Anomalous Properties in the Normal and Superconducting States of LaRu$_3$Si$_2$

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Superconductivity in LaRu$_3$Si$_2$ with the honeycomb structure of Ru atoms has been investigated. It is found that the normal state specific heat $C/T$ exhibits a deviation from the Debye model down to the lowest temperature. A relation $C/T = \gamma_n + \beta T^2 - AT\ln T$ which concerns the electron correlations can fit the data very well. The suppression to the superconductivity by the magnetic field is not the mean-field like, which is associated well with the observation of strong superconducting fluctuations. The field dependence of the induced quasiparticle density of states measured by the low temperature specific heat shows a non-linear feature, indicating the significant contributions given by the delocalized quasiparticles.

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Superconductivity arising from non-phonon mediated pairing, such as through exchanging the magnetic spin fluctuations, has renewed interests in condensed matter physics. The superconducting (SC) mechanism of the cuprates[1] and the iron pnictides[2], although not yet settled completely, should have a close relationship with the electron correlations.[3–5] A similar assessment may extend to many others, like heavy Fermion[6] and organic materials[7]. In this regard, the systems $RT_3$Si$_2$ or $RT_3B_2$ ($R$ stands for the rare earth elements, like La, Ce, Y, etc., $T$ for the transition metals, like Ru, Co and Ni, etc.) provide an interesting platform, since a variety of combinations of chemical compositions allow the system to be tuned between superconducting and magnetic, and sometimes both phases coexist.[8 9]. Among these samples, the LaRu$_3$Si$_2$ has a SC transition temperature as high as 7.8 K[10]. The material of LaRu$_3$Si$_2$ contains layers of Ru with the honeycomb structure sandwiched by the layers of La and Si, forming a $P6_3/m$ or $P6_3$ space group. Preliminary experiment found that the SC transition temperature drops only 1.4 K with the substitution of 16 % La by Tm (possessing a magnetic moment of about 8$\mu_B$), suggesting that the superconductivity is robust against the local paramagnetic moment. By doping the La with Gd, a coexistence of superconductivity and the spin glass state[11] was observed. In CeRu$_3$Si$_2$, the SC transition temperature drops to about 1 K and a valence fluctuation model was proposed for the pairing[12]. Since the Ru atom locates just below the Fe in the periodic table, a key player in the iron pnictide superconductors, therefore it is very curious to know whether the superconductivity here is induced by the electron-phonon coupling, or by other novel mechanism, such as the electron correlations. In this paper we report the results of transport and specific heat on samples of LaRu$_3$Si$_2$. Our results reveal some novelties in both the SC and normal states of LaRu$_3$Si$_2$.

The samples were fabricated by the arc melting method.[8 12 11] The starting materials La metal pieces (99%, Alfa Aesar), Ru powder (99.9%) and Si powder (99.99%) were weighed and mixed well, and pressed into a pellet in a glove box filled with Ar atmosphere (water and the oxygen compositions were below 0.5 PPM). In order to avoid the formation of the LaRu$_3$Si$_2$ phase, we intentionally let a small amount of extra Ru with the nominal compositions as LaRu$_3$Si$_2$. Three round of welding with the alternative upper and bottom on the pellet was taken in order to achieve the uniformity. After these refined processes, the resultant sample contains

FIG. 1: (color online) X-ray diffraction patterns of the sample LaRu$_3$Si$_2$. All main diffraction peaks can be indexed well by a hexagonal structure with $a = 5.68$ Å and $c = 7.13$ Å with Ru as the impurity phase. For some peaks the difference between the data and the fitting is a bit large because some of the grains of the polycrystalline sample are slightly oriented. The ratio between LaRu$_3$Si$_2$ and Ru is found to be 85:15. The inset gives a sketch of the structure. One unit cell is highlighted by the rhomboic block.
mainly the phase of LaRu$_3$Si$_2$ and small amount of Ru remains as the impurity phase. In Fig.1 we plot the x-ray diffraction patterns (XRD) on one typical sample and the Rietveld fitting using the GSAS program[13]. It is clear that the main diffraction peaks can be indexed well by a hexagonal structure with $a = 5.68 \, \text{Å}$ and $c = 7.13 \, \text{Å}$. Some weak peaks arising from the impurity phase Ru can also be seen. A detailed fitting to the structural data find that the ratio between LaRu$_3$Si$_2$ and Ru is around 85:15 for this typical sample. The sample preparation and the quality characterized by the SC transitions can be repeated quite well. It is found that, some of the LaRu$_3$Si$_2$ phase with a tetragonal structure can be found if the starting material has the nominal composition of LaRu$_3$Si$_2$. In this case, the XRD data exhibit clearly two set of structures and can be easily indexed by the GSAS program. For the present sample, the absolute difference between the experimental data and the fitting curve can be observed for some peaks because part of the grains in the sample are slightly aligned. The resistivity was measured with a Quantum Design instrument PPMS-16T with a standard four-probe technique, while the magnetization was detected by the Quantum Design instrument SQUID-VSM with a resolution of about $5 \times 10^{-8}$ emu.

In Fig. 2(a) we present the temperature dependence of magnetization measured in the zero-field-cooling mode (ZFC) and the field-cooling mode (FC). By considering the demagnetization factor on the ZFC data, the Meissner screening is estimated to be almost 100 %. This indicates that the SC connections between the grains of LaRu$_3$Si$_2$ are very good, although we have slight secondary phase of Ru. The onset $T_c$ determined from the magnetization is around 7.8 K. The majority of the SC transition occurs at about 6.6 K under a magnetic field of 20 Oe. This difference is not induced by the inhomogeneity of the sample, it may be induced by the relatively strong SC fluctuations (see below). Fig. 2(b) shows the magnetization hysteresis loops (MHL) measured at different temperatures. The symmetric and clear opening of the MHLs indicate that it is a type-II superconductor. A roughly linear MHL was observed at 9 K, just above $T_c$, indicating that the normal state has no long range ferromagnetic order. We didn’t observe a magnetization enhancement near $T_c$, which was reported in Tm and Gd doped samples in early publications[8, 11]. Fig.3(a) shows the resistive transitions at zero field (main panel) and different magnetic fields under 4 Tesla (inset). The onset resistive transition temperature is at 7.9 K.

FIG. 2: (color online) (a) Temperature dependence of the DC magnetization measured in the ZFC mode and the FC mode at a magnetic field of 20 Oe. (b) The MHLs measured with a field sweeping rate of 50 Oe/s at different temperatures. At 9 K, the MHL shows a rough linear paramagnetic behavior.

FIG. 3: (color online) Temperature dependence of resistivity at zero magnetic field. The inset shows the resistivity at different magnetic fields: 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 T. (b) Temperature dependence of the critical magnetic field with three different criterions: $H_{c2}$ (squares, 95$\%\rho_n$), $H_{c2}$ (circles, 50$\%\rho_n$) and the irreversibility line $H_{irr}$ (up-triangles, 0.1$\%\rho_n$). There is a large area between the $H_{c2}$ (95$\%\rho_n$) and $H_{irr}$ (0.1$\%\rho_n$), which is probably induced by the strong SC fluctuation.
The normal state resistivity $\rho_n$, and the zero resistivity was achieved at about 6.8 K. By applying a magnetic field, the resistive transition broadens. Taking different criterions of resistivity we determined the upper critical field $H_{c2}(95\%\rho_n)$, $H_{c2}(50\%\rho_n)$, and the irreversibility line $H_{irr}(0.1\%\rho_n)$. It is clear that there is a large difference between the $H_{c2}(95\%\rho_n)$ and $H_{irr}(T)$. We will argue that this may be induced by the strong SC fluctuations.

The raw data of specific heat was shown in Fig.4(a). A SC anomaly appears at about 7.6 K. Since the Ru has a $T_c$ at 0.49 K and a quite small normal state specific heat coefficient $\gamma_n = 2.8 mJ/molK^2$, a slight correction of about 0.42 mJ/molK$^2$ was made to the data. By applying a magnetic field, the SC anomaly shifts to lower temperatures. It is interesting to note that the transition is not shifted parallel down to the low temperatures (the so-called mean-field like), rather the SC anomaly is suppressed. This kind of suppression was clearly seen in the cuprate superconductors Pr$_{0.88}$La$_{0.12}$CuO$_{4-\delta}$ and was ascribed to a strong SC fluctuation. Combining with the resistive broadening under a magnetic field, we would argue that there is also a strong SC fluctuation in LaRu$_3$Si$_2$. As for a three dimensional system judged from our band structure calculations, this kind of strong SC fluctuation may suggest that the superfluid density is low. Another interesting point shown in Fig.4(a) is that the normal state specific heat (SH) coefficient $C/T$ shows a non-linear dependence on $T^2$ down to the lowest temperature (0.38 K). This is clearly deviating from the prediction of the Debye model. Taking the slope of $C/T$ vs. $T^2$ from the low temperature data, we get the Debye temperature $T_D = 284$ K. The phonon contribution calculated based on the Debye model $C_{Debye} \propto (T/T_D)^3 \int_0^{T_D/T} [e^{x^2}/(e^{x^2} - 1)]^2 dx$ is shown by the red dashed line. One can see that the Debye model is seriously violated. It is naturally questioned whether this violation is induced by some electron correlation effect. For a non-Fermi liquid with three dimensionality, the enhanced electron-electron interaction will give an extra contribution to the electronic specific heat $C/T$ vs. $T$.

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![Figure 4](image-url)

**Fig. 4**: (color online) (a) The raw data of specific heat coefficient $C/T$ vs. $T^2$, at different magnetic fields ranging from 0 to 5 T. The normal state data (at 5 T) shows a non-linear feature down to the lowest temperature here, indicating a deviation from the Debye model, as shown by the red dashed line. The solid line represents the fit to the formula including the electron correlations (see text). (b) The electronic specific heat coefficient obtained by subtracting normal state value $C_N/T$ (data at 5 T) from the total. The solid lines are the theoretical fitting curves based on the BCS model. (c) The entropy difference (squares) between the SC state and the normal state, derived from $S_S - S_N = \int_0^T (C_S/T^2 - C_N/T^2) dT$. The condensation energy is calculated by $E_c = \int_0^T (S_S - S_N) dT$. (d) The magnetic field dependence of the field induced electronic specific heat $\Delta \gamma(H)$. The non-linear field dependence is very clear. The red solid line is a fit to the $\sqrt{H}$.
the five Ru 4d orbitals contribute to the conduction in the SDW order is unlikely. Worthy of noting is that all find any strong nesting effect in the Fermi-surface, thus netic instability. The calculation shows that the ferro-level is high as shown in Fig.5 (b). We also perform Fermi level is narrow, and the density of state at Fermi will be presented elsewhere. Since the band closed to level, which leads to complicated 3D Fermi surfaces, this role in the electron conduction and related supercon-sequently all Ru 4d electron should play an important field splitting upon Ru 4d orbitals is quite weak, con-

Further analysis of the calculation shows that the crystal-

field splitting upon Ru 4d orbitals is quite weak, consequently all Ru 4d electron should play an important role in the electron conduction and related supercon-

ductivity. There are several bands crossing the Fermi level, which leads to complicated 3D Fermi surfaces, this will be presented elsewhere. Since the band closed to Fermi level is narrow, and the density of state at Fermi level is high as shown in Fig.5 (b). We also perform spin polarized calculations to check the possible magnetic instability. The calculation shows that the ferromagnetism is not stable for this compound. We cannot find any strong nesting effect in the Fermi-surface, thus the SDW order is unlikely. Worthy of noting is that all the five Ru 4d orbitals contribute to the conduction in LaRu$_3$Si$_2$, which is very similar to the case of the iron in the iron-pnictide superconductors.$^{[18]}$ Actually a Ru-based compound, namely LaRu$_2$P$_2$, is a superconductor with $T_c = 4.1$ K, which has the similar structure of the BaFe$_{2-\delta}$Co$_\delta$As$_2$ superconductor $^{[19]} [20]$, and probably they share the same superconducting mechanism. This reminds us that the correlation effect may play some roles in the superconductivity of LaRu$_3$Si$_2$.

In summary, resistivity, magnetization and specific heat have been measured in a Ru-based superconduc-
tor LaRu$_3$Si$_2$ with $T_c$ of about 7.8 K. The temperature dependence of the normal state specific heat coefficient C/T deviates clearly from the Debye model, but shows the possible evidence of electron correlations. The superconducting transitions measured by both resistivity and specific heat self-consistently present the evidence of strong superconducting fluctuations, resembling that in the cuprates. The field induced quasiparticle density of states show a non-linear magnetic field dependence, which is argued as a gap anisotropy. Combining the nov-
elties found both in the normal state and the supercon-
ducting state, we argue that the electron correlations may play an important role in the occurrence of superconduc-
tivity in LaRu$_3$Si$_2$.

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**FIG. 5:** (color online) (a) The energy bands obtained from the DFT calculations. The dense bands near $E_F$ are derived from the Ru 4d orbitals. (b) The electronic density of states (DOS) from the band structure calculations. It is found that the DOS at the $E_F$ are mainly contributed by the Ru orbitals. The DOS from the La and the Si atoms at $E_F$ are negligible.

In order to have a comprehensive understanding to the data, we did the density-functional theory calculations by using the WIEN2k package$^{[16]}$ utilizing the generalized gradient approximation$^{[17]}$ for the exchange-correlation potential. As shown in Fig.5(a), the bands around Fermi level are mainly contributed by Ru 4d. The Si 3p bands are very wide and have some hybridization with Ru 4d. Further analysis of the calculation shows that the crystal-field splitting upon Ru 4d orbitals is quite weak, consequently all Ru 4d electron should play an important role in the electron conduction and related supercon-
ductivity. There are several bands crossing the Fermi level, which leads to complicated 3D Fermi surfaces, this will be presented elsewhere. Since the band closed to Fermi level is narrow, and the density of state at Fermi level is high as shown in Fig.5 (b). We also perform spin polarized calculations to check the possible magnetic instability. The calculation shows that the ferromagnetism is not stable for this compound. We cannot find any strong nesting effect in the Fermi-surface, thus the SDW order is unlikely. Worthy of noting is that all the five Ru 4d orbitals contribute to the conduction in LaRu$_3$Si$_2$, which is very similar to the case of the iron in the iron-pnictide superconductors.$^{[18]}$ Actually a Ru-based compound, namely LaRu$_2$P$_2$, is a superconductor with $T_c = 4.1$ K, which has the similar structure of the BaFe$_{2-\delta}$Co$_\delta$As$_2$ superconductor $^{[19]} [20]$, and probably

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