Superconductivity in Cubic A15-type V–Nb–Mo–Ir–Pt High-Entropy Alloys

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We report the crystal structure and superconducting properties of new V5+2xNb35−xMo35−xIr10Pt15 high-entropy alloys (HEAs) for x in the range of 0 ≤ x ≤ 10. These HEAs are found to crystallize in a cubic A15-type structure and have a weakly coupled, fully gapped superconducting state. A maximum Tc of 5.18 K and zero-temperature upper critical field Bc2(0) of 6.4 T are observed at x = 0, and both quantities decrease monotonically with the increase of V content x. In addition, Tc shows an increase with increasing valence electron concentration from 6.4 to 6.5, which is compared with other A15-type HEA and binary superconductors.

1 INTRODUCTION

High-entropy alloys (HEAs) consisting of five or more constituent elements have received a lot of attention as an emerging class of multicomponent alloys [1–5]. These alloys are stabilized by the high mixing entropy rather than the formation enthalpy, and often referred to as metallic glasses on ordered lattices. Despite the presence of strong chemical disorder, some HEAs exhibit collective quantum phenomena such as superconductivity [6, 7]. So far, a number of HEA superconductors have been discovered and their crystal structures can be categorized into body-centered cubic (bcc)-type [8–11], α-Mn-type [12, 13], CsCl-type [14], hcp-type [15–17], A15-type [18], and s-type [19]. In particular, the A15-type V1.4Nb1.4Mo0.3Al0.3Ga0.3 HEA has a Tc of 10.2 K and a disorder-enhanced upper critical field of 20.1 T [18], both of which are the highest among HEA superconductors. It is worthy noting that, for binary A15-type superconductors, the Tc values exhibit two maxima at valence electron concentrations (VECs) of 4.7 and 6.5, respectively [20]. Since the VEC of the V–Nb–Mo–Al–Ga HEAs is limited below around 5, it is desirable to search for other A15-type HEA superconductors with VEC close to 6.5.

Motivated by this, we replace Al and Ga in the V–Nb–Mo–Al–Ga HEAs with Ir and Pt to form new V5+2xNb35−xMo35−xIr10Pt15 HEAs. A nearly single A15 phase is found for 0 ≤ x ≤ 10, which corresponds to a VEC range of 6.4–6.5. Physical property measurements indicate that these A15-type HEAs are weakly coupled, fully gapped superconductors with Tc and Bc2(0) up to 5.18 K and 6.4 T, respectively. In addition, their Tc increases with increasing VEC, in contrast to the V–Nb–Mo–Al–Ga HEAs. A comparison of the Tc vs. VEC plots is made between the A15-type HEA and binary superconductors, and its implication is discussed.
2 MATERIALS AND METHODS

The \( V_{5+2x}Nb_{35-x}Mo_{35-x}Ir_{10}Pt_{15} \) HEAs were prepared by the arc melting method. Stoichiometric amounts of high purity V (99.99%), Nb (99.999%), Mo (99.995%), Ir (99.99%), Pt (99.99%) elements were mixed thoroughly and pressed into pellets in an argon-filled glove box. The pellets were then melted in an arc furnace under high-purity argon atmosphere. To ensure homogeneity, the melts were flipped several times, followed by rapid cooling on a water-chilled copper plate. The phase purity of as-cast HEAs was checked by powder x-ray diffraction (XRD) at room temperature using a Bruker D8 Advance x-ray diffractometer with Cu-K\( \alpha \) radiation. The structural refinements were performed using the JANA2006 program [21]. The morphology and elemental composition were examined by a Zeiss field emission scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) spectrometer. The four-probe resistivity and specific heat were measured in a Quantum Design Physical Property Measurement System (PPMS-9 Dynacool). The dc magnetization measurements were carried out in a commercial SQUID magnetometer (MPMS3).

3 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction and Chemical Composition

The XRD patterns for the \( V_{5+2x}Nb_{35-x}Mo_{35-x}Ir_{10}Pt_{15} \) HEAs are displayed in Figure 1A. For all \( x \) values, the major diffraction peaks can be well indexed on a cubic lattice with the \( Pm\bar{n}m \) space group, indicative of a dominant A15 phase. With increasing \( x \), the (004) peak shifts toward higher 2\( \theta \) values. This points to a decrease of the \( a \)-axis with the increase of V content, in consistent with its smaller atomic radius compared with those of Nb and Mo [22]. In addition to the A15 phase, small impurity peaks are observed in the vicinity of main (102) diffraction and probably comes from the NbAl\(_2\)-type sigma phase [18]. In the A15 structure, there are two crystallographic sites (0, 0, 0) and (0.25, 0, 0.5). Following Reference [18], all the five constituent elements are assumed to be distributed randomly on these sites (see the inset of Figure 1A), and their occupancies are fixed by the stoichiometry. This assumption is based on the previous studies of binary A15 compounds, which show that the antisite disorder is the most common point defects [23]. In NbSn, it has been argued that the Nb and Sn atoms occupy randomly the two sites after a certain period of mechanical milling [24]. The refinement profiles are shown in Figures 1B–D and the statistics are listed in Table 1. Both the

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**TABLE 1 | Structural and physical parameters of the \( V_{5+2x}Nb_{35-x}Mo_{35-x}Ir_{10}Pt_{15} \) HEAs.**

| Parameter | Unit | \( x = 0 \) | \( x = 5 \) | \( x = 10 \) |
|-----------|------|-------------|-------------|-------------|
| V Content | –    | 7.1%        | 17.0%       | 26.3%       |
| Nb content | –    | 33.8%       | 28.9%       | 25.4%       |
| Mo content | –    | 37.1%       | 29.2%       | 26.0%       |
| Ir content | –    | 10.7%       | 11.2%       | 10.5%       |
| Pt content | –    | 11.3%       | 13.7%       | 11.8%       |
| \( A \) | Å | 5.0324 | 5.0130 | 4.9848 |
| \( R_{wp} \) | – | 11.8% | 11.2% | 10.9% |
| \( R_p \) | – | 8.4% | 7.5% | 7.3% |
| \( T_c \) | K | 5.18 | 4.49 | 3.61 |
| \( \gamma \) | mJ/molK\(^2\) | 4.59 | 4.94 | 5.03 |
| \( \Phi_0 \) | K | 419 | 440 | 393 |
| \( \lambda_{ab} \) | – | 0.59 | 0.56 | 0.55 |
| \( B_{c2}(0) \) | T | 6.4 | 5.7 | 4.4 |
| \( \xi_{GL} \) | nm | 7.2 | 7.6 | 8.7 |
difference plot and \( R_p \) factor indicate a reasonably good agreement between the observed and calculated XRD patterns, which supports the validity of the employed structural model. Note that a more definitive conclusion requires atomic-level spectroscopies in future. The refined lattice parameter \( a = 5.0324, 5.0130, \) and \( 4.9848 \) Å for \( x = 0, 5 \) and \( 10 \), respectively, close to those of the \( \text{V}_{15}-\text{type} \) HEAs. Figures 2A–C show the typical SEM images for the HEAs, all of which appear to be dense and homogeneous. Indeed, EDX elemental mapping reveals the uniform distribution of V, Nb, Mo, Ir, and Pt, and, as an example, the results for \( x = 0 \) are shown in Figures 2D–H. Furthermore, the EDX measurements allow us to determine the chemical compositions to be \( \text{V}_{7.1}\text{Nb}_{33.8}\text{Mo}_{37.1}\text{Ir}_{10.7}\text{Pt}_{1.2} \), \( \text{V}_{17.0}\text{Nb}_{28.9}\text{Mo}_{29.2}\text{Ir}_{11.2}\text{Pt}_{13.7} \), and \( \text{V}_{26.3}\text{Nb}_{25.4}\text{Mo}_{26.0}\text{Ir}_{10.5}\text{Pt}_{11.8} \) for the HEAs with \( x = 0, 5 \), and \( 10 \), respectively. These agree well with the nominal compositions within the experimental error of \( \pm 2.5 \) at%.

### 3.2 Resistivity and Magnetic Susceptibility

Figures 3A, B show the temperature dependencies of resistivity \( (\rho) \) and magnetic susceptibility \( (\chi) \) for the \( \text{V}_{5+2x}\text{Nb}_{35-x}\text{Mo}_{35-x}\text{Ir}_{10}\text{Pt}_{15} \) HEAs, respectively. For each \( x \) value, a sharp drop in \( \rho \) and strong diamagnetic \( \chi \) are observed, signifying a superconducting transition. As indicated by the vertical dashed line, the midpoint of \( \rho \) drop coincides well with the onset of diamagnetic transition. By this criterion, \( T_c \) is determined to be 5.18, 4.49, and 3.61 K for the HEAs with \( x = 0, 5 \) and \( 10 \), respectively. Below \( T_c \), there is a clear bifurcation between the zero-field cooling (ZFC) and field cooling (FC) \( \chi \) data measured under an applied field of 1 mT, which is characteristic of a type-II superconductor. At 1.8 K, the ZFC data correspond to superconducting shielding fractions ranging from 101 to 174%. Although the demagnetization effect is difficult to correct due to irregular sample shapes, these large values suggest bulk superconductivity in these HEAs.

### 3.3 Specific Heat

To confirm the bulk nature of superconductivity, the \( \text{V}_{5+2x}\text{Nb}_{35-x}\text{Mo}_{35-x}\text{Ir}_{10}\text{Pt}_{15} \) HEAs were further characterized by specific heat \( (C_p) \) measurements, whose results are shown in Figure 4. As can be seen in Figures 4A, a \( C_p \) jump is indeed detected around \( T_c \) for these HEAs. Above \( T_c \), the data are analyzed by the Debye model

\[
\frac{C_p}{T} = \gamma + \beta T^2 + \delta T^4, \tag{1}
\]

where \( \gamma \) and \( \beta(\delta) \) are the Sommerfeld and phonon specific heat coefficients, respectively. With \( \beta \), the Debye temperature \( \Theta_D \) is calculated as...
\[ \Theta_D = \left(12\pi^4 R/5\beta^2\right)^{1/3}, \]

where \( R \) is the molar gas constant 8.314 J/molK\(^2\). This gives \( \beta = 4.59, 4.94, \) and 5.03 mJ/molatomK\(^2\), and \( \Theta_D = 419, 440, \) and 393 K for \( x = 0, 5, \) and 10, respectively. Figure 4B shows the normalized electronic specific heat \( C_{el}/T \) after subtraction of the phonon contribution. For all HEAs, the \( \Delta C_{el}/T \) are significantly smaller than the BCS value of 1.43 [25]. Nevertheless, the \( C_{el}/T \) data can still be fitted by a modified BCS model or the \( \alpha \)-model [26] with \( \alpha = 1.39, 1.41\) and 1.56 for \( x = 0, 5 \) and 10, respectively, where \( \alpha = \lambda_0/T_c \) and \( \lambda_0 \) is the gap size at 0 K. These results suggest that the \( V_{5+2x}Nb_{35-x}Mo_{35}Ir_{10}Pt_{15} \) HEAs are BCS-like superconductors in the weak coupling regime. This is corroborated by their electron-phonon coupling constants \( \lambda_{ep} \) in the range of 0.55–0.59, as calculated using the inverted McMillan formula [27],

\[ \lambda_{ep} = \frac{1.04 + \mu' \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu'\ln(\Theta_D/1.45T_c))} - 1.04 \]

with \( \mu' = 0.13 \) being the Coulomb repulsion pseudopotential. In passing, it is pointed out that the decrease in \( T_c \) with increasing \( x \) is accompanied by the decrease in \( \lambda_{ep} \) but the increase in \( \gamma \). Hence the \( T_c \) in the \( V_{5+2x}Nb_{35-x}Mo_{35}Ir_{10}Pt_{15} \) HEAs is mainly governed by the electron-phonon coupling strength rather than the density of states at the Fermi level. In passing, it is worth noting that the \( T_c \) and \( \lambda_{ep} \) values of the \( V-Nb-Mo-Pt-Ir \) HEAs are very similar to those of the \( (V_{0.5}Nb_{0.5})_{3-x}Mo_{2.5}Al_{0.5}Ga_{0.5} \) HEAs for \( x \geq 1.2 \) [18], pointing to a common phonon-mediated pairing mechanism.

### 3.4 Upper Critical Field

The upper critical fields \( B_{c2} \) of these HEAs were investigated by resistivity measurements under magnetic fields. As an example, the result for the HEA with \( x = 0 \) is shown in Figure 5A. The resistive transition is gradually suppressed to low temperatures as the field increases. For each field, the \( T_c \) is determined using the same criterion as above, and the obtained \( B_{c2} \) vs. \( T \) phase diagrams are displayed in Figure 5B. Extrapolating the \( B_{c2}(T) \) data to 0 K using the Wathamer-Helfand-Hohenberg model [28] yields \( B_{c2}(0) = 6.4, 5.7 \) and 4.4 T for the HEAs with \( x = 0, 5, \) and 10, respectively. These values are well below the corresponding Pauli limiting fields [29] of \( \sim 9.6, \sim 8.4, \) and \( \sim 6.7 \) T, suggesting that \( B_{c2} \) in these HEAs is orbitally limited. In addition, the Ginzburg–Landau coherence lengths \( \xi_{GL} \) can be calculated using the equation

\[ \xi_{GL}(0) = \sqrt{\Phi_0/2\pi B_{c2}(0)}, \]
where $\Phi_0 = 2.07 \times 10^{-15}$ Wb is the flux quantum. This yields $\xi_{GL} = 7.2, 7.6$ and 8.7 nm for the HEAs with $x = 0, 5,$ and 10, respectively. The above results are summarized in Table 1.

### 3.5 VEC Dependence of $T_c$

Figure 6 shows the VEC dependence of $T_c$ for the V$_{5+x}$Nb$_{35-x}$Mo$_{35-x}$Ir$_{10}$Pt$_{15}$ HEAs, together with the data for A15-type V-Nb-Mo-Al-Ga HEA [18] and binary [20] superconductors for comparison. One can see that superconductivity in all these materials occurs near the VEC values of 4.7 and 6.5, consistent with the expectation from the Matthias rule [30]. Compared with the V–Nb–Mo–Al–Ga HEAs, the V–Nb–Mo–Ir–Pt HEAs have higher VEC values in the range 6.4–6.5 and their VEC dependence of $T_c$ is in the opposite trend, increasing monotonically with the increase of VEC. Nevertheless, the maximum $T_c$ is considerably lower for the V–Nb–Mo–Ir–Pt HEAs than for the V-Nb-Mo-Al-Ga ones. This indicates that optimal VEC for $T_c$ in A15-type HEA superconductors is around 4.7, which is reminiscent of the case in binary A15 compounds [20]. Moreover, for similar VEC values, the $T_c$ values for V–Nb–Mo–Al–Ga and V–Nb–Mo–Ir–Pt HEAs are always no more than half those of the binary compounds. It is thus reasonable to speculate that the upper limit of $T_c$ for A15-type HEA superconductors is about one-half the highest $T_c$ in binary A15 superconductors.

### 4 CONCLUSION

In summary, we have studied the structure, electronic, magnetic and thermodynamic properties of the V$_{5+x}$Nb$_{35-x}$Mo$_{35-x}$Ir$_{10}$Pt$_{15}$ HEAs with $0 \leq x \leq 10$. In this $x$ range, the HEAs adopt a cubic A15-type structure and exhibit bulk superconductivity. The analysis of their specific-heat jumps points to a weakly coupled, fully gapped superconducting state. The $T_c$ and $B_{c2}(0)$ reach 5.18 K and 6.4 T, respectively, at $x = 0$, and decrease monotonically with the increase of V content $x$. In addition, $T_c$ increases with increasing VEC from 6.4 to 6.5 and its comparison with isostructural HEA and binary superconductors suggests that the upper limit of $T_c$ for A15-type HEA superconductors is about half that for binary compounds. Our study helps to better understand the effect of chemical disorder in A15-type superconductors.

### DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, upon reasonable request.

### AUTHOR CONTRIBUTIONS

LB synthesized the samples and did the physical property measurements with the assistance from WJF, CYW, ZQQ, XGR. WSQ and CGH contributed in the magnetic measurements. RZ supervised the project and wrote the paper.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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