Discovery of a Superconducting High-Entropy Alloy

P. Koželj,[1] S. Vrtnik,[1] A. Jelen,[1] S. Jazbec,[1] Z. Jagličić,[2] S. Maiti,[3] M. Feuerbacher,[4] W. Steurer,[3] and J. Dolinšek[1,*]
[1]*Faculty of Mathematics and Physics, J. Stefan Institute and University of Ljubljana, Jamova 39, SI-1000 Ljubljana, Slovenia*
[2]*Faculty of Civil and Geodetic Engineering, Institute of Mathematics, Physics and Mechanics and University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*
[3]*Department of Materials, Laboratory of Crystallography, ETH Zürich, Vladimir-Prelog-Weg 5, CH-8093 Zürich, Switzerland*
[4]*Institut für Mikrostrukturforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
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High-entropy alloys (HEAs) are multicomponent mixtures of elements in similar concentrations, where the high entropy of mixing can stabilize disordered solid-solution phases with simple structures like a body-centered cubic or a face-centered cubic, in competition with ordered crystalline intermetallic phases. We have synthesized an HEA with the composition $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ (in at. %), which possesses an average body-centered cubic structure of lattice parameter $a = 3.36$ Å. The measurements of the electrical resistivity, the magnetization and magnetic susceptibility, and the specific heat revealed that the $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA is a type II superconductor with a transition temperature $T_c \approx 7.3$ K, an upper critical field $\mu_0 H_{c2} \approx 8.2$ T, a lower critical field $\mu_0 H_{c1} \approx 32$ mT, and an energy gap in the electronic density of states (DOS) at the Fermi level of $2\Delta \approx 2.2$ meV. The investigated HEA is close to a BCS-type phonon-mediated superconductor in the weak electron-phonon coupling limit, classifying it as a "dirty" superconductor. We show that the lattice degrees of freedom obey Vegard's rule of mixtures, indicating completely random mixing of the elements on the HEA lattice, whereas the electronic degrees of freedom do not obey this rule even approximately so that the electronic properties of a HEA are not a "cocktail" of properties of the constituent elements. The formation of a superconducting gap contributes to the electronic stabilization of the HEA state at low temperatures, where the entropic stabilization is ineffective, but the electronic energy gain due to the superconducting transition is too small for the global stabilization of the disordered state, which remains metastable.

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Within the past several years, a new approach to metallic alloy design with multiple principal elements in equimolar or near-equimolar ratios, termed high-entropy alloys (HEAs), has been proposed [1,2]. According to this concept, the high entropy of mixing can stabilize disordered solid solution phases with simple structures like a body-centered cubic (bcc) or a face-centered cubic (fcc), in competition with ordered crystalline intermetallic phases that often contain structurally complex giant unit cells [3,4]. The HEA structure is characterized by a topologically ordered lattice with an exceedingly high chemical (substitutional) disorder so that an HEA can be conveniently termed as a "metallic glass on an ordered lattice." In order to achieve a high entropy of mixing, the alloys must be composed typically of five or more (up to 13) major elements in similar concentrations, ranging from 5 to 35 at. % for each element, but do not contain any element whose concentration exceeds 50 at. %. This is in contrast to traditional metallic alloy systems, which contain one principal chemical element as the matrix, even though a substantial amount of other elements is incorporated for property/processing enhancement. In a thermodynamic equilibrium, a system will minimize its Gibbs free energy $G = H - TS$, where H is the enthalpy and S is the entropy. For a multicomponent system, mixing of the elements yields a contribution $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$. Following Boltzmann's hypothesis, the mixing configurational entropy of an r-element ideal gas (also valid for certain liquid or solid solutions, where intermolecular forces between every pair of molecular kinds are similar, so that the mixing is completely random) is given by $\Delta S_{\mathrm{mix}} = -nR\sum_{i=1}^{r} x_i \ln x_i$, where n is the total number of moles, $x_i = n_i/n$ is the mole fraction of component i, and R is the gas constant [5]. For equimolar concentrations of elements, $x_i = 1/r$, the entropy of mixing reaches its maximum value $\Delta S_{\mathrm{mix}} = nR \ln r$. For example, for a five-component mixture ($r = 5$) with equimolar ratios of the elements, the mixing entropy per mole amounts $\Delta S_{\mathrm{mix}} = R \ln 5 = 13.4$ J/mol K, which yields at a high temperature such as $T = 2000$ K the entropy term $T\Delta S_{\mathrm{mix}} = 26.8$ kJ/mol. The energy gain of a few 10 kJ/mol is sufficient for the entropic stabilization of a disordered solid solution phase, in competition with ordered crystalline intermetallic phases. At lower temperatures, the importance of the entropy term for the phase stabilization is reduced. However, unfavorable kinetics with sluggish atomic diffusion hinders phase transformations so that the simple high-temperature structure of a disordered solid solution is

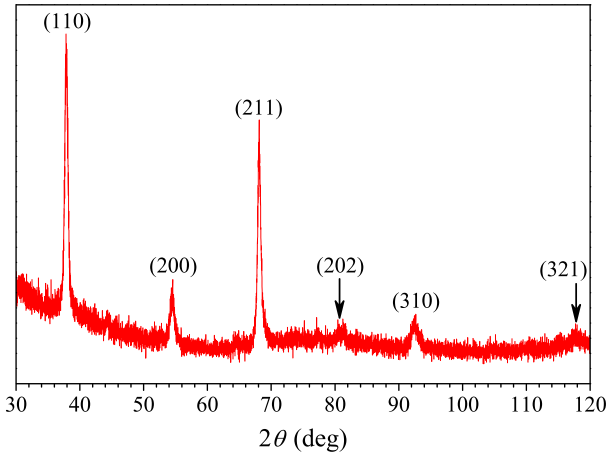

FIG. 1 (color online). X-ray diffraction pattern of the $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA. The peaks are indexed to a bcc crystal lattice.

retained down to low temperatures as a quenched metastable state, whereas ultrafine crystallites of intermetallic phases may precipitate at the nanometric scale within the simple matrices. The low-temperature physical properties of such an out-of-equilibrium state are difficult to predict. It is not clear whether the physical properties of an HEA are just a compositional average of properties of constituent elemental phases (i.e., a "cocktail" effect) or whether they depend on a particular distribution of chemical elements on the HEA lattice. A related question is whether the mixing of elements on a HEA lattice is completely random or some preferential chemical environments form on the scale of nearest neighbor atoms that consequently govern the physical properties.

The number of possible HEAs is virtually unlimited. Examples are HEAs derived within the systems Al-Si-Co-Cr-Cu-Fe-Mn-Ni-Ti [1,2], W-Nb-Mo-Ta-V [6], and Ta-Nb-Hf-Zr-Ti [7]. Most existing studies are focused on the relationship between phase, microstructure, and mechanical properties [1,2,6–11]. A highly disordered lattice scatters electron and lattice waves, which results in reduced electrical and thermal transport similar to bulk metallic glasses [8]. HEAs that contain magnetic transition elements also show rather standard paramagnetism or ferromagnetism [12,13]. In this paper, we report that a five-component HEA derived within the Ta-Nb-Hf-Zr-Ti system shows a spectacular property of type II superconductivity, not observed before in any of the investigated HEAs.

In the investigation of the Ta-Nb-Hf-Zr-Ti system, structural and mechanical properties of a HEA with equimolar ratio of the elements, $Ta_{20}Nb_{20}Hf_{20}Zr_{20}Ti_{20}$, were presented before [7]. Our HEA had quite different composition and was produced from high-purity raw materials, which were arc molten and cast into a cylindrical copper mold. The so produced rod was recast in a zone-melting setup at a feed rate of 5 mm/h at about 2300 °C under 400-mbar Ar atmosphere. The final ingot consisted of a single phase with grain sizes of 200–300 μm. The x-ray diffraction (XRD) pattern obtained with Cu $K\alpha_1$ radiation is shown in Fig. 1, where all diffraction peaks have been identified to belong to a bcc phase. The XRD peaks are quite broad, revealing a distorted lattice with an average bcc structure. This distortion originates from different atomic radii of the constituent elements (Table I), where the atomic radius mismatch between the largest (Zr) and the smallest (Ti) element amounts to $2(r_{Zr} - r_{Ti})/(r_{Zr} + r_{Ti}) = 9\%$. This is below the glass-forming criterion, where it is considered that atomic radius mismatch $\Delta r/r$ greater that 12% between elements of a multicomponent mixture leads to lattice distortions large enough that the energy for retaining the crystalline configuration is too high and the amorphous disorder is energetically preferred [14]. The lattice parameter was determined to be $a = 3.36(2)$ Å. Energy-dispersive spectrometer analysis yielded an average composition of $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ (in at. %), and there was some small compositional variation on the μm scale within ±1 at. % for each element. The theoretical lattice parameter of a HEA can be calculated by assuming validity of Vegard's rule of mixtures [15], $a_{mix} = \sum_i c_i a_i$, valid for completely random mixing of the elements. Here c_i and a_i are the atomic fraction and the lattice parameter of the element i. All five elements in our HEA possess a bcc structure just below their melting temperatures, which is preserved down to room temperature (RT) for Ta and Nb, whereas Hf, Zr, and

TABLE I. Atomic fractions c_i, the RT bcc lattice parameters a, atomic radii $r = a\sqrt{3}/4$ [7], the Debye temperatures θ_D [16], the SC transition temperatures T_c [17], and the linear specific heat coefficients γ [16] of the elements in the investigated $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA. The theoretical parameter values (Theor.) for the HEA were calculated by the rule of mixtures and are compared to the experimental (Exp.) values.

	Ta	Nb	Hf	Zr	Ti	Theor.	Exp.
c_i	0.34	0.33	0.08	0.14	0.11		
a(Å)	3.303	3.301	3.559	3.582	3.276	3.359	3.36
r(Å)	1.430	1.429	1.541	1.551	1.418		
θ_D (K)	246	276	252	290	420	282	243
T_c (K)	4.47	9.25	0.128	0.61	0.40	4.71	7.27
γ(mJ/mol K^2)	5.87	7.8	2.15	2.77	3.36	5.5	8.3

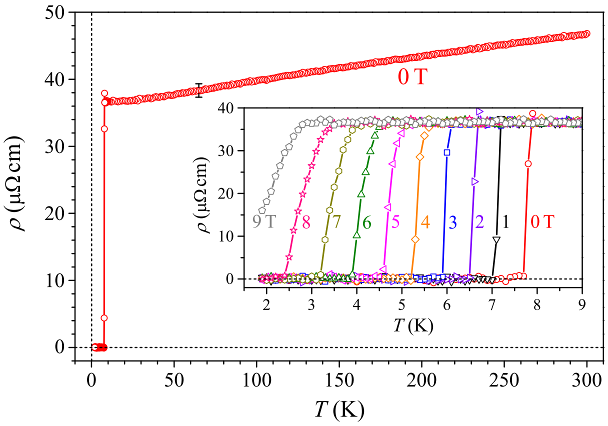

FIG. 2 (color online). Electrical resistivity in zero magnetic field between 300 and 2 K. Magnetic-field dependence of the resistivity in the region of the SC transition for fields up to 9 T is shown in the inset.

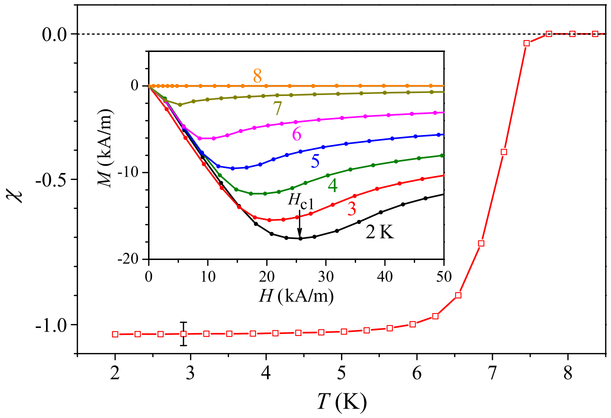

FIG. 3 (color online). The zfc magnetic susceptibility $\chi = M/H$ in a 5 mT field in the region of the SC transition. The inset shows isothermal magnetization $M(H)$ in the low-field range at temperatures between 2 and 8 K. The arrow denotes the lower critical field H_{c1} at $T = 2$ K.

Ti undergo a transformation to a hexagonal close packed (hcp) structure. The bcc lattice parameters of the elements at RT [7], obtained by extrapolating the high-temperature bcc parameters using the reported thermal expansion coefficients, are given in Table 1, yielding the theoretical value $a_{\mathrm{mix}} = 3.359$ Å. This is in excellent agreement with the experimental value of 3.36 Å, indicating random mixing of the elements.

The zero-field electrical resistivity ρ is shown in Fig. 2. $\rho(T)$ exhibits a weak positive temperature coefficient with a RT value of $\rho_{300K} = 46 \pm 1$ $\mu\Omega$ cm. Below 8 K, a sharp drop to a zero-resistivity superconducting (SC) state is observed, whereas the extrapolated normal-state residual resistivity amounts to $\rho_{T\to 0} = 36 \pm 1$ $\mu\Omega$cm. The magnetic-field dependence of the resistivity in the region of the SC transition in fields up to 9 T is shown in the inset of Fig. 2. The SC transition temperature is systematically shifted to lower temperatures in increasing fields.

The low-temperature magnetic susceptibility $\chi(T)$ in a field of 5 mT, measured under zero-field-cooling (zfc) conditions, is shown in Fig. 3. Below about 8 K, a strong diamagnetic response is observed due to Meissner effect and the susceptibility corrected for the demagnetization factor assumes almost the ideal diamagnetic value $\chi = -1$ intrinsic to a superconductor. The isothermal magnetization $M(H)$ curves between 2 and 8 K in the low-field range up to $H = 50$ kA/m are shown in the inset of Fig. 3. Close to the origin, the $M(H)$ relation is linear with the slope -1, whereas at higher fields, the $M(H)$ curves show minimum and then approach the weakly paramagnetic value of the normal state. This behavior is typical of type II superconductors. The field value in the minimum was taken as a measure of the lower critical field H_{c1}. At 2 K, the lower critical field amounts to $\mu_0 H_{c1} \approx 32$ mT.

The specific heat C was measured between RT and 350 mK in magnetic fields between 0 and 9 T. The low-temperature $C(T)$ below 9 K for selected fields is shown in Fig. 4(a). In zero field, a sharp discontinuous jump of $\Delta C(T_c) = 98 \pm 2$ mJ/mol K is observed at the SC transition temperature $T_c = 7.27 \pm 0.07$ K. Since the lattice specific heat does not change at T_c, this difference equals to the change of the electronic specific heat between the SC and the normal states, $\Delta C = C_{es} - C_{en}$. The specific heat can be used to determine the volume fraction of the SC phase. In cases when a vortex state or a mixture of the normal and SC states coexist, the presence of normal regions is reflected in a linear term in the specific heat. Assuming that the normal-state low-temperature specific heat is written as $C = \gamma T + \alpha T^3$, where γ and α are the electronic and lattice specific heat coefficients, we present specific heats in zero field and 9 T in a C/T versus T^2 plot in Fig. 4(b). The analysis of the normal-state specific heat (in 9 T field) below 4.5 K with the expression $C/T = \gamma + \alpha T^2$ (solid line) has yielded the intercept $\gamma = 8.3 \pm 0.1$ mJ/mol K^2 and the slope $\alpha = 0.14 \pm 0.01$ mJ/mol K^4. In contrast, the zero-field specific heat intercepts the vertical axis at $C/T \approx 0$, demonstrating that there is no linear term in the specific heat and that the superconductivity is a bulk effect, where the entire specimen becomes SC below T_c. By considering the nature of the SC state of our HEA (e.g., BCS type or unconventional), the quantity of interest is the ratio $\Delta C(T_c)/\gamma T_c$, which assumes a value 1.43 within the BCS theory valid for phonon-mediated superconductivity in the weak electron-phonon coupling limit [18]. We obtain $\Delta C(T_c)/\gamma T_c = 1.63 \pm 0.06$, which is in reasonable agreement with the BCS prediction, indicating that the investigated HEA is close to a BCS type. The low-temperature zero-field specific heat can be used to check for the presence of an energy gap of width 2Δ in the electronic DOS at the Fermi level ε_F. Within the BCS theory [18], the formation of Cooper pairs leads to a temperature-dependent energy gap $2\Delta(T)$,

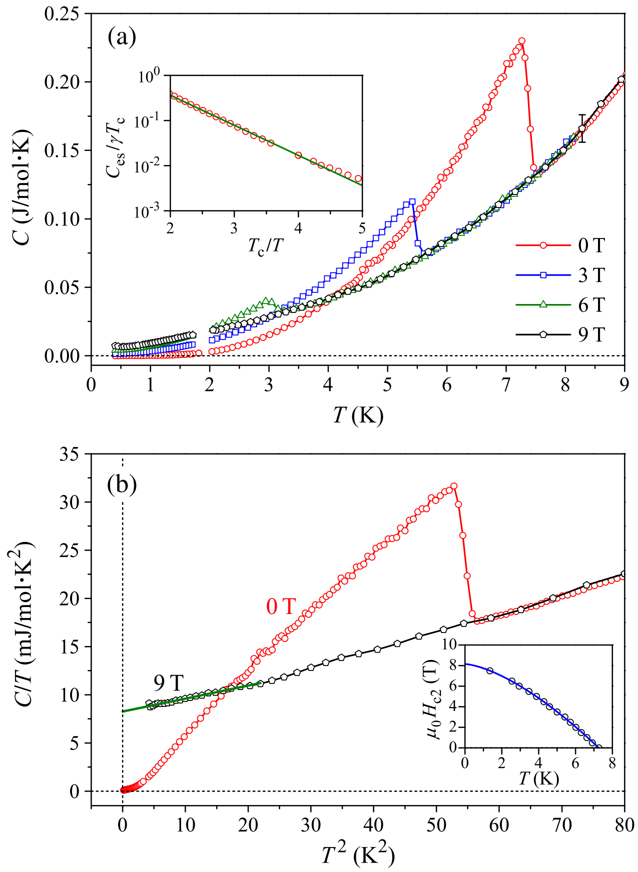

FIG. 4 (color online). (a) Low-temperature specific heat $C(T)$ for selected magnetic fields. The inset shows a semilog graph of $C_{es}/\gamma T_c$ against T_c/T and solid line is the fit $C_{es}/\gamma T_c = 7.9\exp(-1.54T/T_c)$. (b) Specific heat in zero field and 9 T in a C/T versus T^2 plot. The inset shows the upper critical field $\mu_0 H_{c2}(T)$.

which is related to the transition temperature T_c through $2\Delta(0)/k_B T_c = 3.52$. The energy required to break up a Cooper pair is about $2\Delta(0)$, and hence, the number of pairs broken up is proportional to $\exp(-2\Delta(0)/k_B T)$, which leads to an exponential temperature dependence of the specific heat at sufficiently low temperatures. The form predicted by the BCS theory is $C_{es}/\gamma T_c = A\exp(-BT_c/T)$ [16], where A and B are two constants whose values depend on the temperature interval used. For the interval $2.5 < T_c/T < 6$, they are $A = 8.5$ and $B = 1.44$. The graph $\ln(C_{es}/\gamma T_c)$ versus T_c/T should thus be a straight line. The zero-field electronic specific heat $C_{es} = C - \alpha T^3$ is shown in this type of graph in the inset of Fig. 4(a) for the temperature range $2 < T_c/T < 5$. A straight line is indeed observed and the fit yielded the parameter values $A = 7.9 \pm 0.1$ and $B = 1.54 \pm 0.05$, which are close to the BCS prediction. The electronic DOS thus contains an energy gap at ε_F of approximate width $2\Delta(0) \approx 2.2$ meV.

In an applied magnetic field, the jump in C is systematically shifted to lower temperatures in higher fields. Using the peak in C as a measure of T_c, we mapped the temperature dependence of the upper critical field H_{c2} [inset in Fig. 4(b)]. $H_{c2}(0)$ was determined from a fit with the empirical formula $H_{c2}(T) = H_{c2}(0)(1-(T/T_c)^{\beta})$, yielding $\mu_0 H_{c2}(0) = 8.15 \pm 0.05$ T and $\beta = 1.51$. The $\mu_0 H_{c2}(0)$ value is far below the Pauli-paramagnetic limit for weak electron-phonon coupling, $\mu_0 H_{c2} = 1.86 T_c \approx 13.5$ T [19], and supports phonon-mediated superconductivity in our HEA. The lattice specific heat coefficient α yielded the Debye temperature $\theta_D = (12\pi^4 R/5\alpha)^{1/3} = 243 \pm 5$ K.

The investigated $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA is thus a type II superconductor with a transition temperature $T_c \approx 7.3$ K, an upper critical field $\mu_0 H_{c2} \approx 8.3$ T, a lower critical field $\mu_0 H_{c1} \approx 32$ mT, and an energy gap in the electronic DOS at ε_F of $2\Delta \approx 2.2$ meV. Evaluation of different criteria using parameters of the SC state indicates that the investigated HEA is close to a BCS-type phonon-mediated superconductor in the weak electron-phonon coupling limit. The XRD spectrum reveals a distorted bcc lattice with a high degree of chemical (substitutional) disorder so that our HEA classifies as a "dirty" superconductor describable by the theory of Anderson [20]. Since the lattice parameter a ideally obeys the rule of mixtures, suggesting completely random mixing of the five chemical elements on the bcc lattice, it is interesting to check whether other physical properties obey this rule as well, i.e., whether a given physical property of the "mixture" Y_{mix} is a compositional average of the properties Y_i of constituent elements, $Y_{\mathrm{mix}} = \sum_i c_i Y_i$. To see that, we evaluate the departure of the experimental values Y_{exp} from the theoretical values Y_{mix} using the expression $(Y_{\mathrm{exp}} - Y_{\mathrm{mix}})/Y_{\mathrm{mix}} = \Delta Y/Y_{\mathrm{mix}}$. The Debye temperature θ_D is a measure of the lattice dynamics. Taking the literature-reported θ_D data of the elements [16] (Table 1), we obtain $\Delta\theta_D/\theta_D^{\mathrm{mix}} = -14\%$. Since θ_D is not a precisely defined quantity, this mismatch can be considered small, and the rule of mixtures applies reasonably well to the phonon dynamics of the HEA. In view of the high lattice distortion and large degree of chemical disorder, where elements with largely different masses (^{181}Ta, ^{93}Nb, ^{180}Hf, ^{90}Zr, and ^{48}Ti) are randomly positioned on the bcc lattice, this apparently simple phononic picture of the HEA lattice dynamics is surprising. Considering the electronic degrees of freedom (Table 1), we obtain for the normal-state electronic specific heat coefficient $\Delta\gamma/\gamma_{\mathrm{mix}} = 51\%$ and the SC transition temperature (recall that all five elements are SC) $\Delta T_c/T_c^{\mathrm{mix}} = 54\%$. The mismatch in γ and T_c is so large that the rule of mixtures is not obeyed even approximately, and the electronic properties are not a "cocktail" of properties of the constituent elements. Theoretical description of the electronic properties of a HEA is thus a highly complex problem, aggravated by a random local distortion of the lattice and random distribution of five or more electronically inequivalent chemical elements on the otherwise simple average lattice. The formation of a SC gap in the electronic DOS at ε_F contributes to the electronic stabilization of the HEA state at low temperatures, where the entropic stabilization is ineffective, but the electronic energy gain due to the SC transition of the order $(k_B T_c)^2/\varepsilon_F \approx 10^{-5}$ meV per electron (for ε_F of several eV) is too small for the global stabilization of the disordered state, which remains metastable.

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[*] Corresponding author.
jani.dolinsek@ijs.si

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