons. On the other hand, the Bc2(0)/Tc ratio of the A15-type HEAs, which is larger than that of Nb3Sn over a broad x range, provides evidence for a disorder-induced enhancement of the upper critical field. Our results not only present a new type of HEA superconductors, but also provide the first example of

Figure 4 Dependence of Tc on the average number of valence electrons per atom ratio (el/a) for A15-type (V0.5Nb0.5)x−Mo3Al5Ga3,5 HEAs. The data for binary A15 [4] and other structurally different HEA [17–20] superconductors are also included for comparison. The solid lines are a guide to the eyes, and the two Tc maxima for binary A15 compounds are marked by the arrows.

Finally, we briefly discuss the implication of our results. First, these results clearly indicate that HEA superconductors are not limited to transition metal elements, which open more possibilities of combinations of elements to compose superconducting HEAs. Second, the A15-type HEAs represent an alternative way of introducing strong disorder to study the effect of atomic ordering on the physical properties of A15 compounds. Previously, such disorder can be introduced by ball milling [44], rapid quenching [45] and high-energy particle radiation [46], all of which have no influence on the chemical composition. In this regard, the chemical complexity in HEAs is expected to provide a fresh insight into the effect of compositional disorder. For example, one question is how this disorder affects normal state resistivity and magnetoresistance, which requires high magnetic fields to suppress superconductivity completely.
polymorphism-dependent superconductivity in HEAs, which help to understand the interplay between chemical disorder, crystal structure and superconducting properties in these materials.

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Author contributions Wu J conceived the idea, synthesized the samples and did the physical property measurements with the assistance from Liu B, Cui Y, Zhu Q, Xiao G. Wang H helped in the EDX analyses. Wu S and Cao G contributed to the magnetic susceptibility measurements. Ren Z supervised the project and wrote the paper.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Chemical composition of the HEAs, analysis of the specific heat data for x ≥ 0.2, and resistivity under various field for x ≥ 0.4 are available in the online version of the paper.

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