Physical properties of noncentrosymmetric superconductor Ru$_7$B$_3$

Lei Fang, Huan Yang, Xiyu Zhu, Gang Mu, Zhao-Sheng Wang, Lei Shan, Cong Ren and Hai-Hu Wen
National Laboratory for Superconductivity, Institute of Physics and National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, P. R. China
(Dated: November 17, 2008)

Transition metal boride Ru$_7$B$_3$ was found to be a noncentrosymmetric superconductor with $T_C$ equal to 3.3 K. Superconducting and normal state properties of Ru$_7$B$_3$ were determined by a self-consistent analysis through resistivity($\rho_{xx}$ and $\rho_{xy}$), specific heat, lower critical field measurement and electronic band structure calculation. It is found that Ru$_7$B$_3$ belongs to an s-wave dominated single band superconductor with energy gap 0.5 meV and could be categorized into type II superconductor with weak electron-photon coupling. Unusual ‘kink’ feature is clearly observed in field-broadening resistivity curves, suggesting the possible mixture of spin triplet induced by the lattice without inversion symmetry.

PACS numbers: 74.70.Ad, 74.25.Qt, 74.25.Sv

I. INTRODUCTION

Unconventional superconductors have been extensively studied during the past decades for the underlying fundamental physics or the potential industrial applications. Some well known examples are heavy fermion superconductors, cuprates, $\text{Sr}_2\text{RuO}_4$ and the newly discovered iron arsenide. In recent years superconductors lacking of lattice inversion center have received intensive attentions for the possibility of spin-triplet dominated pairing symmetry. An important example is noncentrosymmetric spin-orbit superconductor CePt$_3$Si$_2$. Due to the nontrivial antisymmetric spin-orbit coupling (ASOC) effect induced by the heavy Platinum atom and the lacking of inversion symmetry, unconventional superconducting properties are observed, for instance the high upper critical field far beyond the Pauli-Clogston limit. The subsequent nuclear spin-lattice relaxation rate as well as magnetic penetration depth measurements show line nodes in superconducting gap for CePt$_3$Si$_2$. For a material without inversion symmetry the spin degeneracy is lifted by ASOC, under such a condition, orbital angular momentum(\(\hat{L}\)) and spin angular momentum(\(\hat{S}\)) are not good quantum numbers any more, thus the strict categorization of even-parity spin singlet and odd-parity spin triplet conformed to Pauli’s exclusion and parity conservation is violated, then spin triplet may be mixed with spin singlet. Up to now, several noncentrosymmetric superconductors have been reported, the development concerning such a scope could be consulted a overview given by Sigrist et. al. However strong electronic correlation in some materials complicates the studies on ASOC effect, such as heavy fermion properties of CePt$_3$Si$_2$. Recently the pairing symmetry of Li$_2$Pt$_3$B has been proved to be with line node, such a material is not strongly correlated and could be regarded as an appropriate example for ASOC effect. For more comprehension on ASOC, thus, any efforts searching for new noncentrosymmetric superconductors are worthwhile, especially in the absence of correlation effect.

In the present paper we report a new noncentrosymmetric superconductor Ru$_7$B$_3$ with $T_C$ equal to 3.3 K. Transport measurements as well as electronic band structure calculation gave a detailed description to the properties. As to our best knowledge, neither measurements nor calculations have been embarked except Matthias mentioned only the $T_C$ as 2.58 K in 1950's. Additionally, for the first time we point out the noncentrosymmetric characterization of Ru$_7$B$_3$.

The paper is organized as follows: Section II describes the sample preparation process and the experimental details; then in section III we provide the structure illustration and the measurement of many transport properties, including AC magnetization, resistivity, magnetoeresistance and Hall coefficient; section IV focuses on the specific heat and lower critical field measurements; in the following section V full potential electronic structure calculation is discussed; finally a self-consistent normal state and superconducting parameters are determined in section VI.
The crystal structure of Ru$_3$B$_3$ was determined by Aronsnson in the late 1950’s. It was found that the lattice is hexagonal with a space group $P6_3mc$. There are 20 atoms in one unit cell with effective coordinate Ru$_7$(6c), Ru$_{II}$(6c), Ru$_{III}$(2b) and B(6c), respectively. Thus two formula units exist in one unit cell. In that paper the author gave a relative comprehensive description to the lattice structure of Ru$_3$B$_3$, however, thanks to the complex structure of transition metal boride, a more detailed illustration should be added as a supplement for better comprehension on its properties. As to space group $P6_3mc$, a distinct characterization of the crystal lattice is without inversion symmetry, for example, the center of Boron atoms’ sub-lattice dislocates the counterpart of Ruthenium atoms along c-axis, thus the inversion symmetry is broken along such direction. For more clear understanding on the crystal lattice, we illustrate the structure along two types projection in Fig. 1. Fig. 1(a) shows the ab projection of Ru$_3$B$_3$ structure. It is found that the skeleton consists of metal tetrahedra and metal octahedra and interstitial Boron anions. From such a projection, the lattice with hexagonal rotation symmetry is obvious. Fig. 1(b) is the ac projection illustration. A very interesting phenomenon is that two ‘chains’ are built up by ruthenium ions at different coordinations.

![FIG. 1: (a) a-b projection of Ru$_3$B$_3$ structure, the skeleton is consisted of metal tetrahedra and metal octahedra and interstitial Boron anions. From such a projection, the lattice with hexagonal rotation symmetry is obvious. (b) a-c projection of the lattice, two 'chains' are built up by ruthenium ions at different coordinations.](image)

### III. STRUCTURE ILLUSTRATION AND TRANSPORT PROPERTIES

The crystal structure of Ru$_3$B$_3$ was determined by Aronsnson in the late 1950’s. It was found that the lattice is hexagonal with a space group $P6_3mc$. There are 20 atoms in one unit cell with effective coordinate Ru$_7$(6c), Ru$_{II}$(6c), Ru$_{III}$(2b) and B(6c), respectively. Thus two formula units exist in one unit cell. In that paper the author gave a relative comprehensive description to the lattice structure of Ru$_3$B$_3$, however, thanks to the complex structure of transition metal boride, a more detailed illustration should be added as a supplement for better comprehension on it’s properties. As to space group $P6_3mc$, a distinct characterization of the crystal lattice is without inversion symmetry, for example, the center of Boron atoms’ sub-lattice dislocates the counterpart of Ruthenium atoms along c-axis, thus the inversion symmetry is broken along such direction. For more clear understanding on the crystal lattice, we illustrate the structure along two types projection in Fig. 1. Fig. 1(a) shows the ab projection of Ru$_3$B$_3$ structure. It is found that the skeleton consists of metal tetrahedra and metal octahedra and interstitial Boron anions. From such a projection, the lattice with hexagonal rotation symmetry is obvious. Fig. 1(b) is the ac projection illustration. A very interesting phenomenon is that two ‘chains’ are built up by ruthenium ions at different coordinations. The metal octahedra at each corner of the lattice is built up by Ru$_{II}$(6c), those octahedras share face along c-axis and thus a zig-zag chain is formed as shown in Fig. 1(b). The rest Ru$_7$(6c) and Ru$_{III}$(2b) form two tetrahedras in one unit cell at different (x,y) positions, along c direction two tetrahedras (at the same (x,y) positions) share face and then forming a hexahedra, each hexahedra is connected by Ru$_{III}$(2b) and thus another type of row is formed. The special structure configuration might play an important role in transport properties, also the environment of Ruthenium ions (including the interatomic distance and the number of the nearest boron ions) is very important. Detailed parameters are included in Table 1 as shown below.

![FIG. 2 shows the XRD pattern of the sample Ru$_3$B$_3$, which can be indexed in a hexagonal symmetry with $a = b = 7.4629$ Å and $c = 4.7141$ Å. The indexed indices slightly deviate from the reported parameters $a = b = 7.467$ Å and $c = 4.713$ Å. It is clearly found that most diffraction peaks are indexed except one minor peak possibly from un-reacted boron. From the quality of XRD data, it is estimated that the purity of Ru$_3$B$_3$ we synthesized is about 95%.](image)

### TABLE I: Structure parameters of Ru$_3$B$_3$.

| atom   | cite | x    | z    | No.$^a$ | $l$ (Å)$^b$ |
|--------|------|------|------|---------|-------------|
| Ru$_I$ | 6c   | 0.4563 | 0.318 | 4       | 2.15, 2.15, 2.66, 2.66 |
| Ru$_{II}$ | 6c  | 0.1219 | 0    | 4       | 2.15, 2.16, 2.16, 2.86 |
| Ru$_{III}$ | 2b  | 1/3  | 0.818 | 3       | 2.20, 2.20, 2.20 |
| B      | 6c   | 0.187 | 0.582 | /       | /           |

$^a$No. represents the number of nearest Boron for different cites of Ruthenium.

$^b$l stands for the interatomic distance between Boron ions and Ruthenium ions.
is a constant. Using parameters

\[ \Theta = \frac{k_B T}{\kappa} \]

field strongly depends on the selected resistive criterion. As thus very interesting to note that the determined upper critical superconductivity is depressed completely at about 5 T. It is temperature when sample is bearing 1.1 T magnetic field, while magnetic fields, while the upper parts respond reversely. It quickly to low temperatures showing a strong dependence of transition curves into two parts, the lower part moves sharply to zero at 3.3 K. Thus the resistivity data and AC susceptibility give a self-consistent \( T_C = 3.3 \text{ K} \) for \( \text{Ru}_7\text{B}_3 \), which is slightly higher than the preliminary mentioned \( T_C \approx 2.58 \text{ K} \) by Matthias. Considering the high purity of the sample, a quantitative analysis of normal state resistivity is deserved. We try Wilson’s model for transition metals

\[
\rho(T) = \rho_{sd} = \kappa_{sd} \left( \frac{T}{\Theta_{sd}} \right)^3 \int_0^{\Theta_{sd}/T} \frac{x^3 \, dx}{(e^x - 1)(1 - e^{-x})},
\]

where \( \Theta_{sd} \) is a cutoff similar to the Debye temperature and \( \kappa_{sd} \) is a constant. Using parameters \( \Theta_{sd} = 500 \text{ K} \) and \( \kappa_{sd} = 1350 \), a good fitting is obtained as shown in Fig. 4.

Fig. 5 shows the field-broadening resistivity measurement on polycrystalline \( \text{Ru}_7\text{B}_3 \) down to 100 mK. When magnetic field is applied, the onset parts of transition is rounded very similar to the feature of critical fluctuation in superconductors. While adding fields up to 0.6 Tesla, the rounded part of transition evolves into a ‘kink’ structure as shown clearly in Fig. 5. It seems that the kinks break the superconducting transition curves into two parts, the lower part moves quickly to low temperatures showing a strong dependence of magnetic fields, while the upper parts respond reversely. It is observed that the zero resistivity point approach zero temperature when sample is bearing 1.1 T magnetic field, while superconductivity is depressed completely at about 5 T. It is thus very interesting to note that the determined upper critical field strongly depends on the selected resistive criterion. As shown in Fig. 6, the criterion of 99% \( \rho_2 \) and zero resistivity will lead to two distinct \( H_{C2}(0) \) with a ratio of about 5. A conventional interpretation, as discussed in \( \text{Mg}_{10}\text{Ir}_{10}\text{B}_{16} \), for field broadening transition is filamentary-like superconductivity along grain boundaries, the stronger scattering reduces the mean free path and consequently influences on the coherence length. However, we argue that unlike the case of \( \text{Mg}_{10}\text{Ir}_{10}\text{B}_{16} \) the clear kink feature in \( \text{Ru}_7\text{B}_3 \) complicates the determination for \( H_{C2} \), also the kink doesn’t come from sample inhomogeneity or two phases because of the sharp transition in low fields. As to our knowledge, the unconventional ‘kink’ or ‘step’ features in transition curves have been extensively discussed in single crystals \( \text{MgB}_2 \). Several reasons have been attributed to this effect, including superconducting fluctuation, two superconducting gaps, surface barriers and vortex lattice.

\[ \text{FIG. 2: (Color online) X-ray diffraction of \( \text{Ru}_7\text{B}_3 \), most diffraction peaks are indexed except one minor peak possibly from un-reacted boron, the purity is estimated about 95%. The asterisk marks the peak from impurity phase.} \]

\[ \text{FIG. 3: (Color online) AC susceptibility of \( \text{Ru}_7\text{B}_3 \), a sharp superconducting transition happens at 3.3 K under zero field, a narrow transition width less than 0.3 K indicates the good superconducting quality.} \]

\[ \text{FIG. 4: (Color online) Resistivity of \( \text{Ru}_7\text{B}_3 \) under zero field is measured from 2 K to room temperatures, a good fitting is given by Wilson s-d scattering model. The inset shows the enlargement of superconducting transition, the transition width is less than 0.3 K.} \]
melting, etc. However taking account of the very low $T_C$ and $H_{C2}$, superconducting fluctuation is believed to be weak. For surface barriers and vortex lattice melting, the polycrystalline quality seems to exclude their possibilities. As to the two-gap scenario, the following specific heat and lower critical field measurements oppose such a point of view. Thus we assumed the possibility that spin triplet induced kink feature in the framework of inversion symmetry is broken. It is known that applying fields broke time reversal symmetry and is detrimental to spin singlet, whereas triplet pairing remains unaffected. So for a superconductor with pairing symmetry mixed by singlet and triplet, the kink feature in field broadening resistivity curves could be plausible on certain extent.

In Fig. 6 we plot the phase diagram of Ru$_3$B$_3$, the criteria are taken as below, for resistivity 99% $\rho_n$ and zero resistance, for magnetization 95% diamagnetic signal and the half position of specific heat anomaly for thermodynamic measurement. Thus the derived $dH_{C2}/dT$ equal to -0.43 T/K or -0.277 T/K for criteria 99% $\rho_n$ and zero resistance, respectively. It is found that except 99% $\rho_n$ the other three criteria determined data points overlap almost together. Further consideration is that bulk properties provided by specific heat measurement, thus in the following discussion we use 1.1 T as $H_{C2}(0)$ and -0.277 T/K as $dH_{C2}/dT$ near $T_C$. We also try to use Ginzburg-Landau formula to fit the data points determined by 99% $\rho_n$, 

$$H_{C2}(T) = H_{C2}(0) \frac{1 - t^2}{1 + t^2},$$

where $t$ is the normalized temperature $T/T_C$, it is found that the fitting curve strongly deviates the 99% $\rho_n$ points as shown in Fig. 6, indicating the invalidity of Landau twice order phase transition theory in the present material.

Another distinct characterization of Fig. 5 is the field induced magnetoresistance. Typically magnetoresistance is used to investigate the electronic scattering process and provides useful information on fermi surface (FS) topology. So detailed studies are needed. In Fig. 7 we present the temperature dependence of resistivity under magnetic fields from 0 to 9 T. It is found that the magnetoresistance (MR) is about 16% $[\rho_H(9T) - \rho_H(0)]/\rho_H(0)$ at 5 K, which is one order of magnitude larger than the ratio of recently discovered iron arsenide LaFeAsO$_{1-x}$F$_x$. The latter was regarded as superconductor with multiple bands. A simple verification for the possibility of multigap effect is the scaling based on Kohler’s rule. The Kohler’s rule is written as $\Delta \rho / \rho_0 = F(H/\rho_0)$, where $F$ is a function depending on the nature of the metal itself. For single band metal with symmetric Fermi surface topology Kohler’s law should be conserved. It is shown as Fig. 7(b) that Kohler’s rule is only slightly violated. Unlike typical multi-band superconductor MgB$_2$ and LaFeAsO$_{1-x}$F$_x$, the breakdown of Kohler’s law is trivial in Ru$_3$B$_3$, indicating a dominated single band behavior. The further specific heat and lower critical field measurements further provide the same conclusion. However we believe that the slightly violation of Kohler’s rule could be induced by noncentrosymmetric structure of Ru$_3$B$_3$, due to ASOC, the degenerate spin-up and spin-down bands are split, so Kohler’s rule is slightly broken.

Hall coefficient ($R_H$) measurement was done by sweeping temperature at magnetic field 9 T and reversing field (-9 T). For avoiding the possible temperature hysteresis, increasing temperature mode with a moderate rate 1 K/min was adopted for both positive and negative fields. The Hall coefficient is shown in Fig. 8, it is found that the charge carrier of Ru$_3$B$_3$ is dominated by hole-like carriers with $R_H$ $\sim$ $3 \times 10^{-10}$ m$^3$/C from 2 K to 200 K. For verifying the $R_H$, we also use the val-

![Fig. 5](image.png): Field broadening superconducting transition curves of Ru$_3$B$_3$ from 0.1 K to 4 K, a clear kink feature appears as the field exceeds 0.6 T. The drop of resistivity is totally suppressed by 5 T magnetic field. Distinct magnetoresistance is observed.

![Fig. 6](image.png): Phase diagram of Ru$_3$B$_3$, a non-trivial flux flow area for criteria 99% $\rho_n$ and zero resistance is formed by kink shape of transition curves. 95% diamagnetic signal from AC susceptibility and one half points of specific heat jumps are also selected as criteria to estimate the intrinsic value of $H_{C2}(0)$. It is shown that except for the criterion of 99% $\rho_n$ the other points from different criteria overlap together, thus the experimental data 1.1 T is determined as $H_{C2}(0)$. It is found that the estimation of $H_{C2}$ from WHH formula fits experimental data very well, whereas Ginzburg-Landau formula fails to describe the upper bound of $H_{C2}$.
ues derived from sweeping field at three temperature points 2 K, 100 K and 200 K. The low temperature $R_H$ is consistent with the value from sweeping temperature, while error bars exist in high temperatures. The charge carrier density calculated by $n=1/(R_H e)$ is about $1 \times 10^{12}$ cm$^{-2}$, which is two order of magnitude larger than low carrier density superconductors, for example, cuprates and hole doped iron arsenide $(\text{La}_{1-x}\text{Sr}_x)\text{FeAsO}_4$. We also notice the nonlinear temperature dependence of $R_H$, however, the relative change of $R_H$ from 2 K to 200 K is small as shown in Fig. 8. Moreover, it is known that the hall effect is very sensitive to the temperature dependent scattering rate, local fermi velocity and complex FS topology, thus considering the polycrystalline quality detailed analysis on temperature dependent Hall coefficient would not be discussed here.

![Fig. 7: (Color online) (a) Temperature dependence of resistivity of Ru$_3$B$_3$ under magnetic fields from 0 to 9 T. (b) the derived magneto-resistance $\Delta \rho/\rho_0$ is 16% at 5 K, it is shown that the scaling of Kohler’s law is slightly violated. The violation is attributed to band splitting by ASOC instead of multiband effect.](image1)

![Fig. 8: (Color online) Hall coefficient measurement of Ru$_3$B$_3$ from sweeping temperature under reversing fields, the charge carrier is dominated by hole from low temperature to 200 K, the density of charge carrier is about $1 \times 10^{12}$/cm$^2$. The squares represent the data measured by sweeping fields at fixed temperatures.](image2)

FIG. 7: (Color online) (a) Temperature dependence of resistivity of Ru$_3$B$_3$ under magnetic fields from 0 to 9 T. (b) the derived magneto-resistance $\Delta \rho/\rho_0$ is 16% at 5 K, it is shown that the scaling of Kohler’s law is slightly violated. The violation is attributed to band splitting by ASOC instead of multiband effect.

FIG. 8: (Color online) Hall coefficient measurement of Ru$_3$B$_3$ from sweeping temperature under reversing fields, the charge carrier is dominated by hole from low temperature to 200 K, the density of charge carrier is about $1 \times 10^{12}$/cm$^2$. The squares represent the data measured by sweeping fields at fixed temperatures.

### IV. Specific heat and lower critical field measurement

#### A. Specific heat

Fig. 9 shows the raw data of specific heat under different magnetic fields from zero to 3 T. With increasing fields the specific heat anomaly near $T_C$ move quickly to low temperatures leaving a background consistent with that above $T_C$ at zero field. Thus the normal state specific heat could be extracted easily with the relation $C/T = \gamma_n + \beta T^2$, where $\gamma_n$ is the normal state specific heat coefficient and $\beta$ corresponds to phonon contribution. It is found that $\beta=0.3732$ mJ/molK$^4$ and $\gamma_n=89.95$ mJ/molK$^2$, however a residual value $\gamma_n \approx 9.8$ mJ/molK$^2$ indicates the existence of about 10% non-superconducting fraction. The non-superconducting fraction could partly come from unreacted boron as inferred from analysis from X-ray diffraction. Thus the normal state Sommerfeld constant could be determined from the relation $\gamma_s=\gamma_n-\gamma_0$ as 80.15 mJ/molK$^2$. Using the relation $\Theta_D=(12\pi^2k_B^2N_A Z/5\beta)^{1/3}$, where $N_A=6.02\times 10^{23}$ the Avogadro constant, $Z=20$ the number of atoms in one unit cell, we get the Debye temperature $\Theta_D=470.18$ K. In the previous section, we obtained a similar value $\Theta_d=500$ K from the resistivity curve fitting, the consistent values prove the reliability of two different measurements. It is noticed that comparing with the values of Mg$_{10}$Ir$_9$B$_{26}$ and Li$_2$Pt$_3$B$_{26}$ $\gamma_n$ in our measurement is relatively high, thus a prudent checking is necessary. For a type-II superconductor, $\gamma_n$ could be estimated as the following relation

$$\frac{\partial^2 C}{\partial T} \bigg|_{T_c} = A \rho_n \gamma_n \eta,$$

(3)
where \( A = 3.81 e^2/\pi^2 k_B=4479.21(T/K)(\Omega m)^{-1}(J/m^3 K^2)^{-1} \), using \( -\delta \mu_0 H c_2(T)/\partial T |_{T_c} = 0.277 T/K, \rho_n = 9 \mu \Omega cm \), and taking \( \eta = 1 \) for the weak coupling case, we have \( \gamma_n = 94 \) \( mJ/molK^2 \) which is very close to the upper bound of the experimental value 89.95 \( mJ/molK^2 \). Further we could estimate the \( \lambda_{e-p_h} \) via McMillan equation: 

\[
T_C = \frac{\Theta_D}{1.45} \exp(-\frac{1.04(1 + \lambda_{e-p_h})}{\lambda_{e-p_h} - \mu^* (1 + 0.62 \lambda_{e-p_h})}),
\]

where \( \mu^* \) is the Coulomb pseudopotential taking 0.11, \( \Theta_D=470.175 \) K and \( T_C=3.3 \) K, we obtain \( \lambda_{e-p_h}=0.48 \). The value indicates that Ru2B3 belongs to a weak coupling superconductors.

For noncentrosymmetric superconductors, novel pairing symmetry could be achieved due to the mixing of spin singlet and spin triplet. Specific heat is a useful tool to investigate the material’s low energy excitation. So, subtracting the contribution of phonon, we present temperature dependence of \( \gamma_e \) under magnetic fields up to 3 T in Fig. 10(a). For the convenience of theoretical analysis, we further subtract \( \gamma_n \) of zero field data as shown in Fig. 10(b). Thus the weak coupling BCS formula could be used:

\[
\gamma_e(T) = \frac{4N(0)}{k_B T^3} \int_0^{\hbar / \rho_0} d\epsilon \int_0^{2\pi} d\theta \frac{e^{\epsilon / k_B T}}{(1 + e^{\epsilon / k_B T})^2} \times (\epsilon^2 + \Delta^2(\theta, T) - \frac{T}{2} d\Delta^2(\theta, T) / dT) d\theta d\epsilon,
\]

where \( \zeta = \sqrt{\epsilon^2 + \Delta^2(T, \theta)} \). In obtaining the theoretical fit we take the implicit relation \( \Delta_0(T) \) derived from the weak coupling BCS theory for superconductors with different pairing symmetries: \( \Delta(T, \theta) = \Delta_0(T) \) for s-wave, \( \Delta(T, \theta) = \Delta_0(T) \cos 2\theta \) for d-wave, and \( \Delta(T, \theta) = \Delta_0(T) \cos \theta \) for p-wave, respectively. The theoretical curve of s wave fits the experimental data very well leading to an isotropic gap value \( \Delta_0 = 0.5 \) meV and \( T_c = 3.22 \) K. The ratio \( \Delta_0/k_B T_c = 1.80 \) obtained here is quite close to the prediction for the weak coupling limit \( \Delta_0/k_B T_c = 1.76 \). In addition, the specific heat anomaly at \( T_c \) is \( \Delta C/\gamma_n T |_{T_c} \approx 1.31 \) being very close to the theoretical value 1.43 predicted for the case of weak coupling.

Condensation energy \( E_C \) is an important parameter for superconductor, thus we calculate \( E_C \) with the following process, firstly the entropy difference between normal state and superconducting state could be obtained by \( S_n - S_s = \int_0^T (\gamma_n - \gamma_s) dT' \), and then \( E_C \) is calculated through \( E_C = \int_0^T (S_n - S_s) dT' \). The resulted temperature dependence of \( E_C \) is shown in Fig. 11, the inset is the entropy difference between normal state and superconducting state. The \( E_C \) is about 192 mJ/mol at 0 K. Alternatively, \( E_C \) could be calculated by the following equation:

\[
E_C = \alpha N(E_F) \Delta_0^2 / 2 = \alpha \frac{3}{4\pi^2} \frac{1}{k_B} \gamma_n \Delta_0^2,
\]

For a BCS s-wave superconductor, \( \alpha = 1 \), taking \( \gamma_n = 80.15 \) mJ/mol-K² and \( \Delta_0 = 0.5 \) meV, we obtain a value 205 mJ/mol, which is close to experimental value 192 mJ/mol. In addition,
the consistence reversely verifies the validity of \( \gamma_n \) and \( \Delta_0 \) determined through our experiment. From condensation energy, the thermodynamic critical field \( \mu_0 H_{C1}(0) \) could be calculated via the relation \( \mu_0 H_{C1}^2(0)/2 = F_N - F_S = \int (\gamma_n - \gamma_c) dT \), yielding \( \mu_0 H_{C1}(0) = 612 \text{ Oe} \). For a comparison, \( \mu_0 H_{C1}(0) \) of another noncentrosymmetric superconductor \( \text{Mg}_{10}\text{Ir}_{10}\text{B}_6 \) is about 300 Oe\textsuperscript{16}.

### B. Lower critical field measurement

Lower critical field \( H_{C1} \) is an important parameter for a superconductor. According to the Ginzburg-Landau theory, \( H_{C1} \) reflects the superfluid density \( \rho_s \) since \( H_{C1} \) is related to London penetration depth \( \lambda \) and thus is a related parameter that \( H_{C1} \sim 1/\lambda^2 \). Moreover, the temperature dependence of \( H_{C1} \), especially the low temperature features, is always used to investigate the superconducting pairing symmetry and multi-gap effect, for instance the node feature for pairing symmetry and gaps’ value for the latter. In this section we used a two dimensional electron gas(2DEG) micro Hall probe to measure local magnetization loops of \( \text{Ru}_3\text{B}_4 \). For weakening the complex effects of the character of field penetration, such as Bean-Livingston surface barriers and geometrical barriers, we used a low field sweep rate of 60 Oe/min to measure isothermal magnetization curves.

Fig. 12 is the initial isothermal M(H) curves over the temperature range from 1.22 K to 3.2 K. It is found that the low-field parts of those M(H) curves overlap almost on one line (red dash line is guided to the eyes in Fig. 12) with a constant slope, which is attributed to Meissner effect and called as Meissner line. Thus \( H_{C1} \) could be determined as the departure between M(H) curve and Meissner line with the same criterion for all curves. The resulted temperature dependence of \( H_{C1}(T) \)(normalized to \( H_{C1}(0) \)) is shown in Fig. 13. The inset of Fig. 13 shows the criterion for determination of the value of \( H_{C1} \) at 1.4 K, a value of 10 Oe was regarded as error bar due to noise induced uncertainty. According to BCS theory for clean superconductors, the normalized \( H_{C1}(T)/H_{C1}(0) \) is expressed as follows\textsuperscript{11}:

\[
\frac{H_{C1}(T)}{H_{C1}(0)} \propto \frac{\lambda^2(0)}{\lambda^2(T)} = 1 - 2 \int_{\Delta(T)}^\infty (-\frac{\partial f(E)}{\partial E}) D(E) d(E), \quad (7)
\]

Where \( \Delta(T) \) is the BCS superconducting energy gap, \( f(E) = 1/[\exp(-E/k_B T) + 1] \) is the Fermi distribution function, and \( D(E) = E/[E^2 - \Delta^2(T)]^{1/2} \) is the quasiparticle density of states. We use above equation to fit the experimental data, \( H_{C1}(0) \) and \( \Delta(0) \) are fitting parameters. It is found that single gap s-wave pairing could give an appropriate fit with fitting values \( H_{C1}(0) = 110 \text{ Oe} \) and \( \Delta(0) = 0.5 \text{ meV} \), the latter is consistent with that of specific heat measurement. Thus the good consistence indicates the reliability of results determined by \( H_{C1} \) measurement, although the lower temperature (less than 1.2 K) experimental data is absent. A possible argument is that the nominal \( H_{C1} \) obtained from experimental data fitting may not reflect the true value due to the inevitable surface barrier and geometrical barrier induced by the polycrystalline quality. Thus in the following paragraph we will do self-consistent checking from superconducting parameters determined by other measurements.

### V. ELECTRONIC STRUCTURE CALCULATION

In this section we present density of states(DOS) and band dispersion results based on full potential linear-muffin-tin-orbital program LMTART by Savrasov\textsuperscript{13,32}. Full potential approximation, Plane wave expansion(PLW), is selected and
believed to give the adequate accuracy. Fig. 14 is the DOS calculation of Ru$_2$B$_3$. The total DOS curve have numerous van Hove singularities, the feature is very similar to that of Mg$_{10}$Ir$_{10}$B$_{16}$ in that paper the author attributed the characterization as large numbers of atom in the unit cell and various interatomic distances. In Ru$_2$B$_3$ only 20 atoms exist in one unit cell, thus the numerous van Hove singularities could stem from the various interatomic distances complicated by the lacking of a inversion center. Another feature is that electronic structure is dominated by Ruthenium 4d states, boron 2p state contributes weakly. It is reasonable to understand from structure aspect that the lattice of Ru$_2$B$_3$ is mainly consists of metal tetrahedra and metal octahedra or ‘chains’ along c-direction, thus charge carries naturally favor those special channels in a crystal lattice. The total DOS at chemical potential for Ru$_2$B$_3$ is 20.988 state/eV per formula unit. For checking the calculated DOS at chemical potential, we could simply estimate the DOS from $\gamma_n$ in the framework of free electron gas.

$$N(0) = \left(\frac{2\pi^2 k_B^2}{3}\right)^{-1} \cdot \gamma_n, \quad (8)$$

where $\gamma_n$ is selected as 80.15 $mJ/molK^2$, $k_B$ is Boltzmann constant=$1.380658\times10^{-23}$ J/K, $N(0)$ represents the density of state. The obtained $N(0)$ is about 17 state/cell per formula, which is close the calculated value 20.988. Fig. 15 is the band dispersion curves near Fermi energy. A distinct feature is that the all bands are doubly accompanied, the feature is due to asymmetric spin-orbit coupling effect, thus the degeneracy of spin-up and spin-down is lifted. It is noticed that at some k-points with high symmetry splitting instead of degeneracy also exists, which could come from problems such as un-adequate optimized parameters at initialization during computation. Nevertheless, it is believed that such stigma can not affect the main results of the present paper.

VI. SELF-CONSISTENCE AMONG SUPERCONDUCTING PARAMETERS

In the discussion of magnetoresistance, the Kohler’s rule was found to be only slightly broken, indicating a symmetric Fermi surface topology. Thus we could deduce the Fermi-wave number($k_F$) from charge carrier density($n$) assuming a single spherical Fermi surface, $k_F=\left(3\pi^2 n\right)^{1/3}=6.6527$ nm$^{-1}$, where $n=0.995\times10^{22}$ cm$^{-3}$. The effective mass is estimated as $m^*=\left(3h^2\gamma_n\right)/(V_{mol}k_F^2)\approx 17 m_el$, where $m_el$ is bare electron mass and molar volume $V_{mol}=136.89$ cm$^3$/mol. Then the Fermi velocity $v_F=h k_F/m^*$ is about 0.47$\times10^5$ m/s. The mean-free-path is evaluated as $l=\hbar k_F/(\rho_0\gamma n)^{1/3}=31.36$ nm. The superconducting penetration depth $\lambda(0) = \sqrt{m^*/\mu_0\gamma}$ is 214 nm. So the coherence length could be estimated using the BCS expression $\xi(0) = 0.18h v_F/(k_B T_C)$ as 19.5 nm$^{1/2}$. Thus the above
superconducting fields could give a stringent checking on experimental data, such as $\xi(0)$ and $H_{C1}$ and $\mu_0H_C(0)$. In the upper critical fields measurement, $H_{C2}(0)$ is determined as 1.1 T, so using $\xi(0)=\sqrt{\phi_0/(2\pi H_{C2}(0))}$, where $\phi_0$ is flux quanta, coherence length is 17.3 nm, such a value is very close to the deduced $\xi(0)$ 19.5 nm. For checking on $H_{C1}$, the following formula is used:\ref{eq:9}

$$\mu_0H_{C1} = \left(\frac{\phi_0}{4\pi\lambda_0^2}\right)\ln\left(\frac{\lambda_0}{\xi_0}\right),$$

yielding $\mu_0H_{C1} = 90.2$ Oe, where $\lambda_0$ and $\xi_0$ are deduced values from charge carrier density. In our lower critical field measurement we obtain $\mu_0H_{C1}=110$ Oe, which is larger than the estimated value $90.222$ Oe. The thermodynamic critical field $\mu_0H_C(0)$ could be obtained from the following formula:\ref{eq:10}

$$H_{C1}H_{C2} = H_C^2(0)ln\left(\frac{\lambda_0}{\xi_0}\right),$$

using $H_{C2}=11000$ Oe, $H_{C1}=90.2$ Oe, $\lambda_0=214$ nm and $\xi_0=17.3$ nm, $\mu_0H_C(0)$ is given as 628 Oe, which is very close to the value of 612 Oe determined by specific heat. For further checking on the experimental value of $H_{C1}(0)$, firstly the experimental values $H_{C1}(110$ Oe) and $\xi(0)(17.306$ nm) are used into Equation 9, the solved $\lambda_0=189.3$ nm, then using that value $H_{C1}(0)$ could be estimated by Equation 10, yielding $\mu_0H_C(0)=711$ Oe, which is about 100 Oe larger than that obtained from specific heat measurement. Therefore it is safe to conclude that the intrinsic value of $H_{C1}(0)$ is about 90 Oe. So in Table II we list the superconducting and normal state properties of noncentrosymmetric material Ru$_2$B$_3$.

In the final part of self-consistent checking on physical parameters of Ru$_2$B$_3$, a brief discussion on the possible exotic properties due to ASOC is necessary. Generally, two criteria for novel superconductivity in the framework of noncentrosymmetry have been established. The first one is Pauli-Clogston limiting field, which could be expressed as $H_{p}(0) = \Delta(0)/2\sqrt{\lambda B} = 1.83Tc$, for Ru$_2$B$_3$ with $Tc$ 3.3 K, yielding $H_{p}(0) \approx 6$ T. In our experiment the upper bound of $H_{C2}(99%\rho_n)$ is found to be about 5 T, the experimental value is obvious below Pauli limit, indicating that $H_{C2}$ is still determined by orbital depairing fields. Nevertheless, the observed kink feature is still a puzzle under the common thinking, such as two bands or superconducting fluctuation scenarios, et. al. Another criterion is the presence of line or point node in the superconducting gap. The good fitting of specific heat data with isotropic s-wave has provided a strong evidence that spin singlet dominated the condensate. The lower critical field measurement also give the same conclusion even though the lower temperature data (less than 1.2 K) is unfortunately absent. Thus a safe conclusion could be given that noncentrosymmetric superconductor Ru$_2$B$_3$ is dominated by s-wave pairing symmetry, minor spin triplet could admix among the majority of spin singlet.

In the end of experiment and discussion, we show magnetization of Ru$_2$B$_3$ from 5 K to 150 K bearing the magnetic field modes of FC(field cooling) and ZFC(zero field cooling) in Fig. 16. It is found that there is a hump at 40 K on the FC

| TABLE II: Superconducting and normal state properties of Ru$_2$B$_3$ |
|-----------------|-----------------|
| parameter       | Ru$_2$B$_3$     |
| $\gamma$ (ml/mol K$^2$) | 80.15           |
| $N(0)$ (state/eV cell spin) | 20.988          |
| $\Delta$ (m eV) | 0.5             |
| $H_{C2}$ (Oe)   | 11000           |
| $H_{C1}$ (Oe)   | 90              |
| $\xi$ (nm)      | 17.3            |
| $\lambda$ (nm)  | 215             |
| $\kappa$        | 12.4            |
| $H_{C}(0)$ (Oe) | 612~628         |
| $\Delta/k_BTc$  | 1.80            |
| $\Delta/\gamma_Tc$ | 1.31           |
| $\beta$ (ml/mol K$^4$) | 0.3735       |
| $\Theta$ (K)   | 470.175         |
| $E_c$ (ml/mol)  | 192~205         |
| $m^*$           | 17m_e           |
| $n$ (cm$^{-3}$) | $1\times10^{22}$ |
| $l$ (nm)        | 31.36           |
| $\rho_0$ ($\mu\Omega$ cm)/4K | 9              |
curves, while for ZFC mode the hump changes into a peak and
moves to higher temperature at about 55 K. For now it is still
hard for us to comprehend the normal state magnetization of
Ru$_2$B$_3$, especially more subtle features adding on ZFC curves
as shown in Fig. 16(b). For comparison we measured room
temperature magnetization of Ruthenium element(not shown
here), it is found that Ruthenium element is paramagnetic at
300 K, lowering temperature an antiferromagnetic transition
happens at 150 K on the paramagnetic background. The den-
sity states calculation have shown that ruthenium contributes
most DOS on FS. Thus from such a point view, the normal
state magnetization of Ru$_2$B$_3$ could be similar to that of ruthen-
ium element. Furthermore for the ruthenium element the
outer shell electron configuration is 4d$^7$/5s$^1$, thus in Ru$_2$B$_3$ the
ruthenium cations with higher spin angular momentum could
be anticipated. However, we could not exclude the possibility
of impurity induced magnetism due to the 10% residual
γ₀ for specific heat measurement. Nevertheless, the studies
on magnetism of Ru$_2$B$_3$ is worthwhile, for example the pos-
sible antiferromagnetic fluctuation induced superconductivity
has been a hot issue in MgCNi$_x$,$^{35}$ for RuSr$_2$GdCu$_2$O$_8^{36}$ the
interplay between ferromagnetism and superconductor is also
very attractive.

VIII. ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of
China, the Ministry of Science and Technology of China
(973 project: 2006CB601000 and 2006CB921802), and the
Knowledge Innovation Project of the Chinese Academy of
Sciences (ITSNEM). The author thanks to T. Xiang for helpful
discussion and Dr. L. Tang for technical support on electronic
structure calculations. Appreciation also give to C. Dong for
the help of structure analysis.

...
29 J. E. Jaffe, Phys. Rev. B 40, 2558 (1989).
30 W. L. McMillan, Phy. Rev. 167, 331 (1968).
31 M. Tinkham, Introduction to Superconductivity, 2nd ed. (McGraw-Hill, New York, 1996), PP. 93.
32 O. K. Andersen, Linear Methods of Band Theory, Phys. Rev. B 12, 3060 (1975).
33 B. Wiendlocha, J. Tobola and S. Kaprzyk, arXiv:cond-mat/0704.1295.
34 M. Kriener, Y. Maeno, T. Oguchi, Z.-A. Ren, J. Kato, T. Muranaka and J. Akimitsu, Phys. Rev. B 78, 024517 (2008).
35 T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, Nature 411, 54 (2001).
36 C. Bernhard, J. L. Tallon, Ch. Niedermayer, Th. Blasius, A. Golnik, E. Brücher, R. K. Kremer, D. R. Noakes, C. E. Stronach and E. J. Ansaldo, Phy. Rev. B 59, 14099 (1999).