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Jiro Kitagawa
Yoshikazu Mizuguchi *Editors*


# High-Entropy Alloy Superconductors

## Exotic Properties, Applications and Materials Design

Springer

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Editors

# High-Entropy Alloy Superconductors

## Exotic Properties, Applications and Materials Design

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# Preface

This book presents a comprehensive survey of the latest research concerning high-entropy alloy (HEA) superconductors, an area of inquiry initiated in 2014 and has since garnered significant attention. Each section is authored by experts who elucidate the exotic properties, applications, and materials design associated with HEA superconductors, drawing upon their original concepts.

HEAs represent a novel class of materials introduced in 2004, renowned for their exceptional mechanical attributes, robust resistance to corrosion, and remarkable thermal stability, among other merits. HEAs are characterized by crystals in which more than four elements randomly occupy a single crystallographic site, thereby augmenting configurational entropy with the increasing number of compositional elements. Presently, the concept of high entropy is extensively applied across various materials, including oxides, chalcogenides, and halides. Moreover, the high-entropy state engenders many enhanced functionalities, such as thermoelectric properties, magnetocaloric effects, catalytic prowess, and more.

Superconductivity has emerged as a particularly prominent subject in this domain following the discovery of a HEA superconductor in 2014. Recent findings have unveiled robust superconductivity under extraordinarily high pressure or ion irradiation. Furthermore, improvement of bulk superconductivity via the high-entropy effect has been documented. Within this realm of research, numerous scholars are endeavoring to discern the distinctions in superconducting properties between HEA superconductors and conventional or unconventional counterparts. Given the expansive compositional space of HEAs, the materials research on HEA superconductors is imperative for identifying unique characteristics associated with the high-entropy state. Additionally, research on the practical applications of HEA superconductors is indispensable for advancing superconducting technology. Consequently, the principal themes of this publication revolve around elucidating the similarities and disparities in superconducting properties between HEA superconductors and other classes of superconductors, as well as exploring applications and materials design for HEA superconductors. From a fundamental perspective, the exploration of the distinctive aspects of HEA superconductors contributes to the establishment of novel principles in superconductivity. Moreover, the research topic holds significant promise for practical applications, such as robust superconducting wires and multifunctional superconductors. Furthermore, the distinctive structural attributes of HEAs render the materials design of HEA superconductors invaluable for achieving a comprehensive understanding of these materials.

The book is organized into 11 chapters. Chapter 1 encompasses the discovery and the current status of HEA superconductors. These HEA superconductors are classified into two primary categories: the first class encompasses alloy systems characterized by body-centered cubic (bcc) and hexagonal close-packed (hcp) structures, while the second class comprises intermetallic types. In each of these classes, we expound upon the exotic properties, applications, and materials design, aligning with the overarching themes of this work. We also elucidate the interdependencies between the topics addressed in this chapter and those explored in the subsequent ten chapters, contributed by leading-edge researchers. Chapters 2–5 delve into bcc HEA superconductors, with Chap. 7 dedicated to hcp HEA superconductors. Chapter 6, on the other hand, offers a comprehensive treatment of both bcc and hcp superconductors. In the domain of high-entropy intermetallic compounds, Chaps. 8–10 delve into NaCl-type, van der Waals-type, and $CuAl_2$-type compounds, respectively. Additionally, the eleventh chapter encompasses both $BiS_2$-based and YBCO-based HEAs.

This publication addresses the novel facets of superconductivity associated with the high-entropy state, the potential applications under consideration, and the intricacies of materials design. These recent discoveries are poised to captivate a myriad of researchers in the fields of materials science, particularly those engaged in high-entropy alloys and the realm of superconducting properties and technology.

Fukuoka, Japan Jiro Kitagawa
Hachioji, Japan Yoshikazu Mizuguchi

The original version of the book has been revised: The affiliation of the second author has been updated. A correction to the book can be found at https://doi.org/10.1007/978-981-97-4129-8_12

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# Chapter 1
# Discovery and Current Status of High-Entropy Alloy Superconductors

**Jiro Kitagawa and Yoshikazu Mizuguchi**

**Abstract** This chapter reviews the discovery and current status of high-entropy alloy (HEA) superconductors. The categorization of HEA superconductors involves bifurcation into two distinct classes based on their crystallographic features. The first class comprises alloy systems represented by body-centered cubic and hexagonal close-packed structures, while the second class pertains to compound types. Within each of these classes, we expound upon the exotic properties, applications, and materials design in alignment with the themes of this book. Furthermore, we elucidate the interrelationships between the subjects addressed in this chapter and those expounded upon in the subsequent ten chapters.

## 1.1 Introduction

A high-entropy alloy (HEA) is characterized as an alloy or crystalline system in which at least four principal elements randomly occupy a crystallographic site. HEAs stand in stark contrast to conventional alloys composed predominantly of one or two principal elements. The innovative paradigm of HEAs has garnered substantial attention due to its rich applications, encompassing exceptional mechanical properties, energy storage capabilities, magnetic refrigeration, soft ferromagnetism, catalytic potential, thermoelectricity, and biocompatibility [1, 2]. The thermodynamic entropy state of an alloy is assessed through configurational entropy, denoted as $\Delta S_{\text{mix}} = -R\sum_{i=1}^{n} c_i \ln c_i$, where $n$ is the number of elements, $c_i$ is the atomic fraction, and $R$ is the gas constant. The threshold of $\Delta S_{\text{mix}}$, which defines HEAs, is now established at 1.0 $R$, generally fulfilled by the presence of four constituent ele-

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ments [3]. HEAs are reputed for their extraordinary attributes, setting them apart from conventional alloy systems. These distinctive properties are collectively referred to as the "four core effects," encompassing the following phenomena:

- high entropy effect, wherein an elevated $\Delta S_{mix}$ confers stability to the solid solution phase
- severe lattice distortion, resulting in solid solution strengthening due to high atomic disorder
- sluggish diffusion, characterized by hindered atomic mobility and reduced diffusion coefficients
- cocktail effect, which denotes a synergistic phenomenon leading to physical quantities exceeding the average values predicted by the mixture rule.

Superconductivity has emerged as a prominent area of interest following the discovery of an HEA superconductor in 2014 [4]. Presently, HEA superconductivity is the subject of extensive exploration, extending diverse structures such as body-centered cubic (bcc) [5, 6], hexagonal close-packed (hcp) [7–9], face-centered cubic (fcc) [10], CsCl-type [11], A15 [12], NaCl-type [13], $\alpha$ (or $\beta$)-Mn-type [14, 15], $\sigma$-phase type [16], $CuAl_2$-type [17], van der Waals-type [18], $BiS_2$-based [19], and YBCO-based [20] structures. The bcc, hcp, and fcc HEAs are categorized as alloy systems, while the remaining structures are classified as high-entropy compounds. Figure 1.1a and b illustrate the bcc HEA and the $CuAl_2$-type high-entropy compound, respectively. Within the bcc structure, a single crystallographic site, known as the 2*a* site, is randomly populated by multiple atoms. In contrast, the $CuAl_2$-type structure possesses the 4*a* and 8*h* sites. In Fig. 1.1b, the 4*a* site is randomly occupied by five transition metals, while Zr atoms occupy the 8*h* site.

The advent of superconductivity in HEA systems was triggered by the discovery of $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ ,which has a bcc structure [4]. This alloy exhibits the cocktail effect, as delineated among the four core effects previously mentioned, for the superconducting critical temperature $T_c$. This discovery has garnered considerable scholarly attention, leading to extensive investigations into alloy-type superconduc-

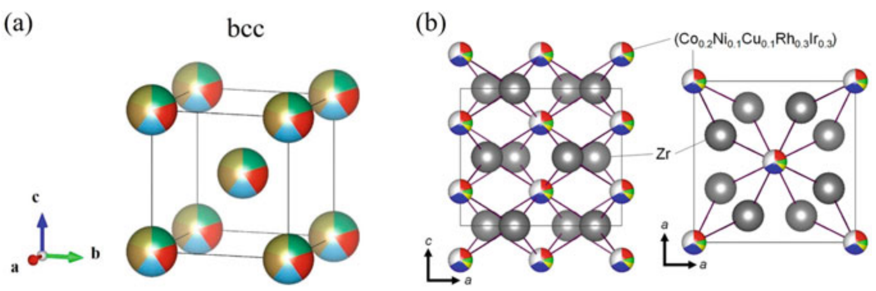


**Fig. 1.1** Crystal structures of high-entropy **a** bcc-type and **b** $CuAl_2$-type compounds. The multi-colored balls indicate random site occupation by several atoms. The solid lines represent the unit cells. Reproduced from [6, 17] under the Creative Commons Attribution License

tors. Notable findings include the robustness of superconductivity against high pressures and irradiation, as well as deviations from the Matthias rule [21–23]. Furthermore, the exploration of potential applications for HEA superconductors holds significance for the advancement of superconducting technology. For instance, several bcc HEAs have demonstrated high critical current densities on par with those observed in commercial Nb-Ti superconducting wires, representing a promising avenue for next-generation superconducting wire technology [22, 24, 25]. Additionally, the high hardness or shape memory effect in some HEAs presents promising prospects for developing multifunctional devices [26, 27].

By extending the HEA material variation to compounds having two or more crystallographic sites, we can explore the effects of HEA sites on various superconducting materials, including high-$T_c$, high-field, unconventional, and low-dimensional superconductors. As shown in Fig. 1.1b, one of the crystallographic sites is the HEA composition in HEA-type compounds. Therefore, various Tr-Zr bonds (Tr: transition metal) are formed in HEA-type $TrZr_2$. The random bond length in HEA-type compounds results in exotic physical properties possibly related to glassy phonons.

Following the brief overview of the discovery of HEA superconductors in both alloy systems and compounds, the subsequent sections of this chapter delve into the current landscape of HEA superconductors. This examination is conducted with a focus on exotic properties, applications, and materials design, all of which are harmonized with the themes of this book. Each class of HEA superconductors will be treated individually in this regard. Furthermore, we elucidate the thematic connections between the topics addressed in this chapter and the subsequent ten chapters contributed by leading-edge researchers.

## 1.2 Discovery of High-Entropy Alloy Superconductors

The first superconductor of the alloy type, $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$, made its debut in 2014 [4]. This compound crystallizes into the bcc structure and manifests itself as a type II superconductor with $T_c$ = 7.3 K. This behavior is comprehensively investigated by the electrical resistivity, magnetization, and specific heat. The specific heat analyses suggest a Bardeen-Cooper-Schrieffer (BCS)-type phonon-mediated superconductor characterized by a weak electron-phonon coupling. The cocktail effect is examined concerning the $T_c$ value, taking into account the $T_c$ values of the constituent elements, which stand at 4.47 K for Ta, 9.25 K for Nb, 0.128 K for Hf, 0.61 K for Zr, and 0.40 K for Ti. Consequently, the composition-weighted $T_c$ is 4.71 K. Remarkably, the experimental $T_c$ significantly surpasses this value of 4.71 K, attributable to the cocktail effect [4].

After the development of HEA superconductors, HEA-type superconducting compounds debuted in 2018. The first example was the layered $BiS_2$-based superconductor $REO_{0.5}F_{0.5}BiS_2$ (RE: rare earth) [28]. The RE site in the material is the solution of RE = La, Ce, Pr, Nd, Sm. Interestingly, the superconducting properties are improved by an increase in RE-site $\Delta S_{mix}$ in the $BiS_2$-based system [19, 28]. This result suggests that the local HEA site can affect the bulk physical properties of layered compounds.

Subsequently, we explore the present state of HEA superconductors, categorizing them into two distinct classes. The first class includes bcc and hcp HEA superconductors, while the second encompasses the compound type. Chapters 2 through 5 survey bcc HEA superconductors, with Chap. 7 dedicated to hcp HEA superconductors. Chapter 6, on the other hand, undertakes the comprehensive treatment of both bcc and hcp superconductors. In the class of high-entropy compounds, Chaps. 8–10 delve into the NaCl-type, van der Waals-type, and $CuAl_2$-type compounds, respectively. Additionally, the eleventh chapter considers both $BiS_2$-based and YBCO-based HEAs.

## 1.3 Body-Centered Cubic and Hexagonal Close-Packed Structures

In this section, we survey the current status of bcc and hcp HEA superconductors, focusing on their exotic properties, applications, and materials design, all harmonized with the themes described within the present book. Within each subsection, we expound upon various topics, many of which will find comprehensive treatment in the ensuing chapters from Chap. 2–7. Table 1.1 summarizes the interrelationships between the subjects addressed in this section and those expounded upon in Chaps. 2 through 7.

**Table 1.1** Interrelationships between topics addressed in this section and those expounded upon in Chaps. 2 through 7

| Topics | Chapter number |
|---|---|
| *Exotic properties* | |
| Deviation from the Matthias rule | 3, 6, 7 |
| Band broadening | 3, 5 |
| Strongly correlated electronic state | 2 |
| Search for breaking of time-reversal symmetry | 4, 6 |
| *Applications* | |
| High critical current density | 2 |
| High hardness | 3 |
| Shape memory and superelasticity | 4 |
| *Materials design* | |
| Semiempirical parameters | 3, 7 |
| First-principles calculations | 5 |

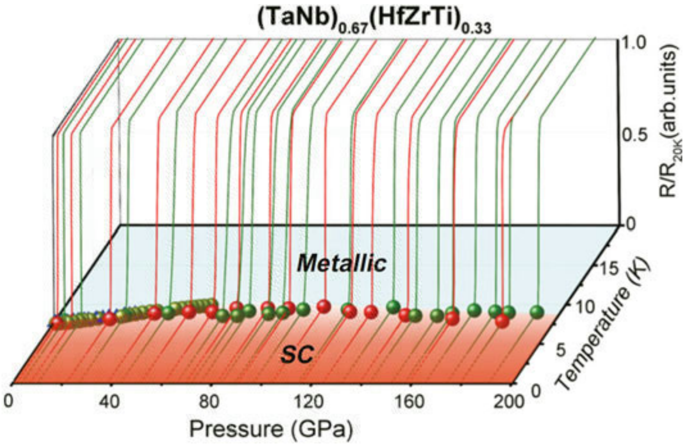


**Fig. 1.2** Phase diagram of $T_c$ vs. pressure up to 190.6 GPa for $(TaNb)_{0.67}(HfZrTi)_{0.33}$, combined with resistance vs. temperature plots. Reproduced with permission from [21]

### *1.3.1 Exotic Properties*

One of the striking and notable characteristics within this class of materials is the remarkable insensitivity of $T_c$ to extremely high pressure. As depicted in Fig. 1.2, the phase diagram of the bcc $(TaNb)_{0.67}(HfZrTi)_{0.33}$ HEA superconductor offers an insightful perspective [21]. This diagram elegantly combines the relationship between $T_c$ and pressure with the evolution of resistivity with respect to temperature. Notably, the value of $T_c$, approximately 8 K, exhibits insensitivity to changes over a wide pressure range, from ambient pressure to an astonishing 200 GPa. Furthermore, interestingly, the $TaNb_2HfZrTi$ bcc thin film demonstrated notably robust superconductivity even when subjected to Kr-ion irradiation [22]. This irradiation introduces a heightened level of atomic disorder, typically leading to a reduction in $T_c$. However, it is noteworthy that the reduction of $T_c$ in $TaNb_2HfZrTi$ remains relatively mild compared to that in famous superconductors such as $Nb_3Sn$, $MgB_2$, and YBCO [22]. These findings regarding $(TaNb)_{0.67}(HfZrTi)_{0.33}$ and $TaNb_2HfZrTi$ have profound implications, positioning superconducting HEAs as promising candidates for materials capable of withstanding extreme conditions, such as those encountered in aerospace applications and nuclear fusion. Furthermore, the robustness of superconductivity in the presence of magnetic elements has been observed, underscoring the versatility of HEA materials [29].

The majority of HEAs showcase conventional s-wave BCS-type superconducting behavior. According to the BCS theory, $T_c$ is intrinsically linked to the density of states at the Fermi energy ($E_F$), expressed as $D(E_F)$, and the strength of the electron-phonon interaction. In the context of bcc and hcp alloy systems, the valence electron concentration per atom (VEC) has a significant relationship with $D(E_F)$. Consequently, the Matthias rule has been established, underscoring the strong correlation

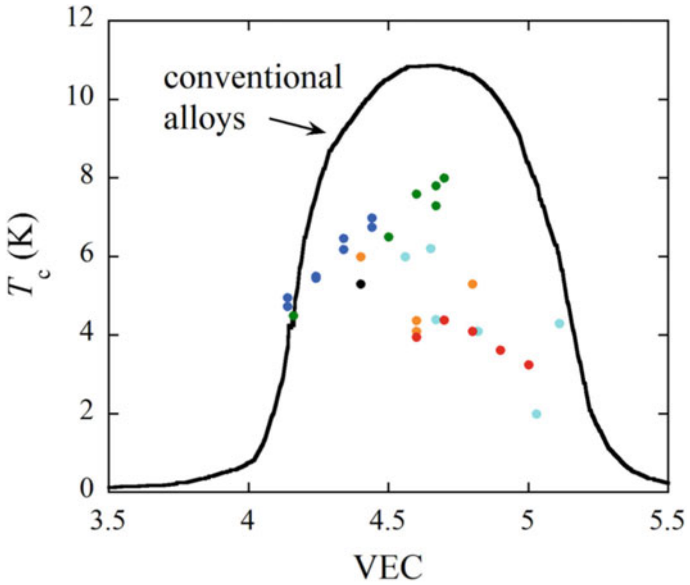


**Fig. 1.3** Comparison between conventional Matthias rule (solid curve) and VEC dependence of $T_c$ values of typical quinary bcc HEA superconductors. The correspondence between color and HEA is as follows: green: nonequimolar Hf-Nb-Ta-Ti-Zr; blue: Al-Nb-Ti-V-Zr; black: $Hf_{21}Nb_{25}Ti_{15}V_{15}Zr_{24}$; orange: HfNbTaTiZr, HfNbReTiZr, HfNbTaTiV, and HfMoNbTiZr; light blue: Nb-Ta-Mo-Hf-W, Ti-Zr-Nb-Ta-W, and Ti-Zr-Nb-Ta-V; and red: Ti-Hf-Nb-Ta-Re. Reproduced from [23] under the Creative Commons Attribution License

between VEC and $T_c$ in binary or ternary superconducting transition metal alloys [30]. As demonstrated in Fig. 1.3, the plot of $T_c$ against VEC, represented by the solid curve, distinctly illustrates a pronounced peak near a VEC value of 4.6 [23]. The dataset for typical quinary bcc HEA superconductors is represented by filled circles of various colors, exemplifying different elemental combinations and their respective studies [23, 26, 31–38]. It is worth noting that the results for HEAs lie beneath the solid curve, revealing that pronounced atomic disorder tends to reduce $T_c$ and lead to deviation from the Matthias rule. Recent electronic and phonon structure calculations have revealed band broadening within electronic and phonon band structures, which can be attributed to substantial atomic disorder [39, 40]. This, in turn, contributes to the decrease in the electron and phonon lifetimes. Various research groups have engaged in discussions to comprehend the influence of this band broadening on superconducting properties [26, 40]. The deviation from the conventional Matthias rule within HEAs suggests that more rigorous treatment of band broadening might be required to explain these phenomena. The impact of atomic disorder, aptly assessed by the value of $\Delta S_{mix}$, on superconducting properties has been an important subject, although conclusive findings have remained elusive. The potential significance of band broadening in this context may be a pivotal factor worthy of exploration.

In the early stages of high-entropy alloy superconductor research, macroscopic measurements such as electrical resistivity, magnetization, and specific heat have proven invaluable. More recently, microscopic techniques such as $\mu$SR spectroscopy have been employed for a more profound elucidation of the Cooper pair mechanism or to explore potential violations of time-reversal symmetry [27, 41, 42]. As of the current state of research, exotic Cooper pairing remains elusive. It should be noted that certain bcc HEA superconductors have exhibited a strongly correlated electronic state. The renowned Kadowaki-Woods ratio, denoted as $A/\gamma^2$, serves as a criterion for assessing the degree of electronic correlation. Here, $A$ is the coefficient of the $T^2$ ($T$:temperature) term in the temperature-dependent electrical resistivity, while $\gamma$ represents the Sommerfeld coefficient. Many heavy fermion compounds containing elements such as Ce or U have established a universal $A/\gamma^2$ value of 10 $\mu\Omega\cdot$cm$\cdot$mol$^2\cdot$K$^2$/J$^2$. Notably, recent findings suggest that bcc HEA superconductors, such as $Ta_{1/6}Nb_{2/6}Hf_{1/6}Zr_{1/6}Ti_{1/6}$ and $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$, also align with this trajectory, mirroring the behavior observed in heavy-fermion compounds [43].

### *1.3.2 Applications*

The practical investigations of bcc and hcp HEA superconductors remain nascent. The assessment of the critical current density ($J_c$) is of paramount importance for the potential application as superconducting wires. Figure 1.4a and b present the field-dependent characteristics of $J_c$ for $HfNb_2TaTiZr$ bcc HEA thin films at temperatures

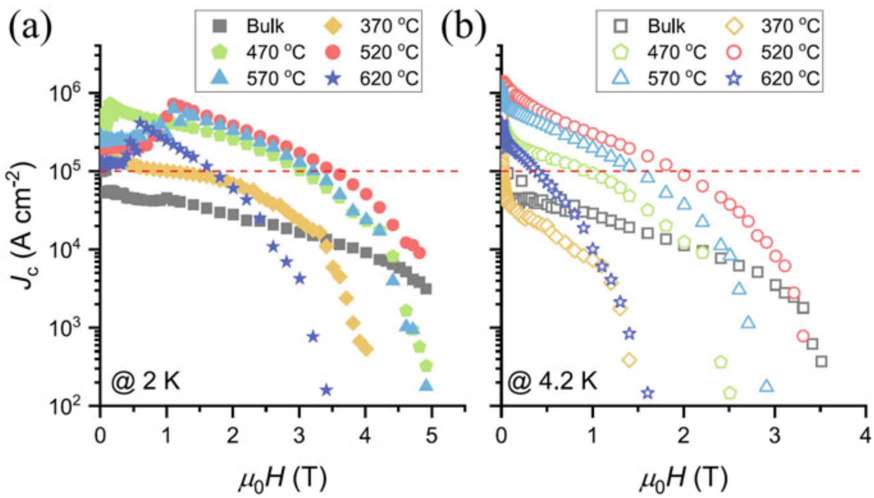


**Fig. 1.4** Field-dependent $J_c$ of $HfNb_2TaTiZr$ thin films fabricated at several temperatures denoted in figure at **a** 2 K and **b** 4.2 K. Reproduced from [22] under the Creative Commons Attribution License

of 2 K and 4.2 K, respectively [22]. Notably, the thin-film samples exhibit exceptionally high self-field $J_c$ values, approximating 1 MA/cm$^2$. The red dashed line in each figure serves as a standard benchmark for large-scale applications, particularly in the context of high-field superconducting magnets. Impressively, the $J_c$ values of $HfNb_2TaTiZr$ thin films surpass the benchmark line up to a magnetic field strength of 2 T at 4.2 K, underscoring their potential as superconducting wires. Another example is $(TaNb)_{0.7}(HfZrTi)_{0.5}$ bulk alloy, which exhibits the unique field-dependent behavior of $J_c$ [24]. In this study [24], the impact of annealing on superconducting properties was explored. Notably, the value of $T_c$ at approximately 7 K remained nearly unaltered after annealing. However, a precipitation phenomenon became evident above an annealing temperature of 500 °C, giving rise to effective flux pinning sites. Although the as-cast sample initially displayed a self-field $J_c$ value less than 0.1 MA/cm$^2$, thermal annealing at 500 °C significantly enhanced $J_c$, elevating it by an order of magnitude. Moreover, the bulk alloy exhibited relatively higher $J_c$ values under elevated magnetic fields due to the fishtail effect [24]. It is worth noting that the popular commercial low-temperature superconducting wire, Nb-Ti alloy, relies on the precipitation of $\alpha$-Ti as flux pinning sites to enhance $J_c$. This necessitates a meticulous precipitation heat treatment to control the microstructure of the $\alpha$-Ti precipitates. Consequently, the prospect of discovering an HEA that can deliver larger $J_c$ even in its as-cast state presents a notable advantage over Nb-Ti alloys.

The concurrent realization of superconductivity and high hardness has been the subject of recent investigations within transition metal carbide-based materials [44, 45], representing a multifunctional superconducting prospect. Given that numerous HEAs are characterized by their inherent high hardness, stemming from the pronounced lattice distortion as part of the four core effects, exploring hardness within bcc or hcp HEA superconductors is valuable. Several reports have underscored the relationship between the Vickers microhardness and VEC in bcc and fcc HEAs [26, 46]. For bcc HEAs with VECs ranging from approximately 4 to 5.5, an increase in VEC tends to yield higher hardness because the hard elements are present at VEC values of $\sim$ 5–7. This behavior has been consistently observed in several bcc HEA superconductors [23, 26]. For instance, the Vickers microhardness of $(Ti_{15}Hf_5)(Nb_{35}Ta_{35})Re_{10}$ with VEC=5.0 has been reported to reach as high as 466 HV [23]. Furthermore, the hardness of HEA superconductors has been examined in $(MoReRu)_{(1-2x)/3}(PdPt)_xC_y$ alloys featuring hcp and fcc structures [10]. In this system, C-doping induces a structural transformation from hcp to fcc, facilitated by covalent bonding between metal and carbon atoms, yielding a Vickers microhardness exceeding 1000 HV.

The intriguing duality of the shape memory effect and superelastic behavior has been recently investigated in the bcc HEA superconductor $Ti_{67}Zr_{19}Nb_{11.5}Sn_{2.5}$ [27]. Figure 1.5a shows the temperature-dependent electrical resistivity of this alloy, revealing zero resistivity below $T_c$ = 4.65 K and a martensite-to-austenite transition occurring within the 150-225 K temperature range. This transition is the driving force behind the shape memory effect. Figure 1.5b displays a representative stress-strain curve, indicating the characteristic hysteresis loop of the superelastic behavior.

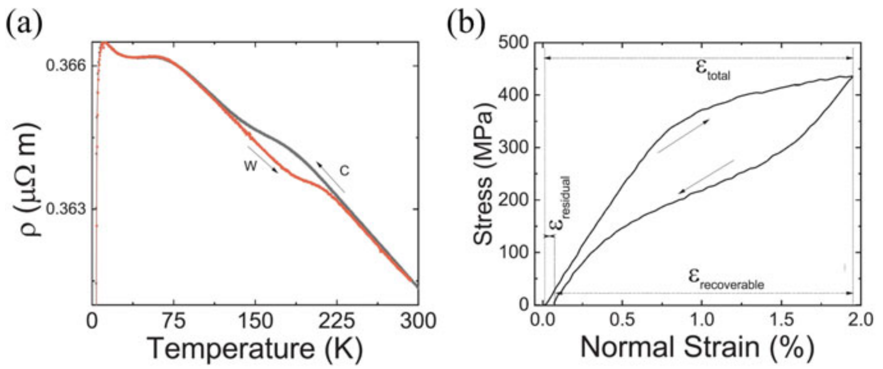


**Fig. 1.5** **a** Temperature dependence of electrical resistivity of $Ti_{67}Zr_{19}Nb_{11.5}Sn_{2.5}$. **b** Typical stress-strain curve showing superelasticity in $Ti_{67}Zr_{19}Nb_{11.5}Sn_{2.5}$ measured at 300 K. Reproduced with permission from [27]

This HEA, composed of biocompatible elements, represents an attractive candidate for developing enhanced functional devices.

### *1.3.3 Materials Design*

In general, the prediction of phase formation in HEAs with bcc and fcc structures has been the subject of extensive research, resulting in the proposition of numerous criteria [1, 2, 47]. These criteria are grounded in evaluating physical, chemical, and thermodynamic parameters. Furthermore, user-friendly and cost-free software tools are available for facilitating such predictions [48]. Conversely, the domain of materials design based on semiempirical parameters specific to bcc and hcp HEA superconductors has received relatively limited attention [5, 6, 9]. Currently, the dominant considerations in materials design are VEC and the constituent elements employed.

Using first-principles calculations with the McMillan formula has emerged as a potent avenue for predicting the $T_c$ of HEAs [40]. Notably, this method has demonstrated its ability to accurately reproduce $T_c$ values for bcc Ta-Nb-Hf-Zr-Ti alloys and even the pressure dependence of $T_c$ [40]. In instances where electronic structure calculations necessitate the preservation of translational symmetry, the atomic disorder inherent in HEAs must be modeled using a supercell structure. On the other hand, electronic structure calculations can be conducted using the Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) without supercell modeling. Moreover, the phonon band structure can be calculated using supercell-based methodologies [39]. Both the electronic and phonon band structures within HEAs exhibit notable band broadening, exerting a discernible influence on the electron and phonon lifetimes. Consequently, including band-broadening effects is highly desirable for enhancing the precision of superconducting parameter predictions of HEAs.

The third and increasingly prominent avenue for materials design in HEAs is machine learning, a field experiencing rapid application [49, 50]. Machine learning methods fundamentally rely on an expansive student-teacher dataset for effective operation. Consequently, in the domain of bcc and hcp HEA superconductors, an inadequately populated dataset poses a substantial obstacle to advancing materials design through machine learning methodologies.

## 1.4 High-Entropy Compounds

In this section, we mention the present state of HEA-type superconducting compounds, with a particular emphasis on their unconventional properties, applications, and materials design. Table 1.2 outlines the interconnections between the subjects deliberated in this section and those elucidated in Chaps. 8 through 11.

### *1.4.1 Exotic Properties*

One of the interesting properties of HEA-type compounds was observed in the $BiS_2$-based layered system $REO_{0.5}F_{0.5}BiS_2$. In the examined samples, the carrier concentration and lattice volume, which affect superconducting properties [51], were fixed by tuning the RE-site composition, and the RE-site $\Delta S_{mix}$ was solely varied [19]. With increasing $\Delta S_{mix}$, in-plane structural disorder was suppressed, and the bulkiness of the superconductivity improved. This is one of the cocktail effects of HEA-type compounds.

Another example of exotic superconducting states was observed in HEA-type MTe (M: Ag, In, Sn, Pb, Bi) [13, 52]. As shown in Ref. [21], the robustness of superconductivity to pressure was observed in an HEA superconductor. Similar robustness

**Table 1.2** Interrelationships between topics addressed in this section and those expounded upon in Chaps. 8 through 11

| Topics | Chapter number |
|---|---|
| *Exotic properties* | |
| Robustness of superconductivity to pressure | 8, 9 |
| Glassy phonons | 8 |
| Cocktail effect | 9, 11 |
| *Applications* | |
| High critical temperature | 11 |
| *Materials design* | |
| Material database | 8, 9, 10, 11 |

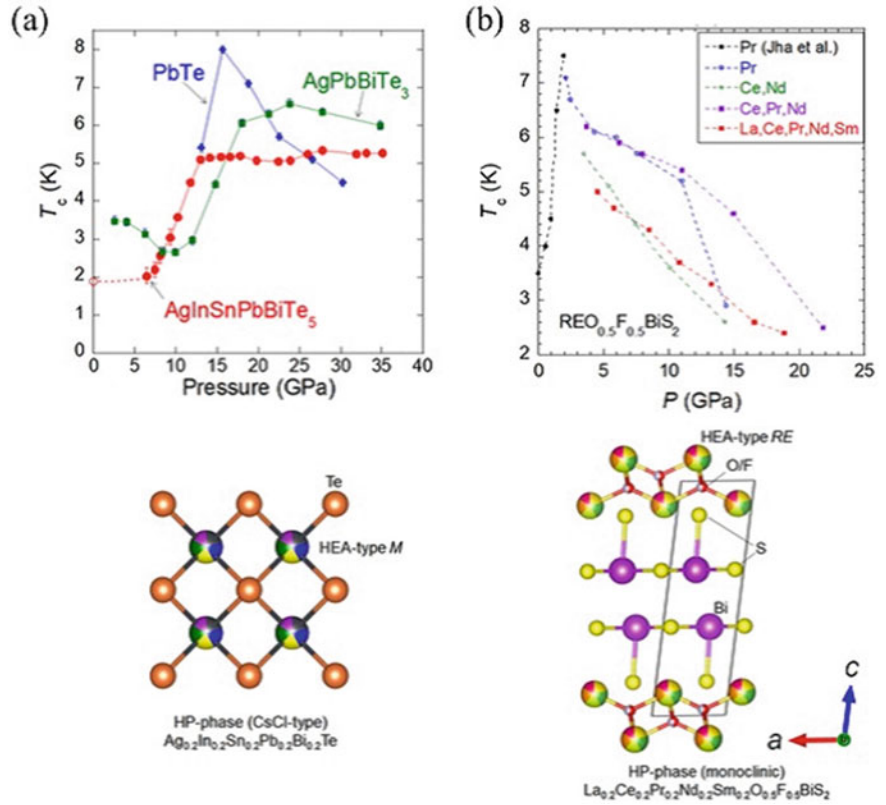


**Fig. 1.6** Pressure dependence of $T_c$ and schematic image of high-pressure (HP-phase) crystal structure for **a** MTe and **b** $REO_{0.5}F_{0.5}BiS_2$. Reproduced from [52, 53] under the Creative Commons Attribution License

was observed for HEA-type MTe, $AgInSnPbBiTe_5$ as shown in Fig. 1.6a [52]. High-pressure electrical resistance experiments, X-ray diffraction, and X-ray absorption spectroscopy revealed that the electronic and crystal structures change with pressure, but $T_c$ does not change with pressure [52]. By molecular dynamics simulation of atomic vibrations and electronic band calculation, glassy phonons and blurry electronic band structure were revealed [53]. These results imply that the observed robust superconductivity to pressure is caused by exotic electron-phonon coupling with glassy phonons. In contrast, HEA-type $REO_{0.5}F_{0.5}BiS_2$ does not exhibit robust superconductivity to pressure, as shown in Fig. 1.6b; a similar pressure dependence of $T_c$ is observed for all the samples with different $\Delta S_{mix}$ [54]. Because of the RE-site alloying, glassy phonons related to the atomic vibrations of the atoms in the superconducting layers are not induced by RE-site alloying, which would be the reason for the lack of robustness. Therefore, HEA-type superconducting compounds can be a good platform for systematically studying superconductivity with glassy to crystalline phonons by selecting crystal structure and its simplicity.