Physical properties of $K_xNi_{2−y}Se_2$ single crystals

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Abstract

We have synthesized $K_{0.95(1)}Ni_{1.86(2)}Se_2$ single crystals. The single crystals contain K and Ni deficiencies not observed in $KNi_2Se_2$ polycrystals. Unlike $KNi_2Se_2$ polycrystals, the superconductivity is absent in single crystals. The detailed physical property study indicates that the $K_{0.95}Ni_{1.86}Se_2$ single crystals exhibit heavy-fermion-like characteristics. The transition to a heavy fermion state below $T ∼ 30$ K results in an enhancement of the electron-like carrier density whereas the magnetic susceptibility shows little anisotropy and suggests the presence of both itinerant and localized Ni orbitals.

(Some figures may appear in colour only in the online journal)

1. Introduction

Even before the discovery of the superconducting $T_c = 26$ K in LaFeAsO$_{1−x}$F$_x$ [1], some nickel pnictide materials (such as LaONiP) [2] had already been found to become superconducting (SC) at low temperatures. Examples of nickel pnictide superconductors also include LaONiAs, LaO$_{1−x}$NiBi, BaNi$_2$P$_2$ and SrNi$_2$P$_2$ [3–6]. However, all nickel pnictide SCs have much lower $T_c (<5$ K) when compared to iron pnictide SCs, of which the $T_c$ values are mostly well above 5 K [7]. The possible reason leading to this difference could be due to different superconducting mechanisms or to different values of material parameters relevant for superconductivity which are not optimized for the nickel pnictides even if the pairing mechanism were to be identical [7].

On the other hand, iron chalcogenide SCs have also been discovered, including FeCh (Ch = S, Se, Te) [8–10], and $A_xFe_{2−y}Se_2$ ($A = K, Rb, Cs, Ti/K$ and Ti/Rb) [11–16]. In contrast to iron chalcogenide SCs, however, corresponding nickel chalcogenide SCs were still missing until recently. NiSe has a NiAs-type structure with space group $P63/mmc$ and this structure is isostuctural to hexagonal FeSe (high-temperature phase). NiSe is a non-superconducting metal with ferromagnetic fluctuations [17]. Similarly, TiNi$_2$Se$_2$ is a Pauli paramagnet without a superconducting transition down to 2 K [18]. However, very recently, it was reported that KNi$_2$Se$_2$ polycrystals are superconducting with $T_c = 0.80(1)$ K [19]. Moreover, KNi$_2$Se$_2$ single crystals feature a heavy-fermion-like state with an increased carrier mobility and enhanced effective electronic band mass below about 40 K. This state should emerge from the proposed local charge density wave (CDW) state, which persists up to 300 K [19].

A study of single crystals is necessary in order to elucidate the anisotropy in intrinsic physical properties of KNi$_2$Se$_2$ and eliminate the influence of grain boundaries and ferromagnetic Ni impurities. Hence, in this work we report the physical properties of $K_{0.95(1)}Ni_{1.86(2)}Se_2$ single crystals. Unexpectedly, we found no evidence for a superconducting transition down to 0.3 K in resistivity measurements. Magnetic, Hall, thermodynamic and thermal measurements suggest that the heavy-fermion-like properties of $K_{x}Ni_{2−y}Se_2$ arise from dominant electron-like carriers.

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onset of the heavy-fermion-like state below 30 K coincides with the increased electron-like carrier concentration below \( T \sim 30 \text{ K} \).

2. Experiment

Single crystals of KNi\(_2\)Se\(_2\) were grown by a self-flux method similar to K\(_x\)Fe\(_{2-x}\)Se\(_2\) [20] with a nominal composition K:Ni:Se = 1:2:2. Briefly, pre-reacted NiSe and K pieces were added into an alumina crucible with a partial pressure of argon gas. The quartz tubes were heated to 1030 °C, kept at this temperature for 3 h, then cooled to 730 °C at a rate of 6 °C h\(^{-1}\). Platelike dark pink colored single crystals with typical size \( 5 \times 5 \times 2 \text{ mm}^3 \) can be grown. A high-energy synchrotron x-ray experiment at 300 K was conducted on X7B beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The setup utilized an x-ray beam 0.5 mm × 0.5 mm in size with a wavelength of 0.3196 Å \((E = 38.7936 \text{ keV})\) configured with a focusing double-crystal bent Laue monochromator and a PerkinElmer amorphous silicon image plate detector mounted perpendicular to the primary beam path. A finely pulverized sample packed in a cylindrical polyimide capillary 1 mm in diameter was placed 377.81 mm away from the detector. Multiple scans were performed to a total exposure time of 240 s. The 2D diffraction data were integrated and converted to intensity versus 2\( \theta \) using the software FIT2D [21].

Structural refinements were carried out using the GSAS modeling program [22] operated by the EXPGUI platform [23]. The elemental analysis was performed using energy-dispersive x-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope. Electrical and thermal transport, heat capacity, and magnetization measurements were carried out in Quantum Design PPMS-9 and MPMS-XL5. The in-plane resistivity \( \rho_{ab}(T) \) was measured using a four-probe configuration on cleaved rectangularly shaped single crystals with the current flowing in the \( ab \)-plane of tetragonal structure. Thin Pt wires were attached to electrical contacts made of silver paste. Thermal transport properties were measured in a Quantum Design PPMS-9 from 2 to 350 K using the one-heater two-thermometer method. The relative error was \( \frac{\Delta \rho}{\rho} \sim 5\% \) and \( \frac{\Delta T}{T} \sim 5\% \), based on a Ni standard measured under identical conditions.

### 3. Results and discussion

Refinement of the synchrotron x-ray diffraction data of KNi\(_2\)Se\(_2\) reveals that the sample is constituted of 97% by weight of KNi\(_2\)Se\(_2\) (space group \( I4/mmm \)) and 3% by weight of SeO\(_2\) impurity (space group \( P42/mmc \)). The SeO\(_2\) impurity phase arises due to sample preparation. Most likely, the oxidation process of KNi\(_2\)Se\(_2\) is similar to \( \beta \)-FeSe [24]. The fit is shown in figure 1(a) and the refinement results are summarized in table 1. The determined lattice parameters are \( a = 3.8707(5) \text{ Å} \) and \( c = 13.591(4) \text{ Å} \). The value for the \( a \) axis is somewhat smaller whereas the \( c \) axis lattice parameter is larger when compared to polycrystalline samples with full occupancies of K and Ni \((a = 3.9098(8) \text{ Å} \text{ and } c = 13.4142(5) \text{ Å}) [25]\). This is in agreement with a previous study which indicated that the deviation from full occupancy can increase the \( c \) lattice parameter with only a minor effect on the \( a \) lattice parameter [25]. On the other hand, both the \( a \) and \( c \) lattice parameters are smaller than those in K\(_x\)Fe\(_{2-x}\)Se\(_2\) \((a = 3.9109 \text{ Å} \text{ and } c = 14.075 \text{ Å}) [20]\). It could be due to the smaller ionic radius of Ni\(^{2+} \) (0.55 Å) than Fe\(^{2+} \) (0.63 Å) with four-fold coordination [26]. The antiferromagnetic state in K\(_x\)Fe\(_{2-x}\)Se\(_2\) can increase the lattice parameters further when compared to the non-magnetic state according to the theoretical calculation [27].

The crystal structure of KNi\(_2\)Se\(_2\) is shown in figure 1(b), where antifluorite-type Ni–Se layers and K cation layers are piled up alternately along the \( c \) axis. XRD pattern of a single crystal (figure 1(c)) reveals that the crystal surface is normal to the \( c \) axis with the plate-shaped surface parallel to the \( ab \)-plane. Figure 1(d) shows the EDX spectrum of a single crystal of KNi\(_2\)Se\(_2\), confirming the presence of the K, Ni, and Se. The EDX results for several single crystals with multiple measuring points indicate that the crystals are rather homogeneous and the determined average atomic ratios are K:Ni:Se = 0.95(1):1.86(2):2.00(1) when fixing the Se stoichiometry to be 2. Although the number of deficiencies is smaller when compared to K\(_x\)Fe\(_{2-x}\)Se\(_2\) crystals [20], it is noticeably higher when compared to KNi\(_2\)Se\(_2\) polycrystals which feature full occupancies of K, Ni and Se atomic sites [25]. The vacancies of K and Fe should be randomly distributed, otherwise the symmetry of the structure (space group: \( I4/mmm \)) should be lower. This is the case for K\(_x\)Fe\(_{2-x}\)Se\(_2\), where the space group changes from \( I4/mmm \) to \( I4/m \) [20]. On the other hand, the deficiencies should have minor effect on the heavy fermion behavior, as

### Table 1. Structural parameters for K\(_{0.95}\)Ni\(_{1.86}\)Se\(_2\) at room temperature.

| Chemical formula | K\(_{0.95}\)Ni\(_{1.86}\)Se\(_2\) | Space group | I4/mmm |
|------------------|-----------------|-------------|--------|
| \( a \) (Å)      | 3.8707(5)       |             |        |
| \( c \) (Å)      | 13.591(4)       |             |        |
| \( V \) (Å\(^3\)) | 203.62(7)       |             |        |

| Atom | \( x \) | \( y \) | \( z \) | \( U_{iso} \) (Å\(^2\)) |
|------|--------|-------|-------|------------------------|
| K    | 0      | 0     | 0     | 0.062(5)               |
| Ni   | 0      | 0.5   | 0.25  | 0.0206(18)             |
| Se   | 0      | 0     | 0.35238(28) | 0.0177(13) |
Figure 1. (a) Refinement of synchrotron x-ray diffraction data of K$_{0.95}$Ni$_{1.86}$Se$_2$: data (solid symbols), structural model (red solid line), difference curve (green solid line, offset for clarity). Vertical tickmarks denote reflections in the main phase (black, top row) and the secondary SeO$_2$ phase (blue, bottom row). (b) Crystal structure of KNi$_2$Se$_2$. The large purple, medium cyan and small red balls represent K, Ni and Se ions. (c) Single crystal XRD of K$_{0.948}$Ni$_{1.86}$Se$_2$. The inset shows a photo of a typical single crystal of KNi$_2$Se$_2$. (d) The EDX spectrum of a single crystal. 

shown below, because this behavior is still observed in the polycrystal sample without significant deficiencies. However, the deficiencies might have a significant influence on the superconductivity which appears in the polycrystal sample.

The temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ of the K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystal exhibits metallic behavior with the residual resistivity ratio (RRR) $\rho_{ab}(295 \text{ K})/\rho_{ab}(0.3 \text{ K}) = 5$. The room-temperature value $\rho_{ab}(295 \text{ K})$ (256 $\mu$Ω cm) is slightly smaller than the value in polycrystals (350 $\mu$Ω cm). However, the RRR value is much smaller than that in polycrystals (RRR $\sim$ 175). Larger residual resistivity $\rho_0$ in crystals could come from the increased impurity scattering due to the deficiencies. The most striking feature is the absence of a superconducting transition down to 0.3 K in K$_{0.948}$Ni$_{1.86}$Se$_2$ single crystals when compared to KNi$_2$Se$_2$ polycrystals with $T_c = 0.80(1)$ K [19]. The absence of superconductivity in single crystals could be related to the deficiencies of K and Ni, implying that the superconductivity in KNi$_2$Se$_2$ is very sensitive to the atomic ratio. There is no metal–insulating transition (MIT) in KNi$_2$Se$_2$ and the absolute values of resistivity are much smaller when compared to K$_x$Fe$_{2-x}$Se$_2$ [20], indicating that Ni orbitals in the former material are more itinerant when compared to Fe orbitals in the latter material. Surprisingly, as shown in the inset of figure 2(b), the $\rho_{ab}(T) \sim T^n$ dependence is observed up to 20 K at temperatures where other types of scattering (e.g. electron–phonon) are usually active or dominant. From the fit using $\rho_{ab}(T) = \rho_0 + AT^n$, we obtain the residual resistivity $\rho_0 = 50.282(2)$ $\mu$Ω cm, the coefficient of the quadratic resistivity term $\Lambda = 0.0079(5)$ $\mu$Ω cm K$^{-2}$, and $n = 1.96(2)$.

Figure 3 presents the temperature dependence of magnetic susceptibility $\chi(T)$ of the K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystal for $H = 1$ kOe along the $ab$ plane and $c$ axis below 300 K. It can be seen that the $\chi_{c}(T)$ is larger than the $\chi_{ab}(T)$ at high temperature. The susceptibility can be fitted
Figure 2. Temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ of the K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystal from 0.3 to 295 K. The inset (a) shows the enlarged part of $\rho_{ab}(T)$ below 2 K. The inset (b) shows the fitted result from 0.3 to 20 K using $\rho_{ab}(T) = \rho_0 + AT^n$, where the red line is the fitting curve.

Figure 3. (a) Temperature dependence of magnetic susceptibility $\chi(T)$ with the applied field $H = 1 \text{kOe}$ along the $ab$ plane and the $c$ axis below 300 K. The inset shows the isothermal magnetization hysteresis loops $M(H)$ for $H \parallel ab$ and $H \parallel c$ at 300 and 1.8 K. Using the Curie–Weiss law $\chi(T) = \chi_0 + C/(T - \theta)$ when a temperature-independent contribution $\chi_0$ is accounted for. Here, $\chi_0$ includes core diamagnetism, Landau diamagnetism, and Pauli paramagnetism, $C$ is the Curie constant and $\theta$ is the Curie–Weiss temperature (solid lines in figure 3). The fitted values for $\chi_0$ are $1.87(5) \times 10^{-3}$ and $4.69(4) \times 10^{-3}$ emu mol$^{-1}$ f.u.$^{-1}$ Oe$^{-1}$ for $H \parallel ab$ and $H \parallel c$, which are much larger than the value in the literature [25]. Because the core diamagnetism is typically on the order of $10^{-6} - 10^{-5}$ emu mol$^{-1}$ Oe$^{-1}$ [28], and $\chi_{\text{Landau}} \approx -1/3 \chi_{\text{Pauli}}$, such large $\chi_0$ values strongly imply there is an enhanced Pauli paramagnetism, i.e. the significant pileup of the density of states at the Fermi level due to $\chi_{\text{Pauli}} \approx \mu_B^2 N(E_F)$. On the other hand, the obtained local moment is about 0.463(3) and 0.615(7) $\mu_B$/Ni for $H \parallel ab$ and $H \parallel c$. This is unlikely to be due to impurities such as Ni$^{2+}$ with $S = 1$ because the corresponding molar fraction would be 16.4(1) and 29.7(3) mol% for $H \parallel ab$ and $H \parallel c$, respectively. Such a large amount of impurities should have been detected in the XRD pattern, hence the origin of low-temperature susceptibility rise should be intrinsic. The contribution of impurity is revealed (figure 3 (inset)) in the magnetization loops for both field directions at 300 and 1.8 K. There is a ferromagnetic component superposed on the paramagnetic background with a very small magnetic moment ($\sim 10^{-2} \mu_B$/Ni). After subtracting the paramagnetic part from the curve for $H \parallel ab$ at 1.8 K, the saturated moment would correspond to $\sim 0.2$ mol% Ni$^{2+}$ or $\sim 1$ mol% Ni impurities. The above analysis indicates that Ni orbitals in NiSe$_4$ tetrahedra are at the boundary of itinerancy and Mott localization with a possible orbital dependent correlation strength, similarly to iron orbitals in iron based superconductors [29].

As shown in figure 4(a), the transverse resistivity $\rho_{xy}(H)$ shows an approximately linear relation against the magnetic field and is negative at all measuring temperatures, indicating that the electron-type carrier is dominant. From the linear fitting of $\rho_{xy}(H) - H$ relation, we obtain the Hall...
coefficients \( R_H = \rho_s(H)/H \) at different temperatures, which is shown in figure 4(b). It can be seen that \( R_H \) is weakly temperature dependent when \( T > 30 \) K and then decreases with temperature. In a single-band scenario, this change suggests that the carrier density increases at about \( T = 30 \) K, since \( R_H = 1/n_e \) (Inset of figure 4(b)). This temperature is close to the observed crossover from the proposed local CDW state to the heavy fermion state in stoichiometric KNi$_2$Se$_2$ polycrystals [19].

On the other hand, the change can also be ascribed to the multiband effect, which has been observed in classic two-band materials such as MgB$_2$ as well as in iron based material Nd(O, F)FeAs [30, 31]. A multiband electronic structure at the Fermi level is also supported by the density function calculations [32]. However, the observed temperature dependence is much weaker than that in Nd(O, F)FeAs single crystal, which exhibits significant multiband behavior. It implies the multiband behavior should be weaker in KNi$_2$Se$_2$ when compared to iron based superconductors.

From the obtained \( R_H \), the corresponding carrier density at 300 K is \( \sim 4 \times 10^{-3} \) carrier per Ni, increasing up to \( \sim 8 \times 10^{-3} \) carrier per Ni. The carrier density is very low, even one order lower than in iron based superconductors, such as LaFeAsO$_{0.88}$F$_{0.12}$\((1\sim 2 \times 10^{21} \text{ cm}^{-3}) \) [33]. Moreover, from the measured resistivity at 5 K (\( \rho_{ab}(5 \text{ K}) = 4.74 \times 10^{-5} \Omega \text{ cm} \)) and the derived carrier density at same temperature (\( n_\text{Si} = 1.46 \times 10^{20} \text{ cm}^{-3} \)), the carrier mobility at 5 K can be roughly estimated using \( \sigma = n e \mu \) and is about 905 cm$^2$/V s$^{-1}$.

It is close to the result derived from magnetoresistance measurements of polycrystals (1070 cm$^2$/V s$^{-1}$), implying that KNi$_2$Se$_2$ has a high carrier mobility. On the other hand, as discussed below, the electron specific heat is large at low temperature, indicating the increased effective mass. Because \( \mu \) is proportional to the mean scattering time and inversely proportional to the effective mass, the mean scattering time could be rather large at low temperatures [19].

Figure 5 shows the temperature dependence of thermoelectric power \( S(T) \) for K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystals measured between \( T = 2 \) and 350 K. At high temperature, the \( S(T) \) is negative, consistent with dominant negative charge carriers. It is interesting that the value of the \( S(T) \) decreases with decreasing temperature and then becomes positive at about \( T_1 = 64 \) K. The sign change implies multiband transport. Even though the Hall coefficient \( R_H \) is unchanged in that temperature range, the sign of \( S(T) \) might change since they have a different dependence on carrier density \( n_e \) \((\nu_b)\), mobility \( \mu_e \) \((\mu_b)\), and \( S_0 \) \((\nu_b)\) in the two-band model \( R_H = 1/c(\nu_b \mu_b^{-1} - \nu_e \mu_e^{-1}) \). \( S = S_0(\nu_b \mu_b^{-1} - \nu_e \mu_e^{-1}) \) [34].

With further decreasing temperature, \( S(T) \) shows a peak at around \( T_m = 27 \) K and then decreases with temperature. Finally it becomes negative again and the temperature corresponding to the second sign reverse is about \( T_2 = 12 \) K. The temperature of \( T_m \) is very close to the temperature where the change of slope in \( R_H \) appears. As we discuss below, the second sign change of \( S(T) \) could be related to the heavy fermion state, where the Fermi surface becomes large with increasing carrier density in electron-type bands.

Figure 6(a) shows the relation between \( C_p/T \) and \( T^2 \) for K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystal at low temperature. It can be seen that there is an upturn in the specific heat as \( T < 3 \) K. This upturn could not be related to the superconducting transition or to a nuclear Schottky anomaly since it appears at much higher temperatures. This might be an intrinsic effect related to magnetic fluctuations due to the deficiencies of K and Ni. Similar behavior has been observed in Ca(Fe$_{0.1}$Co$_{0.9}$)$_2$P$_2$ and Ca(Fe$_{1-x}$Ni$_x$)$_2$P$_2$ \((x = 0.5 \) and 0.6) [35]. In order to obtain the electronic specific heat and Debye temperature, we fit the \( C_p/T - T^2 \) curve between 5 and 10 K by using the formula \( C_p/T = \gamma + \beta_2 T^2 + \beta_3 T^4 \). We obtain \( \gamma = 48(2) \) mJ mol$^{-1}$ K$^{-2}$, \( \beta_2 = 1.06(8) \) mJ mol$^{-1}$ K$^{-4}$, and \( \beta_3 = 5.4(6) \) µJ mol$^{-1}$ K$^{-6}$.

The Debye temperature is estimated to be \( \Theta_D = 209(5) \) K using the formula \( \Theta_D = (12\pi^4 N R/5 \beta)^{1/3} \), where \( N \) is the atomic number in the chemical formula \((N = 5)\) and \( R \) is the gas constant \((R = 8.314 \) J mol$^{-1}$ K$^{-1}$). The Debye temperature \( \Theta_D \) and electronic specific heat \( \gamma \) are close to the results obtained on the KNi$_2$Se$_2$ polycrystals [19]. The large \( \gamma \) implies the mass enhancement at low temperatures and heavy-fermion-like behavior [19]. Moreover, the \( \Theta_D \) is also similar to that of K$_2$Fe$_2$Se$_2$ \((\sim 212 \) K) [36], which could be ascribed to the similar structure and atomic weight.

As shown in figure 6(b), at high temperature the heat capacity approaches the Dulong–Petit value of 3N\( R \) (124.71 J mol$^{-1}$ K$^{-1}$), implying that the electronic specific heat at high temperature is not enhanced when compared to that at low temperature. In order to evaluate the temperature evolution of the electronic specific heat, the \( C_p(T) \) curve is fitted using double-Debye model in different ranges from \( T = 5 \) K to \( T = 52 \) K to 300 K, similar to the discussion for the KNi$_2$Se$_2$ polycrystalline sample [19]. For the double-Debye model, the total specific heat can be expressed by [19]:

\[
C_p(T) = \gamma T + 9R(N - s) \left( \frac{T}{\Theta_D1} \right)^3 \int_0^{\Theta_D1/T} x^4 e^x \left( e^{x-1} \right)^2 dx + 9Rs \left( \frac{T}{\Theta_D2} \right)^3 \int_0^{\Theta_D2/T} x^4 e^x \left( e^{x-1} \right)^2 dx
\]
where Θ_D is the Debye temperature for each sublattice and s is the number of oscillators in one sublattice. We set s = 2, the same as that for the polycrystalline sample. The $C_p(T)$ curve can be fitted well by using this model (figure 6(b)) and the obtained Θ_D and γ are shown in figures 6(c) and (d), respectively. It can be seen that Θ_D increases with decreasing $T$ and Θ_D has the inverse trend, consistent with the result for the polycrystalline sample. On the other hand, the γ values are much smaller than that obtained from the low-temperature fit. Moreover, the γ is about 2.5 mJ mol$^{-1}$ K$^{-2}$ when $T > 35$ K and increases monotonically up to about 6.3 mJ mol$^{-1}$ K$^{-2}$ for $T = 5$ K. The crossover temperature is close to 35 K. The above results imply that the effect of electronic mass enhancement is very weak at high temperature, while it gains strength when cooling below about 30–40 K. Temperature-dependent mass enhancement is consistent with the results for polycrystals [19].

The phonon drag contribution to $S(T)$ gives an $T^3$ dependence for $T \ll \Theta_D$, $\sim 1/T$ for $T \geq \Theta_D$ (where Θ_D is the Debye temperature) and a peak structure for Θ_D/5 [37, 38]. The estimated Debye temperature of our crystals is about 210 K. Since $S(T)$ (figure 5) is nearly constant for $T \ll \Theta_D$, is linear for $T \geq \Theta_D$, and shows no peak structure at Θ_D/5 = 42 K, it is unlikely that the sign change in thermoelastic power is related to the phonon drag effect.

From the obtained Θ and γ, the Kadowaki–Woods (KW) ratio $A/\gamma^2 = 3.43(6) \times 10^{-6}$ μΩ cm mol$^2$ K$^{-2}$ mJ$^{-2}$. This is somewhat smaller than the value for KNi$_2$Se$_2$ polycrystals (1.2 $\times$ 10$^{-5}$ μΩ cm mol$^2$ K$^{-2}$ mJ$^{-2}$) [19], and from the universal value observed in strongly correlated heavy fermion systems (1 $\times$ 10$^{-5}$ μΩ cm mol$^2$ K$^{-2}$ mJ$^{-2}$) [39]. However, it is still larger than that in many intermediate valence Yb-based and several Ce-based compounds with large γ (A/γ$^2$ $\sim$ 0.4 $\times$ 10$^{-6}$ μΩ cm mol$^2$ K$^{-2}$ mJ$^{-2}$) [39]. On the other hand, from the fitted temperature-independent susceptibility $\chi_0$ (1.87(5) $\times$ 10$^{-3}$ and 4.69(4) $\times$ 10$^{-3}$ emu mol f.u.$^{-1}$ Oe$^{-1}$ for $H \parallel ab$ and $H \parallel c$) and the relation of $\chi_{Landau} \approx -1/3 \chi_{Pauli}$ when ignoring the core and orbital diamagnetism, $\chi_{Pauli} \approx 2.81 \times 10^{-3}$ and 7.04 $\times$ 10$^{-3}$ emu mol f.u.$^{-1}$ Oe$^{-1}$ for $H \parallel ab$ and $H \parallel c$. The estimate of the Wilson’s ratio ($R_W = \pi^2 k_B^2 / 3 J (\gamma \chi_{Pauli})$) gives large values $R_W = 4.26$ and 10.68 for $H \parallel ab$ and $H \parallel c$. This value is also larger than that derived from polycrystalline ($R_W = 1.7$) [19]. Such large values have been usually found in the heavy Fermi liquids ($R_W = 1–6$) [40]. However, large $R_W$ values also occur in systems with a magnetic instability or a strong exchange enhanced paramagnetic state [41].

4. Conclusion

In summary, we synthesized K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystals using the self-flux method. Different from polycrystals, there are small K and Ni deficiencies, similar to the iron based counterpart K$_3$Fe$_2$$_{y}$Se$_2$. Resistivity measurements indicate...
that the K$_{0.95}$Ni$_{1.86}$Se$_2$ single crystal does not exhibit a superconducting transition down to 0.3 K, in contrast to polycrystals. Therefore, the superconducting state is rather sensitive to K and Ni stoichiometry, similar to KFe$_2$Se$_2$. Our results suggest a transition to a heavy fermion state at low temperature.

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