Multiband Superconductivity of Heavy Electrons in TlNi$_2$Se$_2$ single crystal

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Superconductivity has been first observed in TlNi$_2$Se$_2$ at $T_C=3.7$ K and appears to involve heavy electrons with an effective mass $m^*\sim14\sim20\ m_e$, as inferred from the normal state electronic specific heat and the upper critical field, $H_C2(T)$. Although the zero-field electronic specific heat data, $C_{sn}(T)$, in low temperatures ($T < 1/4T_C$) can be fitted with a gap BCS model, indicating that TlNi$_2$Se$_2$ is a fully gapped superconductor, the two-gap BCS model presents the best fit to all the $C_{sn}(T)$ data below $T_C$. It is also found that the electronic specific heat coefficient in the mixed state, $\gamma_N(H)$, exhibits a $H^{1/2}$ behavior, which was also observed in some $s$-wave superconductors, although once considered as a common feature of the $d$-wave superconductors. Anyway, these results indicate that TlNi$_2$Se$_2$, as a non-magnetic analogue of TiFe$_2$Se$_2$ superconductor, is a multiband superconductor of heavy electron system.

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The standard heavy fermion compounds containing Ce, Yb and U ions undergo a continuous transition from a high temperature phase in which the $f$-electrons behave as if they are localized to a low temperature heavy Fermion liquid phase in which the $f$-electrons appear to be delocalized with enormous effective masses $m^*$.[1–3]. The heavy Fermi liquid ground state is unstable to fluctuations. It is widely believed that the pairing of the $f$-electrons is mediated by magnetic fluctuations.

An intriguing possibility is the existence of charge order, rather than the usual magnetic order, in proximity to the heavy-fermion state. The materials KNi$_2$Se$_2$[4] and KNi$_2$S$_2$[5], in which Ni ion has a mixed valence Ni$^{+1.5}$, have recently been shown to exhibit several remarkable physical properties. At high temperatures they have high resistivity: the magnetic susceptibility is constant; and structural analysis reveals that they have at least three distinct sub-populations of Ni-Ni bond lengths. Upon cooling below $T_{coh} \sim 20$K, the resistivity rapidly decreases, and the system enters a coherent heavy-fermion state with effective electron mass $m^*\sim10m_e$, eventually giving way to superconductivity below $T_c \sim 1$ K. It was suggested[4, 6] that the formation of a heavy-fermion state at low temperatures is driven by the hybridization of localized charges with conduction electrons, the coherent state competes with a charge-fluctuating state, facilitated by the mixed valency of Ni ions in this system. It raises a question whether the superconductivity in this system is unconventional (i.e., $d$-wave), as that in the standard heavy fermion compounds, or conventional, as that in the Ni-pnictide compounds, such as LaNiAsO ($T_C=2.75$K)[7], BaNi$_2$As$_2$ ($T_C=0.7$ K)[8] or SrNi$_2$P$_2$ ($T_C=1.4$ K)[9]. Due to an unstability in air, a relative lower $T_C$, and the Schottky anomaly corresponding to impurity in the specific heat for this new Ni-chalcogenide superconductors, KNi$_2$Se$_2$ ($T_C=0.8$ K) and KNi$_2$S$_2$ ($T_C=0.46$ K) polycrystalline samples, there have been few reports on the nature of superconductivity.

TlNi$_2$Se$_2$ crystallizes in a tetragonal ThCr$_2$Si$_2$-type structure (space group $I4/mmm$), shown in Fig. 1(a), the same as that of KNi$_2$Se$_2$, Fe-arsenide superconductors, such as (Ba,K)Fe$_2$As$_2$[10], BaFe$_{2-x}$Co$_x$As$_2$[11], Co-based superconductor LaCo$_2$B$_2$[12], as well as the first heavy-fermion superconductor CeCu$_2$Si$_2$[13]. It can be considered one of a non-magnetic analogue of Fe-chalcogenide superconductors recent discovered by us, i.e. TiFe$_2$Se$_2$ compounds with Fe vacancies[14, 15]. TlNi$_2$Se$_2$ compound is a Pauli paramagnetic metal, reported first by A.R. Newmark[16], who did not observe any superconducting transition above 2 K. In this letter, we grew successfully TlNi$_2$Se$_2$ single crystal and rechecked its structure and physical properties. Superconductivity has first been observed in TlNi$_2$Se$_2$ at $T_C=3.7$ K and appears to involve heavy electrons with an effective mass $m^*\sim14\sim20\ m_e$. The zero-field electronic specific heat data, $C_{es}(T)$, in low temperatures ($T < 1/4T_C$) can be described by $C_{es}=C_0 exp(-\Delta)/k_B T$ with $\Delta=3.03$K, indicating that TlNi$_2$Se$_2$ is a fully gapped superconductor, similar to that in the other Ni-arsenide compounds, but different with that in the standard heavy fermion $f$-electron compounds. Furthermore, the two-gap BCS model presents the best fit to $C_{es}(T)$ data below $T_C$, illustrating that TlNi$_2$Se$_2$ is also a multiband superconductor. Another, it is surprising to find that the electronic specific heat coefficient in the mixed state, $\gamma_N(H)$, exhibits a $H^{1/2}$ behavior, which was once
considered as a common feature of the d-wave superconductors, although also observed in some conventional s-wave superconductors. These results indicate that TlNi$_2$Se$_2$ is an example of multiband superconductor of heavy electron system.

Single crystals of TlNi$_2$Se$_2$ were grown using a self-flux method. A mixture with a ratio of Tl:Ni:Se=1:2:2 was placed in an alumina crucible, sealed in an evacuated quartz tube, heated at 950°C for 12 hours, and cooled to 700°C at a rate of 6°C/h, followed by furnace cooling. In each step to prepare the sample, we managed carefully it due to Tl metal poison. Single crystals with a typical dimension of 2×2×0.2 mm$^3$ [see Fig. 1(b)], were mechanically isolated from the flux. Energy Dispersive X-ray Spectrometer (EDXS) was used to determine the crystal composition, and stoichiometric TlNi$_2$Se$_2$ was confirmed, which is different with the analogue of Fe-vacancies existing always [14]. The exact composition of TlFe$_2$Se$_2$ compound, in which Fe-vacancies exists at each sites. Electrical resistivity both in-plane ($\rho_{ab}$) and out-of-plane ($\rho_c$), specific heat $C$, and magnetic susceptibility $\chi$ measurements between 0.5 K and 300K were made using a Quantum Design MPMS or PPMS.

The physical properties of TlNi$_2$Se$_2$ are summarized in Fig. 2. Both $\rho_{ab}$ and $\rho_c$ vs $T$ curves, shown in Fig. 2(a) and inset (i), display a metallic behavior in the normal state before dropping abruptly to zero when superconductivity occurs at $T_C$=3.7 K, which is also confirmed by a large diamagnetic signal [see the inset (ii) of Fig. 2] and a specific heat jump at $T_C$ as shown in Fig. 2(c). At first, we discuss the resistivity in the normal state. $\rho_{ab}$ and $\rho_c$ at 300K is of 68.69 and 108.10 $\mu\Omega$cm, respectively, and $\rho_c/\rho_{ab}$= 1.57, indicating that the anisotropy in TlNi$_2$Se$_2$ is rather small, although the compound has a layer structure. In order to get $\rho_{ab}(T)$ behavior at low temperatures, we measured $\rho_{ab}(T)$ at various magnetic fields above the upper critical field $[\mu_0H_{c2}(0) = 0.802$ Tesla, discussed below]. It was found that no change in $\rho_{ab}(T)$ measured at $\mu_0H \geq$ 1 up to 6 Tesla occurs, indicating no magneto-resistance response in the normal state. Another, we found that $\rho_{ab}(T)$ data below 25K in the normal state can be very well described by a Fermi-liquid behavior, i.e. $\rho_{ab}(T)$= $\rho_0+AT^2$, $\rho_0$=0.615 $\mu\Omega$ cm and $A =4.94 \times 10^{-3}$ $\mu\Omega$ cm/K$^2$ were obtained by fitting $\rho_{ab}(T)$ data measured at 1 Tesla [see the red line in the inset (iii) of Fig. 2]. The residual resistivity ratio $\text{RRR} = \rho_{ab}(300K)/\rho_{ab}(2K)$~103, where $\rho_{ab}(2K)$ obtained from $\rho_{ab}(T)$ data measured at 1 Tesla and superconducting
transition width $\Delta T_C = 0.05$ K reflect the high quality of the single crystals. It is worth to note that no discontinuous change in both $\rho_{ab}(T)$ and $\rho_c(T)$ was observed, which occurs in the iso-structural both BaNi$_2$As$_2$ \cite{18} and SrNi$_2$P$_2$ \cite{9} compounds, corresponding to the structural transition from a tetragonal at higher temperatures to a triclinic at lower temperatures. The powder XRD results (not shown in the paper) at low temperatures provide also an evidence for that no structural transition occurs in TlNi$_2$Se$_2$ compound below 300 K.

Now, we discuss the normal state specific heat $C_N(T)$ measured at a magnetic field $\mu_0 H = 6$ Tesla, as shown in Fig. 2(c). The $C_N(T)/T$ vs $T^2$ plot below 4 K showed a pronounced nonlinear behavior, similar to that observed in KNi$_2$Se$_2$ \cite{3}. We therefore fitted $C_N(T)$ with $C_N(T) = \gamma_N T + \beta T^3 + \delta T^5$, which yields $\gamma_N = 40$ mJ/mol K$^2$, $\beta = 1.65$ mJ/mol K$^4$ and $\delta = 0.135$ mJ/mol K$^6$. The Debye temperature $\Theta_D$ was estimated to be of 175 K. The normal state electronic specific heat coefficient $\gamma_N$ value corresponds to a mass enhancement $m^*/m_b = 14$ (assuming 1.5 carriers/Ni and a spherical Fermi surface). This value is comparable to that of isostructural KNi$_2$Se$_2$ superconductor (44 mJ/mol K$^2$) \cite{4} and $p$-wave superconductor Sr$_2$RuO$_4$ (40 mJ/mol K$^2$) \cite{17}, but is bigger than that in Ni-arsenide superconductors, such as LaO$_{1-x}$F$_x$NiAs (7.3 mJ/mol K$^2$) \cite{7}, BaNi$_2$As$_2$ (12.3 mJ/mol K$^2$) \cite{18}, which is while much smaller than that in the standard heavy-Fermion superconductors, such as CeCu$_2$Si$_2$ (1100 mJ/mol K$^2$) \cite{13}, indicating that the electronic correlation in TlNi$_2$Se$_2$ is stronger than that in Ni-arsenide superconductors, but weaker than that in the standard heavy-Fermion superconductors. The Kadowaki-Woods ratio, $A/\gamma^2$, relates the electronic specific heat to the temperature coefficient in the $\rho_{ab}(T) = \rho_0 + AT^2$, and is typically $\sim 10^{-5}\mu\Omega cm$ [mJ K$^2$] for the standard heavy-fermion systems \cite{13,20}. For TlNi$_2$Se$_2$, we calculate $A/\gamma^2 \sim 0.308 \times 10^{-5}\mu\Omega cm$ [mJ K$^2$] for the metallic properties of TlNi$_2$Se$_2$ with heavy-fermion behavior.

As discussed by T. Takayama et al. \cite{21} for a new strong-coupling superconductor Sr$_2$Pd$_3$P, we analyze the normal state magnetic susceptibility, $\chi(T)$, shown in Fig. 2(b), measured at a magnetic field of 1 Tesla for TlNi$_2$Se$_2$ crystal. $\chi = \chi_0 + \chi_{CW}$, where $\chi_0 = \chi_P + \chi_{VV} + \chi_{core}$ is a temperature independent contribution including a Pauli paramagnetism ($\chi_P$), van Vleck paramagnetism ($\chi_{VV}$) and core diamagnetism ($\chi_{core}$). $\chi_{CW}$ is a Curie-Weiss-
like contribution (< 100 K), very likely from magnetic impurities [as shown as the fitting red line in Fig.2(b) corresponding to < 0.97 mol % of an S=1 impurity, e.g. Ni²⁺]. By subtracting the Curie-Weiss-like contribution, we estimate the temperature independent magnetic susceptibility as \( \chi_0 = 6.064 \times 10^{-4} \text{ emu/mol} \). The core diamagnetic is estimated to be \( -0.76 \times 10^{-4} \text{ emu/mol} \) by using those reported for Ti¹⁺, Ni²⁺ and Se⁴⁺. Then, the Pauli paramagnetic susceptibility is estimated to be \( \chi_P = 6.824 \times 10^{-4} \text{ emu/mol} \) by neglecting \( \chi_{VV} \), which, combined with \( \gamma_N = 40 \text{ mJ/mol K}^2 \), yields the Wilson ratio \( R_W = \pi^2 k_B^2 \chi_P \gamma_N / 3 \mu_0^2 = 1.24 \), typical of many heavy fermion compounds, being comparable to the value of KNi₂Se₂ (\( \gamma_W = 1.71 \)), larger than than the value (\( R_W = 1.0 \)) of the free electron. We note that the Wilson ratio \( R_W \) value may be smaller than the value estimated above without subtracting the van Vleck paramagnetism contribution.

Then, we discuss the electronic specific heat in the superconducting state of TiNi₂Se₂ crystals. Fortunately, no Schottky anomaly in \( C(T) \) measurements, at least at \( T > 0.5 \text{ K} \) and \( \mu_0 H \leq 6 \text{ Tesla} \), was observed for TiNi₂Se₂ single crystal, shown in Fig. 2(c), which let us make the analysis on the specific heat data in the superconducting state. Based on the normal state specific heat \( C_N \) and \( \gamma_N \) obtained above, the electronic specific heat \( C_{es} \) in the superconducting state under zero field was estimated as shown in Fig. 3(a), i.e. \( C_{es} = C(0T) - C_{lat} \), where \( C_{lat} \) is phonon contribution by fitting the \( C \) data measured at 6 T. As fist, we found that low temperature (\( T < 1/4T_c \)) specific heat data can be well described by the \( C_{es} = C_0 \exp(-\Delta/k_B T) \), [see the inset of Fig.3(a)], where \( k_B \) is the Boltzmann constant and the gap \( \Delta = 3.03 K \) obtained by fitting, indicating that TiNi₂Se₂ is a fully gapped superconductor, similar to that observed in the other Ni-arsenide compounds [8, 9], but different with that in the standard heavy fermion \( f \)-electron compounds [13]. Second, it was found that the standard BCS model can not well described all the \( C_{es} \) data below \( T_c \), while the two-gap BCS model presents the best fit to the \( C_{es}/T \) data [see Fig.3(a)]. According to the phenomenological two-gap model, the heat capacity is taken as the sum of contributions from the two bands, each one following the BCS-type temperature dependence [27]. In the Fig. 3(a), we plot the contributions from the two superconducting gaps, \( \Delta_1 = 0.84 k_B T_c \) and \( \Delta_2 = 2.01 k_B T_c \), as well as their sum (black line). The weight contributed from the first gap, \( \Delta_1 \), is about of 0.25. Two gaps behavior in \( C_{es}(T) \) is similar to that observed in PrPt₄Ge₁₂ (\( T_c \approx 5K \)) superconductor [28].

In order to get much information about its superconducting gap, we also measure the low temperature specific heat at various magnetic fields, \( H < 1.07 \text{ T} \), as shown in Fig. 3(b) and the left inset in Fig. 3(b). At \( \mu_0 H = 0 \text{ Tesla} \), zero linear electronic contribution of \( C_{es} \) indicates that almost 100% electrons enter the superconducting state, different with that (50%) observed in the polycrystalline KNi₂Se₂ [4] and KNi₂Se₂ [5] samples. With increasing magnetic field, the magnitude of specific heat jump at \( T_c \) decreases, and the linear electronic specific heat coefficient, \( \gamma_N(H) \), obtained by a linear extrapolation of \( C_{es}/T \) vs \( T^2 \) to \( T = 0 \text{ K} \), increases. In the mixed state, i.e. \( H_C < H < H_{C2} \) where \( H_C \) is the lower critical field, \( H_{C1}(0) \sim 170 \text{ Oe} \) for TiNi₂Se₂, determined by the magnetic hysteresis, \( M(H) \), measurements at different \( T < T_c \), not shown in the paper, the electronic contribution to specific heat is usually attributed to the normal state electrons in the core of vortex. For the \( s \)-wave superconductors, the cores contribute to \( C_{es} \) as a normal metal, then it should be in proportion to the numbers of the cores, i.e. \( \gamma_N(H) = \gamma_0 H / H_{C2} \). However, we found that \( \gamma_N(H) = 58.33 H^{1/2} \), as shown in the right inset of Fig. 3(b), obtained by fitting the \( \gamma_N(H) \) data, which was generally observed in \( d \)-wave cuprate superconductors [22, 23] and some heavy-fermion compounds, such as UPt₃ [24] due to the importance of the Doppler shift to \( d \)-wave superconductivity. The \( \gamma_N(H) \propto H^{1/2} \) behavior was once considered as a common feature of the \( d \)-wave superconductors. In fact, this behavior was also observed in other \( s \)-wave superconductors, such as NbSe₂ [25, 26], V₃Si [27] and CeRu₂ [31] and the organic superconductor (BEDT-TTF)₂Cu[N(CN)₂]Br [31] and the boroncarbide superconductor LnNi₂B₂C [32]. Ramirez [29] suggested that this behavior must be a general feature of all superconductors in the vortex state, independent of the order parameter symmetry, but somehow related the strength of the vortex-vortex interactions.

Finally, we present the analysis of the upper critical field \( H_{C2}(T) \), which give an evidence for superconductivity emerging from the heavy-mass electronic state in TiNi₂Se₂, similar to that described for the standard heavy fermion superconductor, such as for UBe₁₃ [33]. Shown in Fig.4 is the \( H_{C2}(T) \) curve for TiNi₂Se₂ derived from \( \rho_{ab}(T) \) measurements (inset of Fig.3) as a magnetic field applied parallel to \( c \) axis. Using the middle superconducting transition temperature, the zero temperature upper critical field \( H_{C2}(0) \) can be estimated with a formula \( H_{C2}(T) = H_{C2}(0)(1 - t^2)/(1 + t^2) \) [7, 34], where \( t \) is the reduced temperature \( t = T / T_C \), yielding the value of \( \mu_0 H_{C2}(0) = 0.802 \text{ Tesla} \) by fitting [see the main panel of Fig. 4]. The superconducting coherence length \( \xi_0 \) can be estimated from the relation \( \xi_0 = (\Phi_0 / 2\pi H_{C2})^{1/2} \), yielding \( \xi_0 \alpha = 20.3 \text{ nm} \). A value for the Fermi velocity \( v_F = 5.48 \times 10^4 \text{ m/s} \) is then obtained from \( \xi_0 = 0.18 k_B v_F / k_B T_c \) [34] from which \( m^* \) and \( \gamma_N \) can be estimated as follows. Using a spherical Fermi surface approximation, the Fermi wave vector is given by \( k_F = (3\pi^2 Z / \Omega)^{1/3} \), where \( Z \) is the number of electrons per unit cell and \( \Omega \) is the unit cell volume. Assuming that Ni contributes 1.5 electrons (\( Z = 6 \)), we obtain \( k_F = 9.6 \times 10^7 \text{ m}^{-1} \). The expression \( m^* = \hbar k_F / v_F \) yields \( m^* \approx 20 \text{ m}_e \). From the relation \( \gamma_N = \pi^2 N k_B^2 m^* / h^2 k_F^2 \), \( \gamma_N \)
~ 61 mJ/mol K$^2$. The values of $m^*$ and $\gamma_N$ are comparable to the values estimated from the normal state specific heat.

In summary, TlNi$_2$Se$_2$ exhibits superconductivity with $T_C$=3.7 K that appears to involve heavy electrons with an effective mass $m^*$=14~20 $m_b$, as inferred from the electronic specific heat coefficient $\gamma_N$ and the upper critical field, $H_{C2}(0)$. The zero-field electronic specific heat data, $C_{es}(T)$, in low temperatures ($T < 1/4T_C$) can be fitted by a one gap BCS model, indicating that TlNi$_2$Se$_2$ is a fully gapped superconductor, similar to that in the other Ni-arsenide compounds, but different with that in the standard heavy fermion $f$-electron compounds. But the two-gap BCS model presents the best fit to $C_{es}(T)$ data below $T_C$. It is also found that the electronic specific heat coefficient in the mixed state, $\gamma_N(H)$, exhibits a $H^{1/2}$ behavior, which was once considered as a common feature of the $d$-wave superconductors, but also observed in some conventional s-wave superconductors. Anyway, these results indicate that TlNi$_2$Se$_2$, as a non-magnetic analogue of TiFe$_x$Se$_2$ superconductor, is a multiband superconductor of heavy electron system.

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