Superconductivity in a new layered nickel selenide CsNi$_2$Se$_2$

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Abstract
The physical properties of CsNi$_2$Se$_2$ were characterized by electrical resistivity, magnetization and specific heat measurements. We found that the stoichiometric CsNi$_2$Se$_2$ compound undergoes a superconducting transition at $T_c = 2.7$ K. A large Sommerfeld coefficient $\gamma_n$ ($\sim 77.90$ mJ/mol K$^{-2}$) was obtained from the normal state electronic specific heat. However, the Kadowaki–Woods ratio of CsNi$_2$Se$_2$ was estimated to be about $0.041 \times 10^{-5}\mu$cm$^2$/mol K$^2$/mJ$^2$, indicating the absence of strong electron–electron correlations. In the superconducting state, we found that the zero-field electronic specific heat data, $C_n(T)$ ($0.5 \leq T < 2.7$ K), can be fitted well with a two-gap BCS model, indicating the multi-gap feature of CsNi$_2$Se$_2$. The comparison with the density functional theory (DFT) calculations suggested that the large $\gamma_n$ in these nickel selenide superconductors may be related to the large density of states (DOS) at the Fermi surface.

Keywords: nickel selenide superconductor, multi-gap, large Sommerfeld coefficient

(Some figures may appear in colour only in the online journal)
reveal the weak correlation feature in these Ni-chalcogenide superconductors. Instead, they suggested that the large $\gamma$ may be ascribed to the large density states and the Van Hove singularity in the vicinity of the Fermi energy [12–14].

Although the Ni-chalcogenide superconductors have been studied for several years, the superconductivity in the single crystals has only been realized in TlNi$_2$Se$_2$[10] and TlNi$_2$Te$_2$[15] in our group. To understand the intrinsic properties, more superconducting materials, especially the alkali metal compounds, need to be investigated. In this paper, we successfully grew CsNi$_2$Se$_2$ single crystals and conducted the measurements of resistivity, magnetization and specific heat down to $T = 0.5$ K. It was found that the stoichiometric CsNi$_2$Se$_2$ compound undergoes a superconducting transition at $T_{c}^{\text{ onset}} = 2.7$ K, which is very different from that in K$_{0.95}$Ni$_{1.06}$Se$_2$ single crystal [11]. At low temperatures, a large Sommerfeld coefficient, $\gamma_r$ ($\sim$77.90 mJ/mol K$^{-2}$), was obtained from the normal state electronic specific heat. We also found that in the superconducting state, the zero-field electronic specific heat data, $C_V(T)$ (0.5 K $\leq T < 2.7$ K), can be well fitted using a two-gap BCS model, indicating the multi-gap feature of CsNi$_2$Se$_2$. In the end, density functional theory (DFT) calculations were performed for TlNi$_2$Se$_2$, KNi$_2$Se$_2$ and CsNi$_2$Se$_2$, respectively, and the result was compared with their corresponding large $\gamma_r$. It suggested that the large $\gamma_r$ may be related to the large DOS at the Fermi surface in these nickel selenide superconductors.

Large plate-like single crystals of CsNi$_2$Se$_2$ were grown using a self-flux method. First, the precursor Cs$_2$Se was prepared by heating Cs and Se powders at 200°C. Then, Cs$_2$Se, Ni and Se powders were mixed in an appropriate stoichiometry and were put into alumina crucibles and sealed in an evacuated silica tube. The mixture was heated up to 1000°C and kept over 3 hours. Then the melting mixture was cooled down to 700°C at a cooling rate of 3°C h$^{-1}$. Finally the furnace was cooled to room temperature after shutting down the power. The structure of single crystals was characterized by x-ray diffraction (XRD). To avoid exposure to air, the sample was sealed using N2-gas during the XRD data collecting. In the powder XRD patterns (figure 1), all peaks can be well indexed with a ThCr$_2$Si$_2$-type structure (space group: $I4/mmm$). The lattice parameters, $a = 3.988\,\text{Å}$ and $c = 14.419\,\text{Å}$, were obtained by fitting the XRD data, indicating a larger unit cell than that of KNi$_2$Se$_2$ and TlNi$_2$Se$_2$. The elemental analysis was performed using an energy-dispersive x-ray spectroscopy (EDX) in a Zeiss Supra 55 scanning electron microscope. The EDX results indicate that the crystals are rather homogenous and the determined average atomic ratios are Cs:Ni:Se = 1.02:2.03:2.00 when fixing Se stoichiometry to be 2, confirming the stoichiometry of CsNi$_2$Se$_2$. The $ab$-plane $\rho(T)$ measurements were performed by the standard four-probe technique using the Quantum Design Physical Properties Measurement System PPMS-9. Temperatures down to 0.5 K were obtained using a 3He attachment to the PPMS. The heat capacity measurements were carried out using the relaxation method. The magnetic susceptibility was measured using the Quantum Design MPMS-SQUID.

Figure 2(a) shows the electrical resistivity in the $ab$-plane, $\rho_{ab}(T)$, as a function of temperature for CsNi$_2$Se$_2$ crystal. The value of $\rho_{ab}(300\,\text{K})$ and $\rho_{ab}(300\,\text{K})$ (not shown here) is about $204\,\mu\Omega$ cm and $572\,\mu\Omega$ cm, respectively. Then the $\rho_{c}/\rho_{ab}$ is calculated to be 2.8, indicating that the anisotropy is not so large, although CsNi$_2$Se$_2$ has a layered structure. Upon cooling down from room temperature, $\rho_{ab}(T)$ exhibits metallic behavior. In the normal state, no abnormal change in $\rho_{ab}(T)$ was observed, which occurs in both iso-structural BaNi$_2$As$_2$[3] and SrNi$_2$P$_2$[5] compounds, corresponding to the structural transition from a tetragonal at higher temperatures to a triclinic at lower temperatures. At $T_c \sim 2.7$ K, the $\rho_{ab}(T)$ drops to zero abruptly, suggesting that a superconducting transition occurs. It is also confirmed by a large diamagnetic signal (see the inset (iii) of figure 2) and a specific heat jump at $T_c$ as shown in figure 2(d). The residual resistivity ratio (RRR = $\rho_{ab}(300\,\text{K})/\rho_{ab}(3\,\text{K}) \sim 37$) and superconducting transition width $\Delta T_c \sim 0.1$ K reflect the high quality of the single crystals. At low temperatures (3 K $\leq T < 20$ K), it was found that the $\rho_{ab}(T)$ can be well fitted using the equation $\rho_{ab}(T) = \rho_{0} + AT^2$, where $\rho_{0} = 5.368\,\mu\Omega$ cm and $A = 2.474 \times 10^{-10}\mu\Omega$ cm K$^{-2}$, suggesting a Fermi liquid ground state. Combining the values of the Sommerfeld coefficient $\gamma_r$ discussed below, the Kadowaki–Woods ratio, $A/\gamma_r^2$, was estimated to be $0.041 \times 10^{-5}\mu\Omega$ cm(mol K$^2$/mol m$^2$). This value is one order of magnitude smaller than that for the standard heavy-fermion systems ($\sim 10^{-2}\mu\Omega$ cm(mol K$^2$/mol m$^2$)), and is quite similar to that for many transition metals ($\sim 0.04 \times 10^{-5}\mu\Omega$ cm(mol K$^2$/mol m$^2$)).[17, 18] We suggest that this result may indicate the absence of strong correlation in this compound, which is consistent with the previous results [12–14].

Figure 2(b) is the $\rho_{ab}(T)$ of CsNi$_2$Se$_2$ at low temperatures measured at various magnetic fields applied in the $c$ axis. The transition temperature $T_c$ shifts to a lower temperature in external magnetic fields. Using the middle superconducting transition temperature in $\rho_{ab}(T)$, the upper critical field $H_{c2}$ is plotted as a function of temperature in the inset (ii) of figure 2(b). According to the Ginzburg–Landau theory, the zero temperature upper critical field $H_{c2}(0)$ can be estimated.
by using the formula \( H_{c2}(T) = H_{c2}(0)(1 - t^2)/(1 + t^2) \), where \( t \) is the reduced temperature \( t = T/T_c \). The fitting result yields the value of \( \mu_0 H_{c2}(0) = 2 \) Tesla, which is 2.5 times that of TI\sub{Ni\textsubscript{2}Se\textsubscript{2}}\cite{10}. The superconducting coherence length \( \xi_0 \) can be estimated from the relation \( \xi_0 = [\mu_0 / 2\pi H_{c2}]^{1/2} \), yielding \( \xi_0 = 12.8 \) nm. The normal state magnetic susceptibility, \( \chi_{ab}(T) \), for CS\sub{Ni\textsubscript{2}Se\textsubscript{2}} crystal, is plotted as a function of temperature in figure 2(c). It seems nearly temperature independent at high temperatures, consistent with previous reports of Pauli paramagnetism \cite{16}. At low temperatures, it exhibits a Curie-tail-like behavior, which may be due to the existence of magnetic impurity (as shown as the fitting blue line in figure 2(b)) corresponding to < 1.00 mol % of an \( S = 1 \) impurity, e.g. Ni\textsuperscript{2+}). However, we cannot exclude the effect of spin fluctuation at low temperatures, which may play an important role in the emergence of superconductivity.

In the nickel chalcogenide superconductors, superconductivity always accompanies a large Sommerfeld coefficient \( \gamma \) at low temperature, which may imply the non-trivial pairing mechanism. So we carried out detailed measurements of the specific heat \( C(T, H) \) for CS\sub{Ni\textsubscript{2}Se\textsubscript{2}} crystal. Figure 2(d) shows the \( C(T, H)/T \) as a function of \( T^2 \), measured under 0 T, and 2 T field, respectively. For the normal state specific heat \( C_N(T) \), a linear fit of the data from 0.5 K to 8 K to \( C(T) = \gamma + \beta T^2 \) gives \( \gamma = 77.90 \text{ mJ/mol K}^{-2} \) and \( \beta = 3.32 \text{ mJ/mol K}^{-4} \), which implies a Debye temperature \( \Theta_D \) of 139 K.
Compared with the value of KNiSe₂ (~44 mJ/mol K⁻²) [6] and TlNi₂Se₂ (~84 mJ/mol K⁻²) [10], the Sommerfeld coefficient γᵣ for CsNi₂Se₂ is much larger. It can even be compared with that for KFe₃As₂ (~94 mJ/mol K⁻²), which is widely believed to be an unconventional superconductor [19].

The electronic specific heat, Cₑ(T), in the superconducting state is obtained by the deduction of phonon contribution (βT⁴) from the total C(T). As shown in figure 3(a), the normalized specific heat jump at Tₑ (∆C/(γᵣTₑ)), is about 1.44, consistent with the theoretical value (1.43) of the well-known BCS theory. Then, we analyze the data by fitting Cₑ(T) with different gap functions. First, we consider the case of a single gap ∆₁(T). The temperature dependence is taken to be the same as in the BCS theory, i.e. ∆(T) = ∆₁e⁻¹(B/T) , where β is the normalized BCS gap at the reduced temperature T/Tₑ as tabulated by Mühlschlegel [20]. For a standard BCS-type superconductor, the thermodynamic properties, entropy (S) and Cₑ, can be written as:

\[
S = \frac{6\gamma₀}{\pi²} \frac{\Delta₀}{k_B} \int_{0}^{\infty} \ln f + (1 - f) \ln(1 - f) \, df 
\]

\[
Cₑ = \frac{\partial S}{\partial T} 
\]

where f = [exp(βE) + 1]⁻¹ and β = (k_B T)⁻¹. The energy of the quasi-particles is given by E = [ε² + Δ²(ε)]¹/², where ε is the energy of the normal electrons relative to the Fermi surface. The integration variable is y = ε/Δ₀. Considering the multi-band feature of these nickel chalcogenide superconductors as indicated in [12, 13, 21], we also carried out the fitting using a two-gap model, where the total specific heat can be considered as the sum of the contributions of each band calculated independently according to equations (1) and (2).

To obtain more information on the superconducting gap, we also carried out the low-temperature specific heat measurements under various magnetic fields, as shown in figure 3(b). At zero field, the linear extrapolation of C/T versus T² to T = 0 K gives a 'residual' Sommerfeld coefficient of γᵣ = 5.5 mJ/mol K⁻². Considering the air sensitive nature of CsNi₂Se₂, we may ascribe it to the existence of a small fraction (~6.8%) of the non-superconducting phase. With increase of the magnetic field, the magnitude of the specific heat jump at Tₑ decreases, and the linear electronic specific heat coefficient, γ(H), increases. In this study, the field dependence of [γ(H)−γ(0)] obeys the Volovik relation (i.e. ∝H¹/²) very well (see inset), exactly as observed in TlNi₂Se₂. This behavior was once considered a common feature of the d-wave superconductors, where the H¹/² term arises from a Doppler shift of the quasi-particle excitation spectrum in the outer regions of the vortices. Yet this behavior may not be always so unique, because it was also observed in other s-wave superconductors, such as NbSe₂[22, 23], V₃Si [24] and CeRu₂[25].

As mentioned above, CsNi₂Se₂ seems to have similar physical properties to the other nickel chalcogenide superconductors. To deepen our understanding, we summarized the physical properties of KNi₂Se₂, KNi₂S₂, TlNi₂Se₂, TlNi₂S₂ and CsNi₂Se₂, and present them in table 1. It can be seen that the CsNi₂Se₂ exhibits the largest resistivity anisotropy R₆/R₁₀, which could be ascribed to the longer c axis. Most interesting for CsNi₂Se₂ is that it exhibits the largest Sommerfeld coefficient γᵣ and critical field Hₖ compared with the other nickel chalcogenide superconductors and deserves further investigation.
In summary, we have successfully grown CsNi2Se2 single crystals. The measurements of resistivity, magnetization and specific heat were carried out down to $T = 0.5$ K. It was found that the stoichiometric CsNi2Se2 compound is a superconductor with $T_c = 2.7$ K. A large Sommerfeld coefficient, $\gamma_n (\sim 77.90 \, \text{mJ/mol K}^{-2})$, was obtained from the normal state electronic specific heat. However, the Kadowaki–Woods ratio of CsNi2Se2 was estimated to be about $0.041 \times 10^{-5} \, \mu \Omega \text{cm(mol K}^2\text{/mJ)}^2$, comparable with those for transition metals, which may indicate the absence of strong electron–electron correlation. In the superconducting state, we found that the zero-field electronic specific heat data, $C_{es}(T) (0.5 \, \text{K} \leq T < 2.6 \, \text{K})$, can be well fitted with a two-gap BCS model, indicating the multi-gap feature of CsNi2Se2. In the end, density functional theory calculations were performed for TlNi2Se2, KNi2Se2 and CsNi2Se2, respectively. The result indicated that the ratio of the DOS value at $E_F$ is generally consistent with the corresponding ratio of their $\gamma_n$, suggesting that the large $\gamma_n$ may be related to the large DOS at the Fermi surface.

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