

Tuning superconductivity in high entropy nitrides

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The recently investigated nitrogen (N) incorporation into TiNbMoTaW high entropy alloy films leads to a domelike superconducting transition temperature T_C vs nitrogen concentration x (with $x = N/M$ representing the ratio between atomic fractions of nitrogen and metal atoms, $M = \text{Ti} + \text{Nb} + \text{Mo} + \text{Ta} + \text{W}$) in the respective high entropy nitride $(\text{TiNbMoTaW})_{1.0}\text{N}_x$, with a large T_C enhancement. In this study, we report on the effect of N insertion into NbTaHfTiZr films, which show a lower valence electron concentration and a lower configuration entropy than those of TiNbMoTaW. The T_C vs x dependence in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ exhibits a different course, in which T_C first decreases from ~ 6.5 K at $x = 0$ to $T_C \approx 1$ K at $x = 0.25$ and $x = 0.42$, and then starts to increase and reaches a maximum of ~ 8.6 K at $x = 0.81$ followed by a decline to ~ 6.7 K when x approaches the stoichiometric value 1. In this case, the transition of the initial high entropy alloy bcc structure to the fcc structure of high entropy nitrides proceeds slowly and leads to a wide x range in which T_C is suppressed. The analysis shows that the T_C vs x course and the T_C enhancement in high entropy nitrides depend on the valence electron concentration of the initial high entropy alloy, as higher values accelerate the tendency to form a fcc structure and are less sensitive to the localization of otherwise mobile electrons in metallic high entropy alloys due to their bonding to N atoms. However, other parameters, such as the atomic size difference of the metallic constituents and their affinity towards nitrogen, also have to be considered.

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I. INTRODUCTION

Research on superconductivity in compounds containing a transition-metal element and nitrogen started in 1930 with the work of Meissner and Franz [1]. Later, extensive research related to superconductivity in nitrides was performed [2–8] and it was shown that superconductivity can be observed in several transition-metal nitrides and transition-metal alloy nitrides. The highest T_C of 17.3 K has been observed in niobium nitride NbN. It considerably exceeds that for pure niobium of 9.2 K. Nitrides of transition metals being close in the periodic table show lower T_C values, e.g., 6 K was observed in TiN, 10 K in ZrN, 8.2 K in VN, and 13 K in MoN [2–4]. Moreover, the concentration of N also influences their superconductivity, as, e.g., in TiN_x , where T_C increases with increasing N content and reaches the maximum for x close to 1 [9]. Among the alloy nitrides, superconductivity in NbTiN bulk and NbTiN films was mainly investigated [7,10,11]. For sputter deposited NbTiN_x thin films with a thickness of 4–100 nm, a T_C maximum of 15.5 K was

observed for $x \approx 0.91$, where $x = N/(\text{Nb} + \text{Ti})$, while for the stoichiometric ratio $x = 1$, a T_C of 14.7 K was reported [10]. Recent results on bulk superconducting medium and high entropy nitrides (with $x = 1$) are presented in [12,13], where in [12] an ambient-pressure superconductivity onset at 10 K and robust T_C stability under high pressure in a TiNbTa₃ medium entropy nitride were observed. Further results concerning, e.g., the various preparation methods and the application possibilities of superconductors based on nitrides can be found, e.g., in [14–16].

Recently, the effect of N concentration on the superconducting properties of $\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Mo}_{0.2}\text{Ta}_{0.2}\text{W}_{0.2}$ high entropy alloy (HEA) films with a body-centered-cubic (bcc) structure was investigated [17]. The resulting $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ nitride films, where $x = N/M$ is the ratio between the fraction of nitrogen (N) and metal ($M = \text{Ti} + \text{Nb} + \text{Mo} + \text{Ta} + \text{W}$) atoms, were synthesized using high-power impulse magnetron sputtering and had a thickness of ~ 1 μm . These high entropy nitride series showed a NaCl-like face-centered-cubic (fcc) structure already for $x \approx 0.15$. The further increase of x then led to a large increase of T_C : from 0.62 K for $x = 0$ up to 5.02 K for $x = 0.74$. At higher x , the value of T_C decreased and reached 1.08 K at $x = 0.97$, i.e., at the almost stoichiometric concentration. The obtained T_C enhancement and the domelike T_C vs x course were attributed to the phonon frequency increase due to insertion of light N atoms and to the strengthening of the electron-phonon interaction that developed as a result of the occupation of suitable positions by N atoms in HEAs, i.e., due to their high configuration

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entropy ΔS . This entropy, $\Delta S = -R \sum x_i \cdot \ln x_i$, where R is the gas constant and x_i the mole fraction of the i th element in the HEA, is a measure of the number of possible configurations of metal atoms. Thus, a lot of options for N atoms to find the thermodynamically most appropriate positions in the lattice exist, creating a suitable phonon-mode distribution and strengthening the electron-phonon interaction. It should also be noted that in substoichiometric nitrides, i.e., for $x < 1$, the number of different configurations of metal and nitrogen atoms that can be achieved even increases, as the occupied and nonoccupied N sites (N vacancies) can have different positions with respect to the metallic elements (see, e.g., [18,19]). This leads to an additional increase of ΔS in high entropy nitrides.

A domelike T_C vs x course was recently observed also in ZrN_x for nitrogen concentrations $x \approx 0.6$ and $x \approx 1.4$, with a maximum around $x \approx 1$ [20]. There, the increase of T_C from $x \approx 0.6$ to $x \approx 1$, as in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ films, is associated with incorporation of light N atoms and the strengthening of the electron-phonon interaction. The following decrease of T_C for $x > 1$ comes from the localization of otherwise mobile electrons of metallic Zr due to their bonding to the overstoichiometric concentration of N atoms, which, for $x > 1.15$, leads to a strongly insulating state. On the other hand, in TiZrNbTa -based nitride films [21], T_C first decreases from 8 K at $x = 0$ to a value below 1.8 K at $x = 0.42$. Then superconductivity reappears again at $x = 0.64$ with a T_C of about 2 K, and reaches its highest value of 10 K for the slightly overstoichiometric concentration $x = 1.08$. Very recently, an ambient-pressure superconductivity onset at 10 K and robust T_C under high pressure was observed in a TiNbTaTa_3 medium entropy nitride [12]. However, the dependence of T_C on nitrogen concentration was not investigated in this work.

It should be noted that all of the above-mentioned nitrides such as, e.g., ZrN_x , NbN , or NbTiN , as well as high entropy nitrides [4,7,17,21], can be considered as conventional phonon-mediated Bardeen-Cooper-Schrieffer (BCS) superconductors, in which, in the simple case, the T_C relation may be described as $k_B T_C = 1.13 \hbar \omega_D \exp[-1/N(E_F)V]$ (see, e.g., [22]), where ω_D denotes the phonon Debye frequency, $N(E_F)$ the electronic density of states at the Fermi energy E_F , V the electron-phonon interaction potential, and k_B and $\hbar$ the Boltzmann and Planck constant, respectively. Overviews of the superconducting properties of HEAs (without nitrogen) can be found, e.g., in [23–25].

Within this work, we report on the impact of N incorporation into $\text{Nb}_{0.35}\text{Ta}_{0.35}\text{Hf}_{0.10}\text{Ti}_{0.10}\text{Zr}_{0.10}$ -based films, in which the corresponding nitrogen-free HEA film exhibits a lower configuration entropy $\Delta S \approx 1.43 R$, as well as a lower valence electron concentration $\text{VEC} = 4.72$ el./atom than that of the earlier studied $\text{Ti}_{0.20}\text{Nb}_{0.20}\text{Mo}_{0.20}\text{Ta}_{0.20}\text{W}_{0.20}$ HEA (here, $\Delta S \approx 1.61 R$ and $\text{VEC} = 5.2$) and the subsequently formed $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ nitride films [17]. $\text{VEC} = \sum c_i \cdot (\text{VEC})_i$ represents the average number of valence electrons per atom in a particular HEA, with c_i being the concentration and $(\text{VEC})_i$ the valence of the i th element. The obtained experimental results show that the x vs T_C course in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitrides is completely different compared to the domelike dependence observed in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ nitrides. In $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitrides, with increasing x , T_C

first decreases, from ~ 6.5 K at $x = 0$ to $T_C < 1.8$ K values at $x = 0.25$ and $x = 0.42$. Then, at $x = 0.44$, T_C starts to increase and reaches a maximum value of ~ 8.6 K at $x \approx 0.8$, followed by a slight T_C decline to ~ 6.7 K when x approaches the stoichiometric value of 1. We present that the initial drop of T_C (from $x = 0$) with increasing x is associated with the transformation of the bcc structure of the initial (nitrogen-free) HEA to the fcc structure of the subsequent nitrides, which is completed only at concentrations $x > 0.50$. Then, based on the obtained results and those by other authors, we show that the T_C vs x course and the T_C enhancement in high entropy nitrides depend mainly on the VEC of the initial HEA. This is because VEC accelerates the tendency to form a fcc structure and is less sensitive to the localization of otherwise mobile electrons in metallic HEA as N atoms are inserted. However, the impact of other parameters that affect the stability and properties of high entropy nitrides, as the various affinity of different metallic elements towards nitrogen and the lattice distortion arising from the fact that atoms of different sizes occupy a single lattice of these nitrides, are also considered and discussed.

II. METHODS

High-power impulse magnetron sputtering was used to deposit the $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films from a target with the composition $\text{Nb}_{0.35}\text{Ta}_{0.35}\text{Hf}_{0.10}\text{Ti}_{0.10}\text{Zr}_{0.10}$ (in atomic proportions) in an atmosphere of argon and nitrogen. The diameter of the target was 76 mm. The films were grown on single-crystal (1102) Al_2O_3 sapphire and single-crystal (100) Si substrates placed at a distance of 15 cm from the target. Prior to deposition, the vacuum chamber was evacuated to a residual pressure below 0.9 mPa. The power applied to the target was ~ 400 W. The Ar and N_2 gases were introduced into the chamber through mass flow controllers. The Ar flow rate was kept constant at 80 sccm, resulting in a total gas pressure of ~ 1 Pa and monitored with a capacitance manometer. The N_2 flow rate was varied between 0 and 7 sccm, resulting in N_2 partial pressure ratios between 0 and 14%. The pulse on-time for operating the magnetron cathode was set to 100 μs at a repetition frequency of 100 Hz. The thickness of the films was $\sim 350 \pm 100$ nm. No additional heating was applied to the substrates; they were held on ground potential.

Film thickness has been determined on both the sapphire and the Si substrates, using laser confocal microscopy to measure the height step between a coated and an uncoated area of the substrates. The microstructure and chemical composition of the deposited films were investigated using Si substrates, whereas the superconductivity-related properties were investigated on films grown on sapphire substrates. This approach was chosen because the sapphire substrates are nonconductive and therefore do not affect the $R(T)$ electrical resistance vs temperature dependencies. On the other hand, Si is a semiconductor and would influence the $R(T)$ dependencies. However, for comparison, the superconductive properties were also measured on selected film samples grown on Si substrates to illuminate possible strain-induced changes.

The microstructure of the films was characterized using x-ray diffraction (XRD) in Bragg-Brentano geometry with Cu $K\alpha$ radiation. Their chemical composition was determined

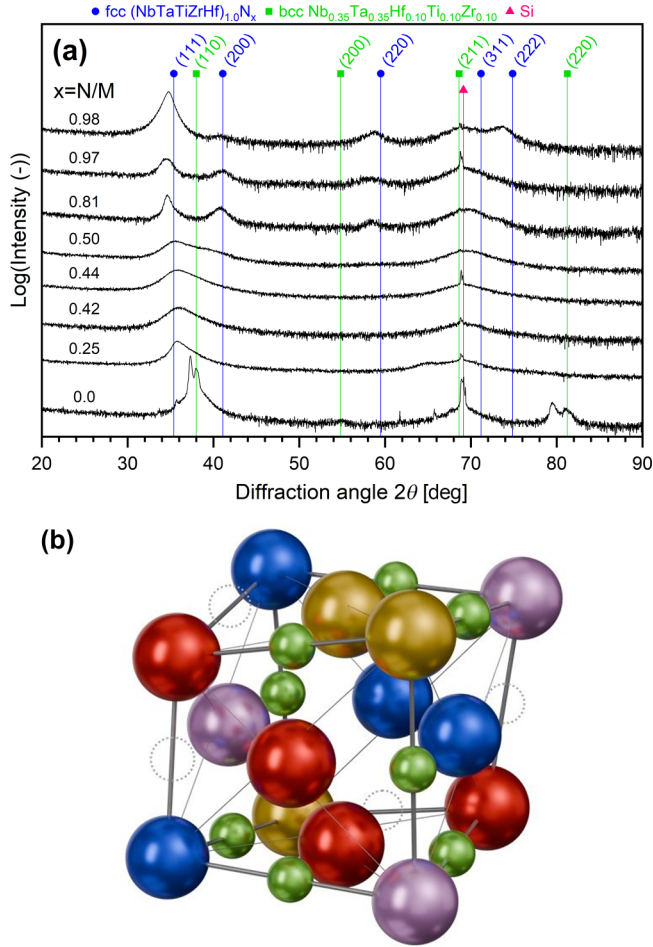


FIG. 1. (a) X-ray diffractograms of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films deposited onto single-crystal Si substrates as a function of $x = \text{N}/\text{M}$, where N and $\text{M} = \text{Nb} + \text{Ta} + \text{Hf} + \text{Ti} + \text{Zr}$ denote the concentrations of nitrogen and metal atoms. One can see that in the concentration range $0 < x < \sim 0.5$, a transition from the bcc structure of the nitrogen-free HEA to the fcc structure of nitrogen-rich nitrides is observed. (b) Schematic illustration of the fcc structure of high entropy nitrides with $x \approx 0.67$. Metal atoms are shown by large spheres of different color, nitrogen atoms by small green spheres, and nitrogen vacancies by dotted empty circles.

by energy-dispersive x-ray spectroscopy (EDX). Since EDX provides limited elemental quantification for light elements such as N, the EDX results were cross-checked by elastic recoil detection analysis (ERDA). ERDA allows one to precisely determine the elemental composition and depth profile of films, ranging from hydrogen to heavy rare-earth elements. This cross-check was carried out so that the EDX sensitivity factors were for a few nitride films adjusted until they matched the atomic composition derived from ERDA. These ERDA measurements were done using a 43 MeV Cl^{7+} ion beam with an angle between the sample normal and the incoming beam of 74.2° and a scattering angle of 29.5° . A Bragg ionization chamber was used to detect recoil atoms and scattered ions, enabling energy measurement and identification of the atomic number of the incoming particles. The original target composition was within a deviation of ~ 1 at.% retained also

in the films. Therefore, for convenience, the nominal target composition is used in the manuscript.

Electrical resistance measurements were performed using a ^4He cryostat with variable-temperature insert, which enabled one to reach temperatures between 1.8 and 300 K. Four probe geometry measurements were carried out using an alternating current (AC) source with an active common mode reduction. During the measurements in a magnetic field, the applied field was oriented perpendicular to the thin-film plane. The electrical contacts were made using four spring contacts with an applied current of $10 \mu\text{A}$. Electrical resistance measurements at temperatures below 1.8 K, down to 0.5 K, were performed using a commercial system (PPMS, Quantum Design) with a He3 insert option. In this case, the contacts were made using silver composition DuPont 4922N. Magnetization measurements in a field of 1 mT and at temperatures between 2 and 300 K were carried out in a commercial (MPMS, Quantum Design) measurement system. More details about these methods can be found in [17,26].

III. RESULTS AND DISCUSSION

A. Film composition and microstructure

Figure 1(a) presents the summary of x-ray diffractograms of the deposited films. As can be seen, the transition from the bcc structure of the initial $\text{Nb}_{0.35}\text{Ta}_{0.35}\text{Hf}_{0.10}\text{Ti}_{0.10}\text{Zr}_{0.10}$ metal film to the NaCl-type fcc structure in corresponding $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitrides takes place in a wide concentration range between $x = 0$ and $x \approx 0.50$. It is noteworthy that the bcc metal film exhibits additional diffraction peaks at 37.2° and 79.5° . These peaks may arise from segregation during film deposition, where compositional fluctuations produce regions with varying atomic fractions within the bcc HEA phase, resulting in slight variations in lattice parameter. The broad diffraction peaks observed in the bcc $\rightarrow$ fcc transition range stem from the coexistence of bcc and fcc phases; however, a gradual shift of the peak center from the bcc to the fcc positions is visible. Table I lists the obtained composition of the as-deposited films determined by EDX. A schematic visualization of the fcc structure of high entropy nitrides with $x < 1$ is shown in Fig. 1(b).

B. Superconducting properties

The low-temperature part of the temperature resistance $R(T)$ dependencies of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films normalized to their resistance values R_0 just above the T_C onset are presented in Fig. 2(a). As the criterion for T_C determination, the temperature value at which $R(T)$ reaches 50% of R_0 was used. The obtained T_C values, together with other properties of the investigated films, are listed in Table I. The corresponding T_C vs x dependence, depicted by red points, is shown in Fig. 2(b). In this figure, parallel to the data of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$, the same dependence for $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ [17] and the approximate dependence for the $(\text{TiZrTaNb})_{1.0}\text{N}_x$ films [21] are also added for comparison. It should be noted that the T_C of high entropy nitrides can also depend on the choice of the substrate [17] and is related to the strain induced by the lattice mismatch between the film and substrate. It turns out that this strain-tuned change of T_C is about $\pm 10\%$, as verified by

TABLE I. Overview of the data obtained from the performed investigations on $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films. In the first column, the composition of the investigated films determined by EDX is given; in the second one, the microstructure determined by XRD is given. In the following columns, $x = \text{N}/M$ denotes the ratio between the atomic concentration of nitrogen and metal atoms ($M = \text{Nb} + \text{Ta} + \text{Hf} + \text{Ti} + \text{Zr}$) and the valence electron concentration (VEC), i.e., the average number of valence electrons per atom in electrons/atom. R_0/R_{300} represents the film resistance ratio between the resistance just above the T_C onset (R_0) and the resistance at 300 K (R_{300}), T_C indicates the superconducting transition temperature, and B_{c2} the upper critical field in Tesla at temperature $T \rightarrow 0$. $R(T, B)$ in the first column stands for the temperature-dependent resistance of films exposed to magnetic fields and $M(T)$ for the temperature-dependent magnetization.

Sample composition, measurements performed	Structure	$x = \text{N}/M$	VEC (el./atom)	R_0/R_{300} ratio	T_C (K)	$B_{c2}(0)$ (T)
$\text{Nb}_{0.40}\text{Ta}_{0.32}\text{Hf}_{0.08}\text{Ti}_{0.10}\text{Zr}_{0.10}$ $R(T, B)$	bcc	0.0	4.718	0.840	6.53	7.26
$(\text{Nb}_{0.39}\text{Ta}_{0.31}\text{Hf}_{0.08}\text{Ti}_{0.11}\text{Zr}_{0.11})_{1.0}\text{N}_{0.25}$ $R(T, B), M(T)$	fcc with bcc	0.25	4.770	0.971	1.03	1.62
$(\text{Nb}_{0.40}\text{Ta}_{0.32}\text{Hf}_{0.08}\text{Ti}_{0.10}\text{Zr}_{0.10})_{1.0}\text{N}_{0.42}$ $R(T, B), M(T)$	fcc with bcc	0.42	4.794	0.970	1.0	1.31
$(\text{Nb}_{0.40}\text{Ta}_{0.31}\text{Hf}_{0.08}\text{Ti}_{0.10}\text{Zr}_{0.11})_{1.0}\text{N}_{0.44}$ $R(T, B), M(T)$	fcc with bcc	0.44	4.802	0.966	~ 1.1 (onset at ~ 2.5)	not deter-mined
$(\text{Nb}_{0.37}\text{Ta}_{0.36}\text{Hf}_{0.06}\text{Ti}_{0.10}\text{Zr}_{0.11})_{1.0}\text{N}_{0.50}$ $R(T, B), M(T)$	fcc with bcc	0.50	4.843	0.970	~ 2.2 (onset at ~ 4.8)	not deter-mined
$(\text{Nb}_{0.41}\text{Ta}_{0.29}\text{Hf}_{0.07}\text{Ti}_{0.12}\text{Zr}_{0.11})_{1.0}\text{N}_{0.81}$ $R(T, B)$	fcc	0.81	4.838	1.059	8.66	10.58
$(\text{Nb}_{0.40}\text{Ta}_{0.29}\text{Hf}_{0.07}\text{Ti}_{0.13}\text{Zr}_{0.11})_{1.0}\text{N}_{0.97}$ $R(T, B)$	fcc	0.97	4.842	1.217	7.49	10.0
$(\text{Nb}_{0.40}\text{Ta}_{0.29}\text{Hf}_{0.07}\text{Ti}_{0.13}\text{Zr}_{0.11})_{1.0}\text{N}_{0.98}$ $R(T, B)$	fcc	0.98	4.847	1.327	6.76	9.78

measurements of the same films deposited on sapphire and Si substrates.

From Fig. 2(b), one can see that the impact of nitrogen incorporation into the initial HEA, which exhibits a valence electron concentration of VEC = 4.72 [here, $\text{VEC} = \sum c_i \cdot (\text{VEC})_i = 0.35 \times 5$ for Nb + 0.35×5 , Ta + 0.1×4 , Hf + 0.1×4 , and Ti + 0.1×4 for Zr] and a configuration entropy of $\Delta S \approx 1.43 R$ is different from that of the $\text{Ti}_{0.20}\text{Nb}_{0.20}\text{Mo}_{0.20}\text{Ta}_{0.20}\text{W}_{0.20}$ HEA [17] with values of VEC = 5.2 el./atom and $\Delta S \approx 1.61 R$ (to learn more about the role of VEC and ΔS in superconducting HEAs, see, e.g., [23,24]). The obtained T_C vs x course in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ does not exhibit a domelike dependence as in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ nitrides [17]; instead, in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ with increasing x , T_C first decreases, from ~ 6.5 K at $x = 0$ to $T_C < 1.8$ K for $x = 0.25$ and $x = 0.42$, then T_C starts to increase at $x = 0.44$ with a T_C onset at ~ 2.75 K. For the film with $x = 0.50$, from the end of the bcc $\rightarrow$ fcc transition range, $R(T)/R_0$ exhibits a T_C onset at ~ 4.8 K and zero resistance is observed only below ~ 2.2 K. At higher concentrations, at $x = 0.81$, T_C reaches a maximum value of 8.66 K, after which there is a slight T_C decline to 6.76 K when x approaches 1.

The observed T_C drop in the concentration range $0 < x < \sim 0.50$ is apparently related to the transition of the bcc structure of the initial HEA to the fcc structure of high entropy nitrides, which is, in our sample set, completed only at $x \approx 0.81$ [see Fig. 1(a) and Table I]. Therefore, we assume that the multiple superconducting transitions in samples with $x = 0.44$ and $x = 0.50$ are related to both structural phases, i.e., the bcc nitride phase having a lower T_C value and the fcc nitride phase exhibiting higher T_C values.

In the earlier investigated $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ films [17], on the other hand, the bcc $\rightarrow$ fcc transition was already completed at $x \approx 0.15$, whereas in the case of $(\text{TiZrTaNb})_{1.0}\text{N}_x$ nitrides [21], where the initial TiZrTaNb HEA has estimated values of VEC ≈ 4.44 el./atom and $\Delta S \approx 1.39$, a concentration above $x \approx 0.64$ is needed to obtain superconductivity in the subsequent nitride. The concentration range, in which the bcc $\rightarrow$ fcc structural transition takes place for

$(\text{NbTaHfTiZr})_{1.0}\text{N}_x$, is very likely a region with a high degree of disorder, which contains a mixture of bcc and fcc clusters. This is reflected in the width of the XRD peaks [see Fig. 1(a)], which is, in this x range, larger than in ranges where the single bcc phase (close to $x = 0$) or fcc phase (for $x \geq 0.81$) dominates. The mentioned high degree of chemical and structural disorder probably leads to superconductivity suppression (see, e.g., [27]).

It should also be noted that in the single fcc phase for $x > 0.50$, there is an increased tendency to the semiconductinglike temperature dependence of resistance, i.e., there is $R_0/R_{300} > 1$ [see Fig 2(c) and Table I]. This comes from the localization of conduction electrons through their bonding to incorporated nitrogen atoms at higher N concentration.

Another feature that may characterize the development of superconductivity in the high entropy nitrides investigated so far is the T_C enhancement, i.e., the ratio $T_C(\text{max})/T_C(0)$, where $T_C(\text{max})$ denotes the highest transition temperature achieved by N incorporation and $T_C(0)$ the transition temperature of the initial (nitrogen-free) HEA. For $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ [17] (with VEC = 5.2 and $\Delta S \approx 1.61 R$), $T_C(\text{max})/T_C(0) \approx 8$; for the present $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ (with VEC = 4.72 and $\Delta S \approx 1.43 R$), $T_C(\text{max})/T_C(0) \approx 1.32$; and for $(\text{TiZrTaNb})_{1.0}\text{N}_x$ nitrides [21] (with VEC = 4.44 and $\Delta S \approx 1.39 R$), $T_C(\text{max})/T_C(0) \approx 1.24$.

From these data, it can be concluded that the T_C vs x course and the T_C enhancement in high entropy nitrides are probably influenced by both the VEC and the ΔS value of the initial HEA. However, we assume that the dominant influence comes from the VEC. As was shown in [28,29], higher VEC leads to enhanced atomic bonding forces, where the atoms (with a higher VEC) forming the HEA or high entropy nitride tend to arrange themselves into an fcc structure, which possesses a higher atomic packing density. Conclusions made in [28] are often referred to as the VEC criterion for the HEA crystal structural stability. And, the revisit of the VEC criterion related to the structure stability of HEAs carried out by high-throughput *ab initio* calculations [30] also shows that this stability criterion not only works for stable structures, but also effectively works for metastable states when both fcc and

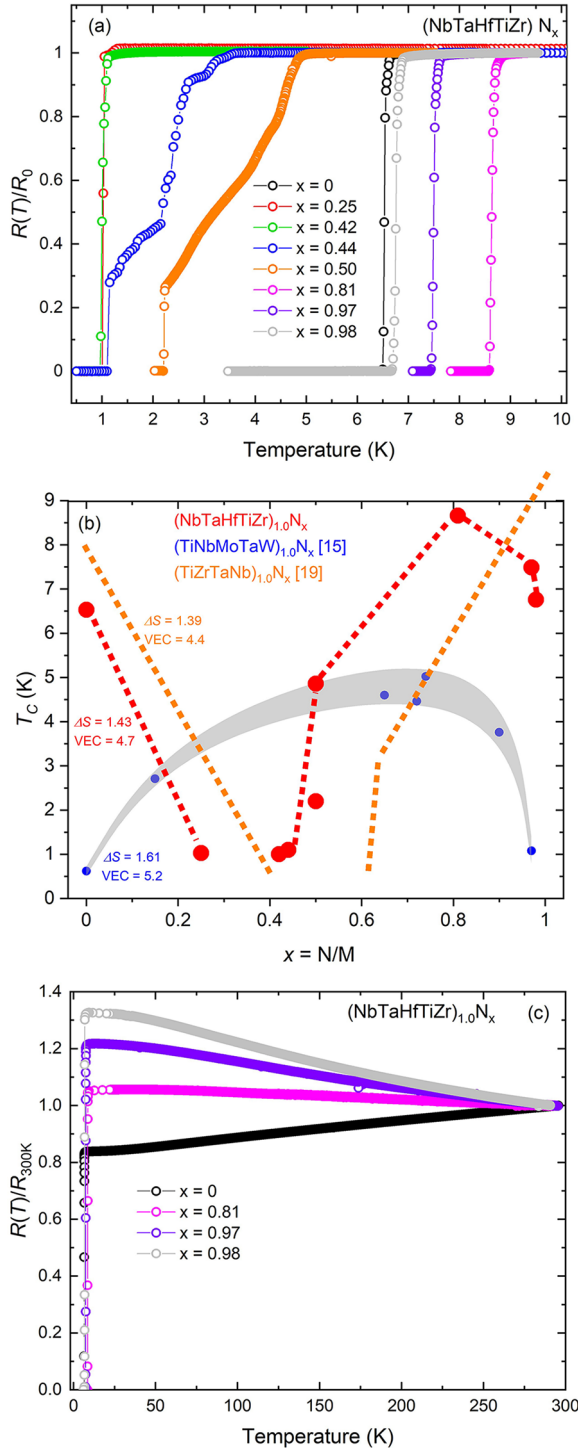


FIG. 2. (a) Temperature dependencies of the normalized electrical resistance $R(T)/R_0$ of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films with different nitrogen concentration $x = \text{N/M}$, where R_0 are the resistance values just above the T_C onset. (b) T_C vs x dependencies for various high entropy nitrides. Red symbols with red dotted lines represent the currently investigated $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films. Blue symbols with the light-gray transparent strip indicate the results obtained on $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ films [17], and the orange dotted lines show approximately the T_C vs x course obtained for $(\text{TiZrTaNb})_{1.0}\text{N}_x$ films [21]. (c) $R(T)/R_{300K}$ dependencies of some samples in the temperature range up to 300 K. Note that samples with $x = 0.81, 0.97$, and 0.98 exhibit a semiconducting behavior.

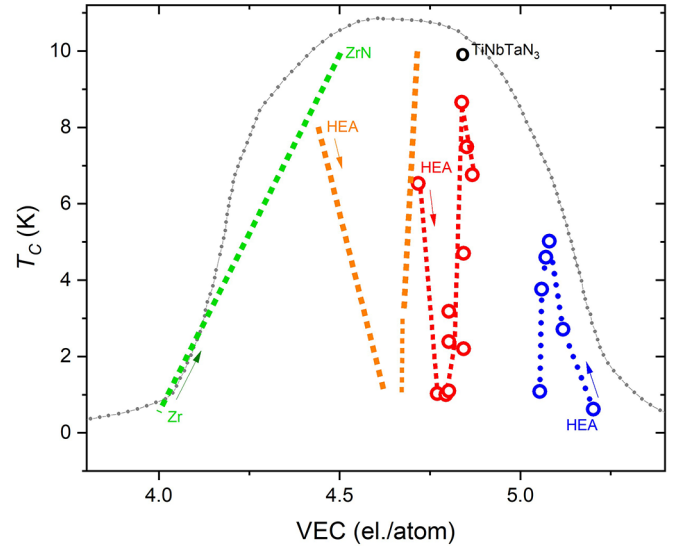


FIG. 3. T_C vs VEC dependencies for various nitrides. The gray dash-dotted line with a domelike shape shows the T_C vs VEC course for transition metals and transition-metal alloys in the crystalline form taken from [31]. Red points represent the $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films, blue points the $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ films [17], orange dotted lines the approximate course for the $(\text{TiZrTaNb})_{1.0}\text{N}_x$ films [21], green dotted line the development in ZrN_x [20], and the upper black point the T_C of TiNbTaN_3 [12]. The HEA marks indicate the position of the initial (nitrogen-free) HEAs; the nearby arrows show the T_C development with increasing N concentration x . The dotted lines are guides to the eyes.

bcc structures are not thermodynamically stable. Results reported in [30], moreover, show that the old VEC criterion [28] fails to work effectively only for compositions containing a high concentration of lightweight metals (such as Al, Mg, Sc, and Li).

Thus, higher VEC values lead to more stable HEA and accelerate the tendency to form a fcc structure. Moreover, the higher VEC is less sensitive to the localization of otherwise mobile conduction electrons in metallic HEAs, which arises due to their bonding to incorporated N atoms (see, e.g., [20]). This localization of conduction electrons is in our case supported, e.g., by the x dependence of the R_0/R_{300} ratio (see Table I), which shows that the metalliclike dependence of the initial HEA (with $R_0/R_{300} = 0.84 < 1$ for $x = 0$) changes gradually to a semiconductorlike one ($R_0/R_{300} > 1$ for $x \rightarrow 1$) with increasing x . Therefore, it appears that the VEC plays a crucial role in the formation of the T_C vs x course and in the enhancement of T_C in high entropy nitrides.

To take a closer look how T_C evolves on the total VEC of high entropy nitrides (i.e., including also N atoms with VEC = 5 el./atom), Fig. 3 represents this dependence for the above-discussed $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$, $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ [17], and $(\text{TiZrTaNb})_{1.0}\text{N}_x$ [21]. In this figure, the dot-dashed gray line with a domelike shape shows the T_C vs VEC course for transition metals and transition-metal alloys in the crystalline form taken from [31]. This course, also named the Matthias rule, shows a maximum of $T_{C\text{max}} \approx 11$ K at VEC ≈ 4.7 el./atom. A second maximum,

not shown in Fig. 3, with a $T_{C\max} \approx 16$ K is located at VEC ≈ 6.5 el./atom; see, e.g., Refs. [24,25].

From the T_C vs VEC dependencies in Fig. 3, one can see that for VEC values of the initial HEA lower than 5, i.e., lower than the VEC of nitrogen [in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ and $(\text{TiZrTaNb})_{1.0}\text{N}_x$ nitrides; see the red and orange courses], with increasing x (as well as with increasing VEC), T_C first goes through a minimum and reaches its highest value only close to the stoichiometric value of $x = 1$. On the other hand, if the VEC of the initial HEA is higher than 5, then with increasing x , the corresponding VEC of the nitride decreases and T_C goes through a maximum at $x < 1$. These results suggest that in order to obtain a T_C enhancement due to N incorporation, a VEC > 5 el./atom of the initial HEA has to be chosen. However, it is interesting that the T_C vs VEC dependence of $(\text{TiNbTaMoW})_{1.0}\text{C}_{1-x}\text{N}_x$ carbonitrides [32] (carbon VEC = 4 el./atom) also shows for VEC < 5 el./atom a domelike course (as in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ nitrides [17] for VEC > 5 el./atom), which indicates that incorporations of N and C into HEAs may have a different impact.

Nevertheless, as the T_C values of all nitrides in Fig. 3 lie inside the dome bordered by the trendline [31] (including Zr and ZrN_x nitrides; see the green dotted line in Fig. 3, as well as the carbonitrides [32]), it is probably difficult to assume that within the range $3.5 < \text{VEC} < 5.5$ el./atom, a high T_C value could be achieved. But, as the T_C of NbN (total VEC = 5 el./atom), MoN (total VEC = 5.5 el./atom), and $(\text{NbTi})_{1.0}\text{N}$ (total VEC ≈ 4.75 el./atom) nitrides reach values of 17.3, 13, and ~ 15 K, respectively [2,3,10], which exceed the value of $T_{C\max} \approx 11$ K, it is not excluded that also some high entropy nitrides will not obey the Matthias rule [31] and provide a higher T_C .

The superconducting transitions in some investigated $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films, with $x = 0, 0.81$, and 0.97 in which sharp $R(T)/R_0$ (percolation) transitions have been observed, were also confirmed by (volumetric) $M(T)$ magnetization measurements. The corresponding results are shown in Fig. 4 as normalized DC magnetization $M(T)/M(2\text{K})$ in magnetic field (B) of 1 mT, where $M(T)$ is the temperature dependence of magnetization and $M(2\text{K})$ the magnetization value at 2 K. The obtained T_C values are in good agreement with those from resistance measurements [see Fig. 2(a)]; however, the shapes of the $M(T)/M(2\text{K})$ dependencies differ. The composition with $x = 0$ exhibits a sharp superconducting transition; on the other hand, the high entropy nitride films with $x = 0.81$ and $x = 0.97$, especially that with $x = 0.81$, show a rather stretched transition, indicating that these samples are not purely single phase and also contain nitrides with compositional and structural inhomogeneities or various phase segregations. This is related to the bcc $\rightarrow$ fcc transition, in which, at a certain nitrogen flow rate, phases with close to x composition or even small fractions of different phases can also form. An important role that is played here is probably the fact that $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitrides contain Zr and Hf atoms (together about 20 at.%), which are considerably larger than the Nb, Ta, and Ti atoms (Zr: $r_a \approx 160.25$ pm; Hf: $r_a \approx 157.75$ pm; Nb: $r_a \approx 142.9$ pm; Ta: $r_a \approx 143$ pm; Ti: $r_a \approx 146.15$ pm). This difference in radii is apparently the main cause of strain and structural distortions or inhomogeneities (even amorphous) that have different T_C values and lead to a stretched superconducting transition (see, e.g., also, [33]). It is

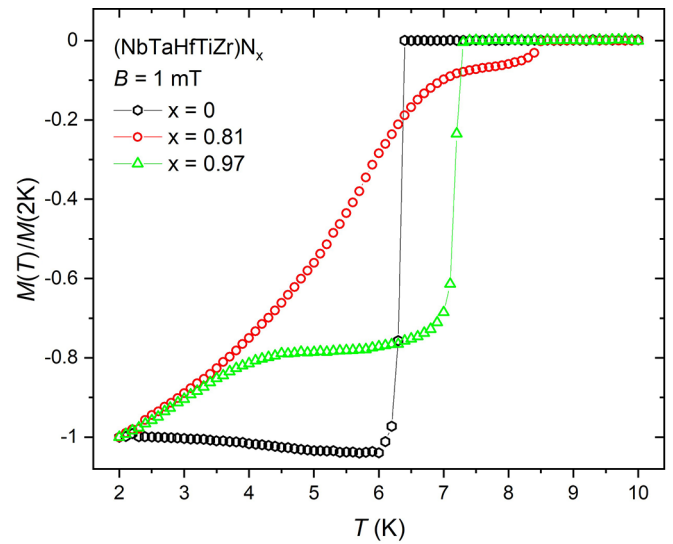


FIG. 4. Normalized DC magnetization $M(T)/M(2\text{K})$ in a magnetic field of 1 mT of selected $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitride films on sapphire substrates. The sample with $x = 0$ shows a sharp superconducting transition, while on the other hand, the high entropy nitride films with $x = 0.81$ and 0.97 exhibit a stretched transition, indicating that the samples are not purely single phase.

worth noting that a similar situation was observed in $(\text{TiZrTaNb})_{1.0}\text{N}_x$ nitride films [21] [see Figs. 2(b) and 3], where a Zr concentration of 15–17 at.% also leads to a wide bcc $\rightarrow$ fcc transition and a very similar T_C vs x dependence. The determination of the detailed microstructure of various nitride films and their relationship to superconducting properties will surely be a subject of future studies; however, it is beyond the scope of this work.

To further investigate the superconducting state in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films, resistance $R(T)$ measurements in different magnetic fields B were carried out. Figure 5(a) shows the $R(T)$ dependence of the $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ film with $x = 0.98$ exposed to magnetic fields between 0.1 and 8 T, demonstrating the decrease of T_C with increasing B . The T_C in magnetic fields [as in the case of Fig. 2(a)] was determined by the temperature at which is $R(T)/R_0 = 0.5$. The obtained T_C values enabled one to construct the upper critical magnetic field B_{c2} vs T phase diagrams for all films [see Fig. 5(b)]. Their dependencies can be described by the Werthamer-Helfand-Hohenberg (WHH) model [34], which, e.g., for N concentration $x = 0$, gives a zero-temperature $B_{c2}(0)$ value of ~ 7.26 T and for $x = 0.81$ a value of ~ 10.6 T. The obtained $B_{c2}(0)$ values (see, also, Table I) provide $B_{c2}(0)/T_C$ ratios which are smaller than 1.86 (T/K), which shows that all the $B_{c2}(0)$ values are within the weak-coupling pair-breaking limit [35,36]. Interestingly, in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ films [17] that exhibited a domelike T_C vs x dependence, the $B_{c2}(0)/T_C$ ratios showed values higher than 2 (T/K).

C. Factors beyond valence electron concentration

In addition to the ΔS and VEC discussed above, there are also other parameters which control the formation and properties of high entropy nitrides. Among others, it is the ability of transition metals to form thermodynamically stable

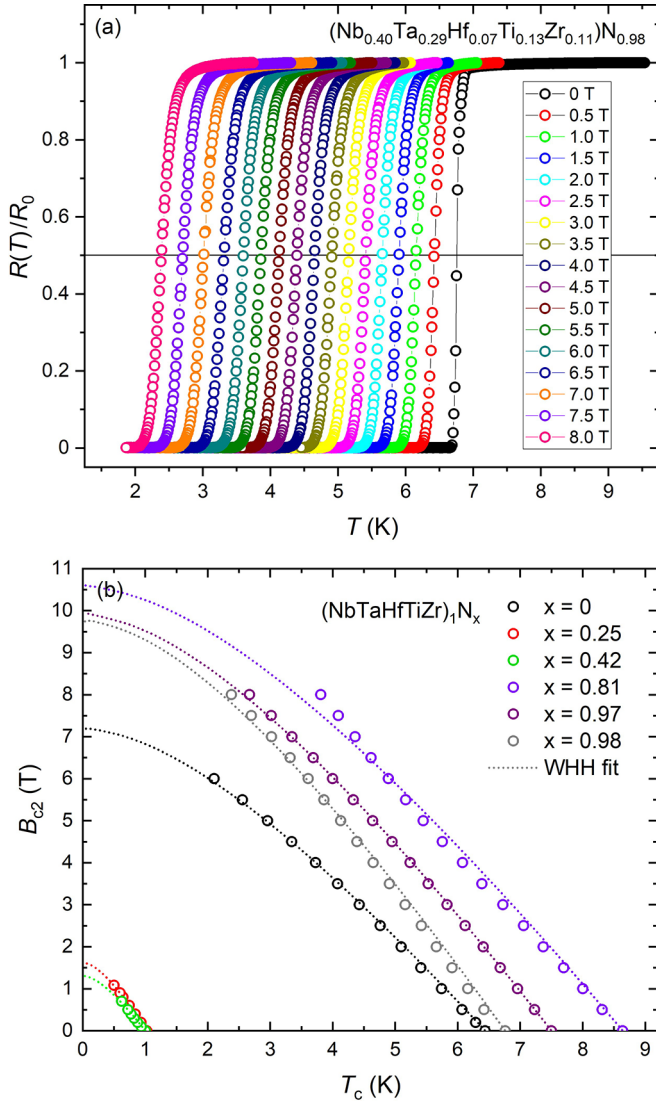


FIG. 5. (a) Temperature dependency of the resistance of a $(\text{NbTaHfTiZr})_{1.0}\text{N}_{0.98}$ film within a magnetic field. (b) Temperature dependencies of the upper critical magnetic field B_{c2} (marked by symbols) for the $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ films together with the WHH model [33] fits (shown by lines). The estimated zero-temperature magnetic fields $B_{c2}(0)$ are given in Table I.

nitride compounds, which varies along the periodic table (see, e.g., [19,37]). This ability points to strong nitride formers found in groups 4–6 of the periodic table, such as, e.g., Ti, Zr, Hf, Nb, Ta. On the other hand, metals in groups 7–11, such as, e.g., Cr, Mo, W, Ru, Rh, Cu, are considered either as weak nitride formers or as unable to form nitrides. Highly stable transition-metal nitrides based on strong nitride formers usually transform at higher N concentrations into a NaCl-type (fcc) crystal structure. As the nitride bond strength decreases towards the right of the periodic table, more complex nitride structures become common. The reason for this trend is the filling of anti- and nonbonding electronic states as the VEC increases [38]. Such structures can be found, e.g., among tungsten nitrides with hexagonal (e.g., WN , W_2N), rhombohedral (e.g., W_2N_3 , W_7N_6), or cubic (W_3N_4) struc-

tures [39]. However, due to the limited mobility of atoms during film deposition, the formation of such nitride structures is not expected. Therefore, the deposition of late or intermediate transition metals in a nitrogen-containing atmosphere usually leads to amorphous structures [19].

In the case of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitrides, all HEA forming elements are strong nitride formers; on the other hand, in the case of $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ (with the domelike T_C vs x course), there are also weak nitride formers (Mo and W) present. It is therefore surprising that the bcc $\rightarrow$ fcc structural transition occurs in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ already at very low N concentration ($x \approx 0.15$), whereas in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$, a considerably higher N concentration ($x > 0.50$) is needed to make it happen.

Another parameter to consider is related to the size differences of atoms forming the HEA. Namely, with increasing atomic size difference, the HEA prefers to form a bcc structure instead of the fcc one (see, e.g., [40,41]). This follows from the ability of the bcc structure to accommodate atoms with larger size differences and lower strain energy. It has been reported (see, e.g., [19,40–42]) that if the average deviation $\delta = [\sum c_i(1 - r_i/r_a)^2]^{1/2}$ from the weighted average atomic radius $r_a = \sum c_i \cdot r_i$, where c_i and r_i are the atomic percentage and atomic radius of the i th element, exceeds a value of $\delta \approx 6.4\%$, HEAs may tend to become amorphous. When looking at this deviation for the current case of $\text{Nb}_{35}\text{Ta}_{35}\text{Hf}_{10}\text{Ti}_{10}\text{Zr}_{10}$, a deviation of $\delta \approx 4.6\%$ can be found in [24]. For $\text{Ti}_{20}\text{Nb}_{20}\text{Mo}_{20}\text{Ta}_{20}\text{W}_{20}$ [17], this deviation was calculated based on atomic radius data taken from [18] (with Ti: $r_i = 146$ pm; Nb: $r_i = 143$ pm; Mo: $r_i = 136$ pm; Ta: $r_i = 143$ pm; W: $r_i = 137$ pm) that lead to a value of $\delta \approx 6.1\%$, and for TiZrTaNb [21], $\delta \approx 4.8\%$. Thus, in all high entropy nitrides under discussion, the deviations δ of the initial HEA compounds have values below the threshold value of 6.4%. Therefore, there should be no obstacles to form the fcc phase in corresponding nitrides (the nitrogen atomic radius is $r_i = 75$ pm [18]).

Of course, apparently not any VEC > 5 eL/atom value of the initial HEA will lead to an increase of the T_C enhancement or a domelike dependence in the derived high entropy nitrides. As in (nitrogen-free) HEAs, where the highest T_C values are observed at certain VEC values, in some cases, even in VEC vs T_C positions that significantly deviate from the Matthias rule (see, e.g., the type “C” HEA superconductors in [23] or the “CsCl” HEA superconductors in [24]), and also in the case of high entropy nitrides, some optimal VEC of the initial HEA will be necessary to reach a pronounced T_C enhancement.

Moreover, recent results performed on superconducting Heusler phases (representing three component intermetallics) [43] show that while a simple VEC value relationship is useful in predicting and tuning these superconducting materials, the inclusion of the symmetry of interacting electron orbitals is also necessary for their understanding. There are also other features in HEAs, such as glassy atomic vibrations or blurry electronic structures created by local structural disorder [44], which can influence the superconductivity in high entropy nitrides. Also, parallel theoretical studies may be useful, as performed recently for superconducting HEAs or off-stoichiometric superconductors [45,46], which could help

to clarify the developments of electronic structure, phonon modes, and electron-phonon interaction as a result of nitrogen incorporation.

We would also like to note that the results obtained for $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ are consistent with those reported in [21], where the authors also observed a decrease of T_C at lower concentrations of nitrogen ($x < 0.62$) and found that the maximum T_C in their $(\text{TiZrTaNb})_{1.0}\text{N}_x$ nitrides appears close to the stoichiometric ratio $x \approx 1.08$. The discrepancy between their and our results [in our case, the highest T_C is observed at $x = 0.81$; see, e.g., Fig. 2(b)] may stem from the lack of experimental data in a relatively large N-concentration range $0.64 < x < 1.08$ in [21], which would clarify how the T_C vs x course behaves in this region.

IV. CONCLUSIONS

The obtained results show that the x (with $x = \text{N}/M$, the ratio between the atomic fractions of nitrogen and metal atoms) vs T_C course in high entropy $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ nitride films is completely different from the domelike course with a high T_C enhancement in $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ [17]. In the discussion, we have shown that in addition to the high configuration entropy ΔS in HEAs, which for the incorporated N atoms provides options to occupy convenient positions in the fcc lattice and form a new phonon mode, the T_C vs x course and the enhancement of T_C in high entropy nitrides depend strongly on the VEC value of the initial HEA. Namely, it turns out that a higher VEC value accelerates the tendency to form a fcc structure and is less sensitive to the localization of otherwise mobile conduction electrons in the metallic HEA due to their bonding to inserted N atoms. However, in nitrides, it is also important to consider the various affinities of transition-metal elements toward nitrogen and the atomic size differences of HEA constituents.

However, as the affinity of metallic elements towards nitrogen decreases when moving in a period of the periodic table from left to right, and a similar dependence also applies to the atomic radii, whereas the VEC values in the same direction increase, a compromise has to be found. This compromise lies between the increasing VEC value, on one hand, and the decreasing affinities to N, on the other hand, also taking into account the difference in atomic radii. Such a balance is necessary to identify a suitable composition of the initial HEA for subsequent nitrides, which should exhibit a domelike

enhancement of the T_C with nitrogen incorporation. From the comparison of $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$, $(\text{TiNbMoTaW})_{1.0}\text{N}_x$ [17], and $(\text{TiZrTaNb})_{1.0}\text{N}_x$ [21], it appears that the VEC of the initial HEA plays an important role for the emergence of a suitable T_C vs x or T_C vs VEC dependence in the corresponding high entropy nitrides. However, as follows from the wide width of the bcc $\rightarrow$ fcc structural transitions in $(\text{NbTaHfTiZr})_{1.0}\text{N}_x$ and $(\text{TiZrTaNb})_{1.0}\text{N}_x$ [21] films, the size of metal atoms also plays an important role since a large difference in their atomic radii leads to structural inhomogeneities and subsequently to the suppression of superconducting properties.

Overall, high entropy nitrides, and their formation, microstructure, and superconducting properties, present a very complex issue. Nevertheless, as there is a large number of HEAs of various types reported in the literature, with various VECs, and different atomic radii and nitrogen affinities, the obtained results on the role of the VEC may open up a search for high or medium entropy nitrides with a high T_C enhancement and a high T_C . And, as superconducting high entropy nitrides are very stable and exhibit a high resistance to displacement damage, these materials may have a promising potential for applications under extreme conditions as well as in corrosive environments.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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- [1] W. Meissner and H. Franz, Measurements with liquid helium IX Superconductivity of carbides and nitrides, *Z. Phys.* **65**, 30 (1930).
 - [2] B. T. Matthias and J. K. Hulm, A search for new superconducting compounds, *Phys. Rev.* **87**, 799 (1952).
 - [3] L. E. Toth, C. P. Wang, and G. M. Yen, Superconducting critical temperatures of non-stoichiometric transition metal carbides and nitrides, *Acta Metall.* **14**, 1403 (1966).
 - [4] H. Rietschel, H. Winter, and W. Reichardt, Strong depression of superconductivity in VN by spin fluctuations, *Phys. Rev. B* **22**, 4284 (1980).
 - [5] T. Shiino, S. Shiba, N. Sakai, T. Yamakura, L. Jiang, Y. Uzawa, H. Maezawa, and S. Yamamoto, Improvement of the critical temperature of superconducting NbTiN and NbN thin films using the AlN buffer layer, *Supercond. Sci. Technol.* **23**, 045004 (2010).
 - [6] K. Makise, H. Terai, M. Takeda, Y. Uzawa, and Z. Wang, Characterization of NbTiN thin films deposited on various substrates, *IEEE Transact. Appl. Superconduct.* **21**, 139 (2011).
 - [7] M. V. Burdastiy, S. V. Postolova, T. Proslir, S. S. Ustavshikov, A. V. Antonov, V. M. Vinokur, and A. Yu. Mironov,

- Superconducting phase transitions in disordered NbTiN films, *Sci. Rep.* **10**, 1471 (2020).
- [8] Y. Zou, Q. Jin, Y. Wang, K. Jiang, S. Wang, Y. Li, E.-J. Guo, and Z. G. Cheng, Tuning superconductivity in vanadium nitride films by adjusting strain, *Phys. Rev. B* **105**, 224516 (2022).
 - [9] W. Spengler, R. Kaiser, A. N. Christensen, and G. Müller-Vogt, Raman scattering, superconductivity, and phonon density of states of stoichiometric and nonstoichiometric TiN, *Phys. Rev. B* **17**, 1095 (1978).
 - [10] L. Zhang, W. Peng, L. X. You, and Z. Wang, Superconducting properties and chemical composition of NbTiN thin films with different thickness, *Appl. Phys. Lett.* **107**, 122603 (2015).
 - [11] S.-Z. Chen, J.-W. Yang, T.-Y. Peng, Y.-C. Chu, C.-C. Yeh, I.-F. Hu, S. Mhatre, Y.-J. Lu, and C.-T. Liang, Disorder-induced 2D superconductivity in a NbTiN film grown on Si by ultrahigh-vacuum magnetron sputtering, *Supercond. Sci. Technol.* **35**, 064003 (2022).
 - [12] L. Zeng, J. Wang, H. Liu, L. Li, J. Qin, Y. Li, R. Chen, J. Song, Y. Hou, and H. Luo, Ambient-pressure superconductivity onset at 10 K and robust T_C under high pressure in TiNbTa_N₃ medium-entropy nitride, *Adv. Sci.* **12**, e06089 (2025).
 - [13] S. Das, V. Drozd, A. Durygin, M. S. I. Sozal, W. Li, X. Bai, Y. Ding, Y. Guan, Z. Mao, M. Cinibulk, and Z. Cheng, Reactive flash sintering and characterization of bulk high entropy nitrides, *J. Eur. Ceram. Soc.* **45**, 117157 (2025).
 - [14] I. Ohkubo, Z. Hou, J. N. Lee, T. Aizawa, M. Lippmaa, T. Chikyow, K. Tsuda, and T. Mori, Realization of closed-loop optimization of epitaxial titanium nitride thin-film growth via machine learning, *Mater. Today Phys.* **16**, 100296 (2021).
 - [15] N. Cucciniello, D. Lee, H. Y. Feng, Z. Yang, H. Zeng, N. Patibandla, M. Zhu, and Q. Jia, Superconducting niobium nitride: A perspective from processing, microstructure, and superconducting property for single photon detectors, *J. Phys. Cond. Matter.* **34**, 374003 (2022).
 - [16] S. Miyajima, T. Yamashita, M. Tanaka, N. Takeuchi, K. Inomata, and H. Terai, Fabrication process for monolithic integration of a nitride superconductor-based superconducting qubit with a single flux quantum control circuit, *IEEE Trans. Appl. Supercond.* **33**, 1 (2023).
 - [17] G. Pristáš, G. C. Gruber, M. Orendáč, J. Bačkai, J. Kačmarčík, F. Košuth, S. Gabáni, P. Szabó, C. Mitterer, and K. Flachbart, Multiple transition temperature enhancement in superconducting TiNbMoTaW high entropy alloy films through tailored N incorporation, *Acta Mater.* **262**, 119428 (2024).
 - [18] D. B. Miracle and O. N. Senkov, A critical review of high entropy alloys and related concepts, *Acta Mater.* **122**, 448 (2017).
 - [19] E. Lewin, Multi-component and high-entropy nitride coatings - A promising field in need of a novel approach, *J. Appl. Phys.* **127**, 160901 (2020).
 - [20] F. Chen, X. Bai, Y. Wang, T. Dong, J. Shi, Y. Zhang, X. Sun, Z. Wei, M. Qin, J. Yuan, Q. Chen, X. Wang, Xu Wang, B. Zhu, R. Huang, K. Jiang, W. Zhou, N. Wang, J. Hu, Y. Li, K. Jin, and Z. Zhao, Emergence of superconducting dome in ZrN_x films via variation of nitrogen concentration, *Sci. Bull.* **68**, 674 (2023).
 - [21] R. Shu, X. Zhang, F. Tasnádi, W. Olovsson, S. G. Rao, G. Greczynski, A. le Febvrier, M. Magnuson, and P. Eklund, Stoichiometry effects on the chemical ordering and superconducting properties in TiZrTa_NN_x refractory high entropy nitrides, *Ann. Phys.* **536**, 2300470 (2023).
 - [22] M. Tinkham, The BCS theory, in *Introduction to Superconductivity* (Dover, Mineola, New York, 2004), Chap. 3.
 - [23] L. Sun and R. J. Cava, High-entropy alloy superconductors: Status, opportunities, and challenges, *Phys. Rev. Mat.* **3**, 090301 (2019).
 - [24] J. Kitagawa, S. Hamamoto, and N. Ishizu, Cutting edge of high-entropy alloy superconductors from the perspective of materials research, *Metals* **10**, 1078 (2020).
 - [25] Y. He, K. Maa, J. You, Md. S. A. Hossain, M. Nadeem, and X. Wang, High entropy superconductors, *Phys. Rep.* **1144**, 1 (2025).
 - [26] G. Pristáš, J. Bačkai, M. Orendáč, S. Gabáni, F. Košuth, M. Kuzmiak, P. Szabó, E. Gažo, R. Franz, S. Hirn, G. C. Gruber, C. Mitterer, S. Vorobiov, and K. Flachbart, Superconductivity in medium- and high-entropy alloy thin films: Impact of thickness and external pressure, *Phys. Rev. B* **107**, 024505 (2023).
 - [27] T. R. Kirkpatrick and D. Belitz, Suppression of superconductivity by disorder, *Phys. Rev. Lett.* **68**, 3232 (1992).
 - [28] S. Guo, C. Ng, J. Lu, and C. T. Liu, Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys, *J. Appl. Phys.* **109**, 103505 (2011).
 - [29] R. Chen, G. Qin, H. Zheng, L. Wang, Y. Su, Y. L. Chiu, H. Ding, J. Guo, and H. Fu, Composition design of high entropy alloys using the valence electron concentration to balance strength and ductility, *Acta Mater.* **144**, 129 (2018).
 - [30] S. Yang, G. Liu, and Y. Zhong, Revisit the VEC criterion in high entropy alloys with high-throughput *ab initio* calculations: A case study with Al-Co-Cr-Fe-Ni system, *J. Alloys Comp.* **916**, 165477 (2022).
 - [31] B. T. Matthias, Empirical relation between superconductivity and the number of valence electrons per atom, *Phys. Rev.* **97**, 74 (1955).
 - [32] L. Zeng, X. Hu, Y. Zhou, Y. Liu, M. Boswell, W. Xie, K. Li, L. Li, P. Yu, C. Zhang, W.-M. Guo, D.-X. Yao, and H. Luo, Superconductivity and non-trivial band topology in high-entropy carbonitride Ti_{0.2}Nb_{0.2}Ta_{0.2}Mo_{0.2}W_{0.2}C_{1-x}N_x, *Innov. Mater.* **1**, 100042 (2023).
 - [33] X. Lu, H. Li, J. Liang, D. Huo, C. Liu, M. Hu, and Y. Yang, A review of high-entropy nitrides: Preparation methods, properties, and applications, *Mater. Today Commun.* **47**, 113092 (2025).
 - [34] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Temperature and purity dependence of the superconducting critical field, H_{c2}. III. Electron spin and spin-orbit effects, *Phys. Rev.* **147**, 295 (1966).
 - [35] K.-Y. Ma, K. Gornicka, R. Lefevre, Y. Yang, H. M. Rønnow, H. O. Jeschke, T. Klimczuk, and F. O. von Rohr, Superconductivity with high upper critical field in the cubic centrosymmetric η -carbide Nb₄Rh₂C_{1- δ} , *ACS Mater. Au* **1**, 55 (2021).
 - [36] F. N. Womack, D. P. Young, D. A. Browne, G. Catelani, J. Jiang, E. I. Meletis, and P. W. Adams, Extreme high-field superconductivity in thin Re films, *Phys. Rev. B* **103**, 024504 (2021).
 - [37] A. Friedrich, B. Winkler, E. A. Juarez-Arellano, and L. Bayarjargal, Synthesis of binary transition metal nitrides, carbides and borides from the elements in the laser-heated diamond anvil cell and their structure-property relations, *Materials* **4**, 1648 (2011).
 - [38] J. Häglund, A. Fernández Guillermet, G. Grimvall, and M. Körling, Theory of bonding in transition-metal carbides and nitrides, *Phys. Rev. B* **48**, 11685 (1993).

- [39] S. Wang, X. Yu, Z. Lin, R. Zhang, D. He, J. Qin, J. Zhu, J. Han, L. Wang, H. Mao, J. Zhang, and Y. Zhao, Synthesis, crystal structure, and elastic properties of novel tungsten nitrides, *Chem. Mater.* **24**, 3023 (2012).
- [40] S. Guo, Q. Hu, C. Ng, and C. T. Liu, More than entropy in high-entropy alloys: Forming solid solutions or amorphous phase, *Intermetallics* **41**, 96 (2013).
- [41] S. A. Kube, S. Sohn, D. Uhl, A. Datye, A. Mehta, and J. Schroers, Phase selection motifs in high entropy alloys revealed through combinatorial methods: Large atomic size difference favors BCC over FCC, *Acta Mater.* **166**, 677 (2019).
- [42] Y. Zhang, Y. J. Zhou, J. P. Lin, G. L. Chen, and P. K. Liaw, Solid-solution phase formation rules for multi-component alloys, *Adv. Eng. Mater.* **10**, 534 (2008).
- [43] K. Górnicka, X. Gui, J. R. Chamorro, T. M. McQueen, R. J. Cava, T. Klimczuk, and M. J. Winiarski, Superconductivity – electron count relationship in Heusler phases - the case of LiPd_2Si , *Chem. Mater.* **36**, 1870 (2024).
- [44] Y. Mizuguchi, H. Usui, R. Kurita, K. Takae, M. R. Kasem, R. Matsumoto, K. Yamane, Y. Takano, Y. Nakahira, A. Yamashita, Y. Goto, A. Miura, and C. Moriyoshi, Glassy atomic vibrations and blurry electronic structures created by local structural disorders in high-entropy metal telluride superconductors, *Mater. Today Phys.* **32**, 101019 (2023).
- [45] K. Jasiewicz, S. Gutowska, and J. Tobola, Electron-Phonon Coupling Calculations for bcc HEA Superconductors, in *High-Entropy Alloy Superconductors: Exotic Properties, Applications and Materials Design*, Springer Series in Solid-State Sciences Vol. 202, edited by J. Kitagawa and Y. Mizuguchi (Springer Nature, Singapore, 2024), p. 103.
- [46] P. N. Ferreira, R. Lucrezi, I. Guilhon, M. Marques, L. K. Teles, C. Heil, and L. T. F. Eleno, *Ab initio* modeling of superconducting alloys, *Mater. Today Phys.* **48**, 101547 (2024).