Comparative studies on superconductivity in Cr$_3$Ru compounds with bcc and A15 structures

Zhengyan Zhu, Ying-Jie Zhang, Yiwen Li, Qing Li*, Wen Duan and Hai-Hu Wen*

Center for Superconducting Physics and Materials, National Laboratory of Solid State Microstructures and Department of Physics, Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing 210093, People’s Republic of China

E-mail: liqing1118@nju.edu.cn and hhwen@nju.edu.cn

Received 14 July 2022, revised 27 August 2022
Accepted for publication 26 September 2022
Published 5 October 2022

Abstract
Chromium (Cr) is a transition metal element with 3$d$ orbital electrons. In most compounds containing Cr, due to the correlation effect, twofold features, namely localization and itinerancy are expected. The localization gives rise to a magnetic moment, while the latter exhibits as the effective coherent weight for conductivity. Here we report the physical properties of Cr$_3$Ru compounds with body-centered cubic (bcc) and A15 structures by using multiple experimental tools. The resistivity measurements show sharp superconducting transitions at $T_c = 2.77$ K and $T_c = 3.37$ K for the bcc and A15 structures, respectively. A high residual resistivity exists in both phases. Magnetization measurements also show rather narrow superconducting transitions, with a clear hump feature in the intermediate temperature region (about 150 K), which may be ascribed to the remaining antiferromagnetic spin fluctuations. A pronounced second peak effect has been observed in magnetization hysteresis loops in the superconducting state only for samples with bcc structure. The specific heat coefficient reveals a clear jump at critical temperatures ($T_c$). We find that s-wave gaps can be adopted to fit the low temperature specific heat data of both samples yielding ratios of $2\Delta/k_B T_c$ about 3.6, indicating a moderate pairing strength. Interestingly, the Wilson ratios $R_W = A\chi_0/\gamma_n$ are 3.81 and 3.62 for the bcc and A15 phases, suggesting a moderate correlation effect of conducting electrons in the normal state. Besides, for samples with A15 structure, another specific heat anomaly occurs at about 0.85 K and is sensitive to magnetic fields. In addition, by applying high pressures, both systems will exhibit an enhancement of $T_c$ with a rate of about 0.019 K GPa$^{-1}$ and 0.013 K GPa$^{-1}$ for the bcc and A15 phases, respectively. Our combinatory results point to unusual behavior of both superconducting and normal states in these two Cr based alloys.

* Authors to whom any correspondence should be addressed.

Original Content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Keywords: Cr–Ru alloys, superconductivity, magnetic properties, electrical transport properties, specific heat, high pressure physics

Some figures may appear in colour only in the online journal

1. Introduction

Cuprates [1] and iron-based superconductors [2], as unconventional superconductors with high critical temperatures ($T_c$), all have strongly correlated 3d electrons. The relationship between unconventional superconductivity (SC) and strong correlation effect of 3d electrons with magnetic interactions and spin fluctuations has aroused great interest in the past decades. In recent years, lots of research have been conducted on unconventional SC in those materials which contain 3d transition-metal elements [3–9]. Chromium (Cr) is one of 3d transition-metal elements, and the ionic state of Cr usually has a strong magnetic moment. Thus Cr-based superconducting compounds may have rich and novel electronic behavior. For compounds containing 3d transition-metal chromium, many works have been carried out based on a class of CrAs-based superconductors. CrAs itself is an antiferromagnet which exhibits SC when applying pressure [10, 11]. Then a big family of CrAs-based superconductors was discovered. There are accumulated evidence to show that some of these materials, such as RbCr$_3$As$_3$ and K$_2$Cr$_3$As$_3$, may be candidates for multiband superconductors with spin-triplet pairing state [12–14]. Thus, the study of SC in Cr-based materials always attracts much attention. For example, the studies on Pr$_2$Cr$_{10–x}$N$_{11}$ and CrB$_2$ in recent years has shown that they have novel SC and are possible unconventional superconducting materials [15, 16]. Moreover, 4d transition element Ruthenium (Ru) is one of iron’s relatives with strong itinerant electron magnetism [17, 18]. In addition to Sr$_2$RuO$_4$ [19] as a possible candidate for spin-triplet superconductors [20], other Ru-based compounds also have unusual SC, such as Ru$_7$B$_3$ as a non-centrosymmetric superconductor [21] and LaRu$_2$P$_2$ with an intricate Fermi surface topology [22]. Actually in the early years, there was great interest in SC in the transition metal alloys [23], especially for the alloys with 3d transition metals such as Cr–V system [24]. And the influence of ferromagnetism on SC has always been a matter of concern [25]. The SC of chromium alloys can form various kinds of superconducting phases with different $T_c$ by doping distinct proportions of other metal elements [26]. Due to the possibility of coexistence of superconducting and antiferromagnetic (AFM) order, some binary Cr-based alloys such as body-centered cubic (bcc) Cr–Re alloys and bcc Cr–Ru alloys are of particular interest, but detailed studies on physical properties of these materials are lacking [27, 28]. All of these inspire us to conduct detailed studies of physical properties on Cr–Ru binary alloys.

According to previous report, with the substitution of Ru, the AFM order of Cr vanishes and SC emerges gradually. Interestingly, there are two kinds of structures for Cr–Ru alloys. One is the bcc structure where Cr atoms and Ru atoms arbitrarily occupy each site [28]. And the other is the cubic A15 crystal structure achieved after long time annealing the bcc phase of Cr$_3$Ru at a high temperature [29]. It was found that, with 25% Ru doping in Cr, the two phases (AFM and SC) coexist [28]. Another study on different Cr$_{1−x}$Ru$_x$ alloys has discussed the relationship between the AFM spin density wave (SDW) and SC [30], and found that the AFM, SDW and SC states are exclusive. On the boundary of the two phases, there may exist strong spin fluctuations. The band structure calculations of Cr$_3$Ru in either phases reveal multiple sets of Fermi surfaces which are mainly contributed by the 3d orbital electrons of chromium. The A15 structure was reported in favor of the existence of SC in many compounds [31]. According to the literature [32], the slight excess of Ru is more conducive to obtain pure phase of Cr$_3$Ru with A15 structure, thus we synthesized two kinds of polycrystal samples with a ratio of Cr : Ru = 72 : 28 and carried out comparative studies with various experimental tools.

In this paper, we report the comparative studies of Cr$_3$Ru superconductors with bcc and A15 structures. The crystal structure, chemical composition, magnetization and resistance measurements are carried out to confirm the high quality of the samples with $T_c$ (bcc) = 2.82 K and $T_c$ (A15) = 3.39 K, respectively. The resistance measurements both show strong residual resistance with negligible magneto-resistance. And the magnetization measurements show clear hump structures at around 150 K for two kinds of samples. The sharp specific heat jumps for both samples can be fit well with $s$-wave gaps of $2\Delta/k_B T_c$ around 3.6. But the Wilson ratios are large, about $R_W$(bcc) = 3.81 and $R_W$(A15) = 3.62 in these two samples. In magnetization hysteresis loops (MHLs), a second peak effect has been observed only in samples with bcc structure. Also, with the increase of the external pressure, the $T_c$ enhances linearly for two samples.

2. Experiments

The polycrystalline samples of Cr$_3$Ru with bcc structure were prepared by using arc-melting method. The chromium (99.98%, Alfa Aesar) and ruthenium (99.9%, Alfa Aesar) with a mole ratio of 72 : 28 were weighed, ground and pressed into pellets in a glove box. Then the pellets were melted in the arc-melting furnace filled with pure argon. To improve the homogeneity of samples, each ingot was remelted at least three times. After that, the Cr–Ru alloy with bcc structure was obtained. Then the ingot of Cr$_3$Ru was placed into an evacuated quartz tube and annealed at 1000 °C for one month. The samples with A15 structure can then be obtained.

The x-ray-diffraction (XRD) measurements were carried out on a Bruker D8 Advanced diffractometer with the Cu-Kα radiation. The TOPAS 4.2 software was used to refine the crystal structures by Rietveld analysis. The micrographs and the chemical composition analysis of the samples were taken by
a Phenom ProX scanning electron microscope (SEM). The magnetization was measured using a SQUID-VSM (Quantum Design). The resistivity was measured by the standard four-probe method using a physical property measurement system (PPMS 16T, Quantum Design). And the resistance down to 0.4 K was measured with an additional 3He insert. The specific heat was measured with the thermal-relaxation method by another option of PPMS with the 3He insert. The resistance data under high pressure were collected by our PPMS equipment with an option of using a diamond-anvil-cell (cryoDAC-PPMS, Almax easyLab) module with a four-probe van der Pauw method.

3. Results

3.1 Sample characterization

Figures 1(a) and (b) show the XRD patterns for two kinds of polycrystalline samples of Cr$_3$Ru and the corresponding Rietveld fitting curves. The Rietveld refinements indicate that the samples are assigned to be the cubic structure (space group: $Im\bar{3}m$ (No. 229) for bcc and $Pn\bar{3}m$ (No. 223) for A15) with the lattice parameters of 2.937 Å and 4.637 Å, respectively. The schematic crystal structures are also plotted in the insets in which the blue and yellow spheres represent Cr and Ru, respectively. In the inset of figure 1(a), Cr and Ru occupy the positions as bcc structure in a random way, but after high temperature annealing, the crystal structure becomes A15. In figure 1(a), except for a tiny peak of Cr$_3$Ru with A15 structure at around $2\theta = 38^\circ$, all other peaks can be indexed to bcc structure. In figure 1(b), except for a minor peak of impurities of Cr–O, all other peaks can be indexed to Cr$_3$Ru with A15 structure. The SEM images with backscattered electron mode of the two samples are shown in the left panel of figures 1(c) and (d). They respectively illustrate the morphology of the sample surfaces within a 30 µm area of view. We can only see some scratches caused by physical cuts on the surfaces of the samples. In order to determine the exact element composition of the samples, we also perform energy dispersive x-ray spectra (EDS) on a larger scale. The element compositions for two samples are Cr : Ru = 71 : 29 and 69 : 31 for bcc and A15 structure, respectively. The atomic ratios are close to our nominal value.

The temperature dependence of resistivity at zero magnetic field for two kinds of samples are shown in figure 2(a). The onsets of the superconducting transition temperatures are almost the same. Then with the decrease of temperature, the sample with A15 structure shows a very sharp superconducting transition. But the superconducting transition width is relatively wider for the sample with bcc structure. The obtained $T_c$ from 10% of the normal state resistivity are 2.77 K for bcc, and 3.37 K for A15 structures, respectively. It should be pointed out that, according to previous reports [28], the $T_c$ of Cr$_3$Ru with bcc structure about 2.4 K is significantly lower than that of A15 structure about 3.25 K, which is consistent with our present results. And the superconducting transition temperatures of both samples are comparable with the previously reported values. The similar onsets of superconducting transition temperatures for bcc and A15 structures observed in our study may be due to the extra components of A15 structure in sample with bcc structure during the synthesis process. This is also confirmed by the redundant minor diffraction peak of A15 structure on XRD pattern in figure 1(a). Figure 2(b) presents the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves with the applied magnetic field of 10 Oe. Obtained $T_c$ from magnetization are 2.82 K (bcc) and 3.39 K (A15). The superconducting volumes calculated from the magnetization data are both larger than 100% due to the demagnetization effect. All of these confirm the high quality of our samples.

3.2. Magnetic and electrical transport properties

To investigate the magnetization behavior of Cr$_3$Ru in the normal state, we present the temperature dependent magnetic susceptibility curves under high fields in figures 3(a) and (b). We can see that the $\chi$–$T$ curves of both samples exhibit paramagnetic Curie–Weiss behavior in the low temperature region. And in high temperature range, the
magnetic susceptibility does not change significantly with temperature. Note that the background signal near 50 K due to frozen oxygen has been subtracted by doing a Gaussian fitting. Then we fit them from 2 K to 50 K using the Curie–Weiss law, as shown by the red lines. For Cr$_{0.72}$Ru$_{0.28}$, the magnetic moments per unit molecule are 0.02 $\mu_B$/f.u. (bcc) and 0.027 $\mu_B$/f.u. (A15) for the two samples. We all know that Cr ions usually have a relatively large magnetic moment, but the magnetic moment of Cr–Ru alloys are very small. And the Pauli paramagnetic susceptibility $\chi_0$ were estimated to be $3.56 \times 10^{-4}$ emu·mol$^{-1}$·f.u.$^{-1}$ (bcc) and $3.82 \times 10^{-4}$ emu·mol$^{-1}$·f.u.$^{-1}$ (A15), respectively. Interestingly, figures 3(a) and (b) exist hump structures in $\chi$–$T$ curves for both samples in the intermediate temperature region. Under lower magnetic fields, the hump structure becomes more obvious for both samples. The insets in the figures show the magnetic susceptibility with an applied magnetic field of 100 Oe. Both samples show broad hump structures in wide temperature regions centered around 150 K in the ZFC and FC curves which are similar to previous reports [28]. The hump feature in $\chi$–$T$ curves may suggest the existence of AFM ordering or spin fluctuations [30]. Since such humps are much weaker in the magnetization curve at higher magnetic fields, we believe that the humps in the magnetization curve may be related to the AFM fluctuations.

Figures 4(a) and (b) present the temperature dependence of resistivity for the two kinds of samples in the temperature range from 2 K to 300 K. Both samples exhibit sharp superconducting transitions at zero field. When the magnetic field up to 9 T is applied, the SC is completely suppressed, and the resistivity shows normal metal behavior. It is found that $\rho$ exhibits a $T^2$ dependence below 100 K. The residual resistivity ratio ($\rho_{300 K}/\rho_{2 K}$, RRR) is 1.186 for the sample with bcc structure and is 1.377 for the sample with A15 structure. To our surprise, for both kinds of samples, the temperature dependence of resistance is very weak, and large residual resistances are present. In order to explore the possible causes of the large residual resistivity, we conducted the following analysis of our data. First, the normal state resistivity at 0 T and 9 T overlap well in figures 4(a) and (b). This indicates that the magnetoresistance of the samples is almost negligible. Therefore, the large residual resistance should result from non-magnetic scattering due to impurities or defects. As we can see from the SEM images of the two samples in the left panel of figures 1(c) and (d), the alloy samples are very dense and have no discernible grains. Thus, the possibility of grain boundary scattering can be ruled out for the large residual resistivity. Considering all facts mentioned above, we argue that it may be due to some intrinsic scattering in samples such as chemical disorder and some defects. Note that in some high-entropy alloys (HEAs), there is also a small residual resistivity ratio similar to that in our samples [33]. It is known that in HEAs the atoms are highly disordered. In such alloys, the effect of disorder induced scattering is larger than that of electron–phonon scattering [34]. Such large residual resistance in our samples may also be caused by
electron scattering due to atomic disorder. In addition, it is also possible that there is an insufficient amount of Cr compared with the stoichiometry, so that the lattice structure may have some defects which can cause strong scattering. The deficient Cr atoms make the original crystal structure local noncentrosymmetric which may also influence the electron scattering. The insets of figures 4(a) and (b) show the temperature dependent resistance from 6 K down to 0.4 K under different magnetic fields. With the increase of applied magnetic field, the superconducting transition temperature decreases gradually. Figures 4(c) and (d) show the upper critical field at different temperatures. We obtain the values of upper critical field from the $R-T$ curves by using criterions of 90% $R_n$ (the resistance in the normal state). By fitting the data of upper critical field $H_{c2}(T)$ with the Ginzburg–Landau theory, it is obtained that the upper critical field at zero temperature is $\mu_0 H_{c2}(0) = 4.12 \text{T}$ for samples with bcc structure and $\mu_0 H_{c2}(0) = 5.05 \text{T}$ for samples with A15 structure. None of their upper critical fields exceed the Pauli paramagnetic limit $H_p(T) = 1.84 T_c$ about 5.76 T (bcc) and 6.22 T (A15) [35, 36]. Using the formula $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi^2(0)$, the coherence lengths for the two kinds of samples are 9 nm (bcc) and 8 nm (A15), respectively.

3.3. Specific heat

The temperature dependence of specific heat of Cr$_3$Ru samples with bcc and A15 structures down to 0.4 K are given in figures 5(a) and (b). The data are plotted as $C/T$ versus $T$. A sharp specific heat jump can be seen at about 2.37 K for samples with bcc structure and 3.32 K for samples with A15 structure. For Cr$_3$Ru with bcc structure, the superconducting transition temperature determined by specific heat is slightly lower than that determined by magnetization and resistivity. This is consistent with the behavior reported previously [28]. Surprisingly, for samples with A15 structure, another anomaly of specific heat occurs at about 0.85 K, as shown clearly in the inset of figure 5(b). We fit the data of the normal state using the equation $C_n/T = \gamma_n + \beta T^2 + \eta T^4$, where $\gamma_n$ is the normal state electronic specific heat coefficient, called the Sommerfeld coefficient, and $\beta T^2 + \eta T^4$ are the phonon contributions according to the Debye model. Taking the parameters arising from the fittings of normal state, we find that the entropy conservation can be well satisfied for both samples. For Cr$_{0.72}$Ru$_{0.28}$, the Sommerfeld coefficient $\gamma_n(\text{bcc}) = 6.81 \text{ mJ (mol K}^{-1}\text{)}$ and $\gamma_n(\text{A15}) = 7.66 \text{ mJ (mol K}^{-1}\text{)}$ for the two kinds of samples. Using the equation $\Theta_D = (12\pi^4 k_B N_a Z/5\beta)^{1/3}$, the Debye temperatures estimated here are about 485 K (bcc) and 476 K (A15) respectively, where $k_B$ is Boltzmann constant, $N_a$ is Avogadro constant, $Z$ is the number of atoms in one unit cell. For Cr$_{0.72}$Ru$_{0.28}$, we use $Z = 1$. The specific heat jumps at $T_c$, namely $\Delta C/\gamma_n T_c$ with $\Delta C$ estimated by entropy conservation near $T_c$, are about 1.2 for both of them. These are smaller than 1.43 which is predicted by the Bardeen-Cooper-Schrieffer (BCS) theory in the weak-coupling limit. This finding is consistent with the weak temperature-dependent resistivity associated with the weak electron-phonon scattering. The density of the states near the Fermi level obtained by the equation $N(\varepsilon_F) = 3\gamma_n/\pi^2 k_B^2$ is 2.9 states eV$^{-1}$ for samples with bcc structure and is 3.3 states eV$^{-1}$ for samples with A15 structure.
Figure 5. Temperature dependence of specific heat at zero magnetic field from 0.4 K to 10 K (a) for samples with bcc structure and (b) for samples with A15 structure. The red lines are the fitting curves of the normal state based on the Debye model. The inset of (b) shows the enlarged view of the anomaly around 0.85 K. The electronic specific heat under different fields (c) for samples with bcc structure and (d) for samples with A15 structure. The inset of (d) shows the temperature dependence of the anomaly under different magnetic fields. The temperature dependence of electronic specific heat coefficient at zero field and the fitting curves of different gap structures (e) for samples with bcc structure and (f) for samples with A15 structure. The inset of (f) shows the fitting curve for the specific heat anomaly at low temperature using the BCS formula.

eV$^{-1}$ for samples with A15 structure. In comparison with the density of states on the Fermi surface from the band structure calculations [37], 5.2 states eV$^{-1}$ for Cr$_6$Ru$_2$ with A15 structure, we can calculate the carrier effective mass $m^*/m_e = 5.1$. A slightly large effective mass means the strong electron-electron interaction. Using the Pauli paramagnetic susceptibility estimated above and the Sommerfeld coefficient here, the Wilson ratio can be calculated as $R_W = \frac{4\pi^2}{3\chi_0} \frac{T_c}{T_c^*} = 7.28 \times 10^4 \chi_0$. For the two kinds of samples, the Wilson ratios are 3.81 and 3.62, respectively. These values are much larger than $R_W = 1$ for the case of free-electron approximation. Therefore, this result implies moderate electron correlations in these materials.

Shown in figures 5(c) and (d) are the electronic specific heat under different magnetic fields for the bcc and A15 samples obtained by subtracting the normal-state background at zero field derived above. With increasing magnetic field, the specific heat jumps become broader for samples with bcc structure, but the specific heat jumps remain steep for samples with A15 structure. And the field induced specific heat coefficient increases gradually with the increase of magnetic field at the low temperature limit. In addition, the inset of figure 5(d) shows an enlarged view of the second anomaly at 0.85 K under different magnetic fields for the A15 sample. It is clear that this anomaly shifts to lower temperatures with increasing magnetic field, thus it is also sensitive to magnetic fields. The XRD on the A15 sample shows that the polycrystalline sample is quite pure, and the only impurity CrO is not superconductive. We are not clear at this moment about the possible cause of the second specific heat anomaly in the A15 samples. It looks more like a superconducting transition, but it remains unclear whether it is due to an intrinsic superconducting transition of the sample,
Figure 6. Magnetization hysteresis loops (MHLs) at different temperatures (a) for samples with bcc structure and (b) for samples with A15 structure. The insets of (a) and (b) show the temperature dependent lower critical fields. Magnetic field dependence of critical current density estimated by the Bean critical state model (c) for samples with bcc structure and (d) for samples with A15 structure. The inset of (c) shows the zoom-in view of MHLs with clear second peak effect.

or due to some tiny impurity superconducting phase at low temperatures.

In order to obtain more information about the superconducting gap structure, we use the BCS formula to fit the electronic specific heat in the superconducting state. The superconducting electronic specific heat is obtained by subtracting the normal state data following the Debye model. Based on the formula of specific heat given by the BCS theory, we use different kinds of gap structures to fit our data: a single s-wave gap $\Delta(T, \theta) = \Delta_0(T)$, a single d-wave gap $\Delta(T, \theta) = \Delta_0(T) \cos 2\theta$, and a single extended s-wave gap $\Delta(T, \theta) = \Delta_0(T)(1 + \alpha \cos 2\theta)$ where $\alpha$ is the parameter that represents anisotropy. The optimized fitting parameters according to different gap structures are shown in figures 5(e) and (f) as different fitting curves. One can see that both the single isotropic s-wave model and the single extended s-wave model can well describe the experimental data for two kinds of samples, even considering the anomaly around 0.85 K. These results indicate that one gap model is sufficient to describe the data. And the anisotropy of the superconducting gaps for the two samples is also very weak. The superconducting gaps are about 0.365 meV (bcc) and 0.52 meV (A15) for the two samples, respectively. The calculated ratios of $2\Delta/k_B T_c$ are about 3.6 for the two samples, indicating a moderate pairing strength. We also try the BCS fit for the possible small superconducting gap at low temperature. As shown in the inset of figure 5(f), the specific heat anomaly can also be fitted by a small s-wave gap, and the fitted energy gap is about 0.15 meV. Although this cannot be used as solid evidence for superconducting transition, it can be used as a reference. We obtain the entropy by integrating the electronic specific heat, and then obtain the condensation energy of the superconductor through integrating the entropy from zero temperature to $T_c$. For Cr$_{0.72}$Ru$_{0.28}$, the condensation energy is 7.4 mJ mol$^{-1}$ for samples with bcc structure, and 17.3 mJ mol$^{-1}$ for samples with A15 structure. According to the BCS fit of the electronic specific heat, we can get the zero-temperature residual specific heat coefficients of two samples, which are about 1.02 mJ (mol·K$^2$)$^{-1}$ (bcc) and 0.784 mJ (mol·K$^2$)$^{-1}$ (A15). Assuming that this residual term is due to the non-superconducting impurity phase, we can calculate their superconducting volume from specific heat measurement by using $(\gamma_n - \gamma_0)/\gamma_n$, yielding about 85% for samples with bcc structure and 90% for samples with A15 structure. These also confirm the bulk SC in Cr$_3$Ru.

3.4. Magnetization hysteresis loops and vortex properties

Figures 6(a) and (b) show the MHLs measured at different temperatures for the two kinds of samples. The insets show the lower critical field for the bcc and A15 samples, respectively. The lower critical fields at different temperatures are determined where $M(H)$ deviates from the linear line corresponding to the Meissner state. The lower critical fields of the samples are very small, which means that the quantized flux can very easily enter the superconductors. The samples with bcc structure at different temperatures have a pronounced second magnetization peak effect as can be seen in the inset of figure 6(c). And the position of the second peak gradually
Figure 7. Temperature dependence of resistance for the two kinds of samples at different external pressures (a) for samples with bcc structure and (b) for samples with A15 structure. The insets of (a) and (b) show the enlarged views of $R-T$ curves around the superconducting transitions. Temperature dependence of resistance under different magnetic fields (c) at 52.4 GPa for samples with bcc structure and (d) at 49.4 GPa for samples with A15 structure. (e) The upper critical field (symbols) and fitting curves (lines) by the GL theory for the two samples at the pressure of about 50 GPa. (f) Pressure dependence of superconducting transition temperatures for the two samples.

shifts to lower fields with the increase of temperature. But the second peaks can only exist below 2.2 K. Besides, the second peak effect has not been observed for samples with A15 structure. The compositions of the two samples are almost the same, only their structures are different. Therefore, the cause of second peak effect is elusive, which depends on the intrinsic properties of the samples. We assume that additional pinning centers are formed in the samples with bcc structure when increasing magnetic field which lead to the anomalous increase in superconducting current. The MHLs at fixed temperatures are symmetrical around the horizontal axis, indicating a dominant bulk pinning, therefore the Bean critical state model is applicable in this case. From these MHLs, we calculate the critical current density $J_c$ based on the formula according to the Bean critical state model $J_c = \frac{20 \Delta M}{|a(1 - a/3b)|}$, as seen in figure 6(c), where $\Delta M$ is the width of MHLs with the unit of emu cm$^{-3}$, $a$ and $b$ are the width and length of the samples. With increasing temperature, the critical current decreases gradually. At 1.8 K, we obtain the values of $J_c = 1.2 \times 10^4$ A cm$^{-2}$ (bcc) and $J_c = 5.2 \times 10^4$ A cm$^{-2}$ (A15) for samples, respectively. These $J_c$ values are rather high in terms of the very low $T_c$ values. As we all know, impurities and other defects will form vortex pinning centers, which will hinder the moving of vortices. Therefore, the more flux pinning centers, the greater critical current density of the sample. The large critical current density of the two samples indicates the existence of many defects in the samples, which is consistent with the high residual resistivity in our electrical resistance measurements. We can also see that as the temperature increases slowly, the critical current of sample with bcc structure decreases rapidly while the critical current of sample with A15 structure decreases slowly. This may also mean that there are different flux pinning centers and vortex pinning landscape for the two samples.
3.5. Evolution of superconducting properties at high pressures

Figures 7(a) and (b) show the temperature dependence of resistance for the two kinds of samples under different external pressures. We can see a large residual resistance for all applied pressures, and the RRR does not change much with increasing pressure. But the superconducting transition temperature increases gradually with the increase of pressure for the two samples, and the superconducting transition remains steep, as shown in the insets of figures 7(a) and (b). Under the maximum pressure in our present study (about 50 GPa), the $T_c$ can reach about 4 K. We obtain the values of $T_c$ from the $R$–$T$ curves by using criteria of 90$\%$ $R_0$ and 10$\%$ $R_0$ for all samples and plot them in figure 7(f). Compared with samples with A15 structure, with the increase of pressure, the ratio of increasing $T_c$ is greater for samples with bcc structure. Surprisingly, the relationship between $T_c$ and pressure shows a roughly linear behavior and the increase is unsaturated up to the highest pressure in our measurement. In some alloys like NbTi and (Sc,Zr)NbTa$h_0$RhPd$k_4$, the $T_c$ is robust against large volume shrinkage and shows a monotonous increase with pressure [33, 38]. We believe that the situation in Cr$_3$Ru may also share some similarity with them. In figures 7(c) and (d), we present the temperature dependence of resistance under different magnetic fields at the highest pressure for both samples. Although the $T_c$ of the two samples at the highest pressure are very close, the upper critical fields are different. For samples with bcc structure, with the increase of pressure, the upper critical field of the sample does not increase, which is still about $\mu_0 H_{c2}(0) = 4.1$ T. But for samples with A15 structure, the upper critical field changes from $\mu_0 H_{c2}(0) = 5.05$ T at ambient pressure to $\mu_0 H_{c2}(0) = 6.15$ T at 49.4 GPa.

4. Discussions

For two kinds of Cr$_3$Ru samples with bcc and A15 structures, most of their physical properties show similar unusual features. Firstly, very large residual resistivity is found in resistance measurements. The origin of the large residual resistance can be ascribed to the strong scattering in the samples. If we consider the order of magnitude of the carrier concentration of a normal metal, and we calculate the mean free path of the samples according to the formula $l_{ab} = h(3n^2)^{1/2}/e^2\rho_0 n^{1/2}$, where $\rho_0$ is the residual resistivity at zero temperature and $n$ is the carrier concentration [39]. The mean free paths of both samples are very small, about 1–2 nm. According to the Abrikosov–Gorkov pair-breaking theory, scattering induced by magnetic impurities will lead to pair-breaking, thus will destroy SC [40]. This occurs when the mean free path and the superconducting coherence length are of the same order of magnitude. Considering that the mean free path we obtained for both samples is about 1–2 nm, which is much smaller than the coherence length of about 8–9 nm, it is inconceivable that SC is still survive in our present systems if the impurities would have strong magnetic moments. Therefore, we tend to believe that the atomic defects in the system lead to some strong scattering, but they possess very weak magnetic moments, as evidenced by the fitting to the magnetization under a high magnetic field using the Curie–Weiss law. In addition, the strong inter-grain coupling may also influence the transport properties. From the SEM observation, we find that the samples are very dense and continuous without granular structures or grain boundaries in the scale of sub-micrometer. Sometimes we see tightly compacted grains in scanning tunneling microscope (STM) image after Ar etching on the surface, the grain sizes are about 20–30 nm. Considering that the mean free path is much smaller than the grain size, we would conclude that the major scattering is induced by the intrinsic collision of electrons with disorders within the grains, although the scattering with the grain boundaries may also play some role in leading to the large residual resistivity. Secondly, we find strange humps in the $M(T)$ curves under a high magnetic field in the intermediate temperature region. According to previous reports [28, 30], the cause of the humps may be the AFM ordered phase or the spin fluctuations near the AFM phase boundary. Because such humps are less obvious in higher field magnetization curves, we tend to attribute it to some AFM spin fluctuations which are suppressed under high magnetic field [41]. Thirdly, using the parameters obtained by magnetization and specific heat, the Wilson ratios of the samples are calculated, they are about 3.6–3.8 being much larger than 1 predicted for free-electron system. Combined with the calculated carrier effective mass, we conclude that there may be moderate electron correlations in these materials.

We have also tried scanning tunneling spectrum measurements on these samples at 400 mK. It is found that the suppression of the density of states within the gap for the samples is rather weak, together with a pair of very low and blurred coherence peaks. This may be induced by the strong scattering on the sample surface, which diminishes the coherent weight of the Bogoliubov quasiparticles. The STM data are not presented here. Because of such strong scattering in the samples, one may argue about the purity of them. We want to emphasize that the specific heat, resistivity and magnetization results all confirm very sharp superconducting transitions, and the estimated superconducting volume is also big, thus we believe the samples are very pure. Furthermore, from the XRD patterns, only small amount of impurities can be seen. Considering a slight excess amount of Ru atoms comparing with the stoichiometry, it is easy to understand that partial Cr sites are occupied by Ru atoms, this may lead to local structural distortion, and even induce non-centrosymmetric arrangement of atoms. All these can lead to strong scattering on conducting electrons.

The samples exhibit several properties which are consistent with conventional SC. On one hand, the low temperature electronic specific heat can be well fitted by $s$-wave gap function, and the value of $2\Delta/k_B T_c \approx 3.6$. Meanwhile, the upper critical field at zero temperature is under the Pauli paramagnetic limit in both samples. Thus we conclude that the Cr$_3$Ru compounds either in bcc and A15 structures may satisfy the weak-coupling BCS picture. On the other hand, however, some properties are still difficult to be described by the normal metal with Fermi liquid properties. First, the temperature dependence of the normal state magnetic susceptibility is non-monotonic. In the intermediate temperature region,
the magnetization exhibits a strange hump for both bcc and A15 samples. Secondly, although the samples exhibit weak electron–phonon coupling, the calculated Wilson ratios of normal state are large, indicating a moderate correlation effect of conducting electrons. Thirdly, the elements involved here, Cr and Ru, are usually magnetic in nature due to the d orbital electrons. It is widely perceived that unconventional SC may arise in compounds with magnetic elements which yield the magnetic spin fluctuations. We highly suspect that the Cr elements in the present two compounds may also contribute spin fluctuations, as suggested by the sizable and non-monotonic temperature dependence of magnetic susceptibility in the normal states. All these may add something at odd with the conventional SC arising from a Fermi liquid background. Interestingly, the properties of these Cr–Ru alloys are very similar to high entropy alloys in many respects [33]. Cr–Ru alloys are also composed of mixed atoms of two different elements, the disorder degree of atoms in the samples are large like the HEAs. Therefore, they all have large residual resistance in their normal state. For HEAs, the $T_c$ exhibits a slow increase with the increasing external pressure and then saturates under higher pressure. This is also the same of the Cr–Ru alloys.

The two kinds of materials with different structures also show some distinctions in some physical properties. Only the samples with bcc structure exhibit a pronounced second magnetization peak effect below $2.2 \, \text{K}$ in the MHLs. This difference may be induced by the different micro-structures and vortex pinning landscape in these two materials. Besides, only the samples with A15 structure have shown a second specific heat jump in the low temperature region. This anomaly shifts to lower temperature with increasing magnetic field, thus it is most likely corresponding to a superconducting transition. We can not completely rule out the possibility that this second specific heat jump is due to some secondary impurity phase. The XRD patterns show only the tiny impurity phase of Cr oxide which is not superconductive. Considering that our samples do not contain other metal elements and are of high purity, and the samples with A15 structure are obtained only by high temperature annealing of samples with the one of bcc structure, we thus intend to believe that this additional specific heat jump is an intrinsic property due to another superconducting transition. However, as mentioned above, there is also another possibility that this signal arises from a secondary phase which may not be detectable by the XRD due to the limited resolution. It is also irrelevant to attribute this transition to any possible AFM order developed below $T_c$, since this anomaly can be easily suppressed by a weak magnetic field. If it would correspond to an AFM order, a higher magnetic field is needed even the Neel temperature is only 0.85 K. This second specific heat jump may be understood by a phase transition due to unconventional SC. Thus we consider the possibility of a second superconducting transition in this Cr–Ru with A15 structure. According to the theoretical study [42], a hidden transition from an $s + d$ state to an $s + e^{\eta/d}$ state may occur, leading to a second jump of specific heat far below $T_c$. Due to the magnetic nature of the Cr atoms and the correlation effect, together with the substitution of Cr by Ru in the sample, the system may be locally non-centrosymmetric, which leads to the partially component of chiral SC. If these can be further confirmed, that may suggest the existence of unconventional SC in Cr–Ru.

5. Conclusions and perspectives

In summary, we have successfully synthesized polycrystalline superconducting samples of Cr–Ru with bcc and A15 structures. The XRD and EDS analyses confirm the high quality of our samples. And the magnetization and resistivity measurements all exhibit sharp superconducting transitions with $T_c = 2.82 \, \text{K}$ (bcc) and $T_c = 3.39 \, \text{K}$ (A15), respectively. The two kinds of samples show many similar but unusual physical properties. In magnetization measurements, clear hump structures exist at around 150 K, which are possibly related to AFM spin fluctuations. The resistance measurements show a strong residual resistivity for the two samples, indicating an intrinsic strong scattering effect. The low temperature specific heat can be fitted by the $s$-wave gap for the two samples, and the calculated ratio $2\Delta/k_B T_c$ is around 3.6, indicating a moderate pairing strength. Yet the Wilson ratios are estimated to be 3.81 and 3.62 for the bcc and A15 samples, suggesting moderate electron correlation effect. The two kinds of samples exhibit small lower critical fields and moderate critical current densities. Furthermore, the superconducting transition temperatures are both enhanced slightly under external high pressures. On the other hand, these two kinds of samples with different structures show distinctions of some physical properties. A pronounced second peak effect of magnetization hysteresis has been observed only in samples with bcc structure in the superconducting state. And only in the samples with A15 structure, we observed the second specific heat jump at about 0.85 K, and it is sensitive to magnetic fields.

The Cr–Ru compounds either in bcc and A15 structures may be conventional superconductors, although the normal state magnetic susceptibility exhibits some anomalous features. Thus, the SC in Cr–Ru alloys is very interesting with paradoxical performances, on one hand the superconducting state shows consistency with the picture of an $s$ wave gap and weak electron-phonon coupling, on the other hand, the normal state shows strong scattering, moderate electron correlations and probably the AFM spin fluctuations. Further studies are highly desired in order to understand these interesting features and improve the $T_c$ higher.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

We are grateful for the useful discussions with Joerg Schmalian and Ilya Eremin. This work was supported by the National Natural Science Foundation of China (Grant Nos. 11927809 and 12061131001), and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB25000000).
