CuNNi$_3$: a new nitride superconductor with antiperovskite structure

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Abstract

We have successfully synthesized a new Ni-based antiperovskite nitride, CuNNi$_3$, which exhibits superconductivity with a transition temperature $T_c$ of 3.2 K. This compound is the second nitride superconductor in the Ni-based antiperovskites. We report the synthesis and physical properties of CuNNi$_3$, characterized via x-ray diffraction, magnetization, resistivity, and heat capacity measurements. The temperature dependence of the specific heat is consistent with an isotropic s-wave gap ($\Delta_0 = 0.42$ meV). The estimated electron–phonon coupling strength ($\lambda_{ep} = 0.53$) suggests that the superconductivity in CuNNi$_3$ is induced by electron–phonon coupling, and the gap ratio ($2\Delta_0/k_B T_c$) of 3.05 indicates that it is a weak coupling superconductor. Furthermore, the relatively high Ginzburg–Landau parameter ($\kappa = 24.6$) signifies that CuNNi$_3$ is a type II superconductor.

1. Introduction

Since the superconductivity of MgCNi$_3$ was discovered [1], many experimental and theoretical studies have been made to find new superconductors among the antiperovskite compounds MXNi$_3$, where M is mostly a divalent or trivalent metal and X is C or N. Among the MCNi$_3$ ($M = \text{Cd, Zn, Al, Ga, In}$) carbide antiperovskites [2–6], only CdCNi$_3$ demonstrates superconductivity with a $T_c$ of 3.4 K. Recently, several new nitride antiperovskites, MNNi$_3$ ($M = \text{Zn, In, Cd}$), have been synthesized [7–11], and superconductivity with a $T_c$ of 3 K was found in ZnNNi$_3$. Both InNNi$_3$ and CdNNi$_3$ exhibit metallic behavior and show no superconductivity down to 2 K [10, 11]. The discovery of superconductivity in ZnNNi$_3$ has led us to study other nitride antiperovskites, MNNi$_3$. The mechanical and electronic properties of MNNi$_3$ ($M = \text{Zn, Mg, Cd, Al, Ga, In, Sn, Sb, Pd, Cu, Ag, Pt}$) have been studied using various theoretical methods [12–22]. First principle band calculations for ZnNNi$_3$ revealed that a large and narrow peak of mainly Ni 3d character is located just below the Fermi energy ($E_F$) in the density of states (DOS) curves [12, 13, 21]. According to the rigid band approximation, hole doping in ZnNNi$_3$ could increase the density of states at the Fermi level. If we consider CuNNi$_3$ as a hole doped ZnNNi$_3$, the $E_F$ of CuNNi$_3$ should be located closer to the Ni 3d peak, i.e., in the region of quite high DOS, which is favorable for superconductivity. Helal and Islam studied the elastic, electronic, and optical properties of MNNi$_3$ ($M = \text{Zn, Sn, and Cu}$) by first-principle calculations in 2011 [21]. They found that the electronic band structures of SnNNi$_3$ and CuNNi$_3$, two ‘hypothetical’ compounds at that time, show metallic behavior just like the superconducting ZnNNi$_3$, and expected that their calculations would motivate experimental study on SnNNi$_3$ and CuNNi$_3$. There is no information in the current literature concerning the preparation and superconductivity of CuNNi$_3$. In this paper we report the synthesis, crystal structure and superconducting and normal-state properties of CuNNi$_3$. From the experimental data, we determined the lower
critical field $H_c(0)$, upper critical field $H_{c2}(0)$, coherence length $\xi(0)$, penetration depth $\lambda(0)$, Ginzburg–Landau (GL) parameter $\kappa(0)$, electronic specific-heat coefficient $\gamma$ and Debye temperature $\Theta_D$ for CuNNi$_3$.

2. Experimental details

Polycrystalline samples of CuNNi$_3$ were synthesized by solid–gas reactions. Stoichiometric Cu (99.7%) and Ni (99.8%) powders were mixed and ground thoroughly. The mixture was heated in a tube furnace at 673 K for 3 h in flowing NH$_3$ (99.9%, 80 ml min$^{-1}$). The as-prepared powders were thoroughly reground, pelletized, initially sintered at 773 K for 6 h and finally sintered at 833 K for 6 h in flowing NH$_3$. The powder x-ray diffraction (PXRD) data of the sample were collected on an MXP18A-HF diffractometer with Cu Kα radiation. The Rietveld refinement of the diffraction data was performed using the program RIETAN-2000 [23]. The chemical composition of the sample was analyzed by an energy dispersive x-ray spectrometer (EDXS) attached to a scanning electron microscope (XL30 S-FEG). Additionally, an elemental analyzer (Elementary Vario Micro Cube) was used to analyze the nitrogen content. Magnetic measurements were performed in a superconducting quantum interference device magnetometer (MPMS XL-7, Quantum Design). All $M(H)$ curves were taken in the zero-field-cooled (ZFC) mode with initial temperature up to 6 K. A low-field sweep rate of 20 Oe min$^{-1}$ was selected to measure isothermal magnetization curves.

3. Results and discussion

Our CuNNi$_3$ sample is a stoichiometric compound based on the results of the EDX analysis, elemental analysis and the Rietveld refinement of the PXRD data. EDX analysis revealed that the actual Cu/Ni atomic ratio is consistent with the nominal composition (CuNNi$_3$) within the experimental error. The elemental analysis showed that the weight percentage of nitrogen is 5.5%. This result corresponds to $y = 0.99$ in CuNNi$_3$. The diffraction peaks could be indexed well with a cubic antiperovskite unit cell. Using the antiperovskite structure as a starting model, the lattice parameter and the occupancy of the nitrogen atom were refined using the Rietveld method. The occupancy of the nitrogen atom was refined together with other structural parameters. The Rietveld refinement pattern for CuNNi$_3$ is shown in figure 1. The refined structural parameters and $R$ factors are listed in table 1.

Figure 3 shows the specific heat divided by the temperature ($C/T$) as a function of $T^2$ under different magnetic fields from 0 to 1 T. The bulk nature of the superconductivity and the good quality of the sample are confirmed by a sharp anomaly at 3.2 K under $H = 0$, which is consistent with the $T_c$ determined by the susceptibility and resistivity data. Regarding the relatively low $T_c$ of the sample, the normal-state specific heat could be extracted easily with the simple relation $C/T = \gamma_n + \beta T^2$, where the first and the second terms correspond to the electronic and phonon contributions, respectively. The solid line in figure 3 shows the curve fitted by the formula $C/T = \gamma_n + \beta T^2$. From this fitting, $\gamma_n$ and $\beta$ are estimated to be 39.27 mJ (mol K$^2$)$^{-1}$ and 0.392 mJ (mol K$^2$)$^{-1}$, respectively. By extrapolating the low temperature data for zero field down to 0 K, a small residual value $\gamma_0 = 0.75$ mJ (mol K$^2$)$^{-1}$ is obtained, indicating a small non-superconducting volume fraction of

![Figure 1. The Rietveld refinement pattern for CuNNi$_3$. The crosses (+) correspond to the experimental data. The solid line represents the calculated pattern. The short vertical lines mark the positions of allowed reflections. The curve at the bottom of the plot gives the difference between the experimental and calculated patterns. The inset shows the crystal structure of CuNNi$_3$.](image)

![Table 1. Refined structural parameters for CuNNi$_3$.](image)
about 2%. The normal state Sommerfeld constant for the present sample could be determined from the relation $\gamma_\text{c} = \gamma_n - \gamma_0$, yielding 38.52 mJ (mol K$^2$)$^{-1}$. It is noticeable that the value of $\gamma_\text{c}$ determined in our measurement is higher than that of ZnNNi$_3$ [7], indicating the higher density of states in CuNNi$_3$. Using the relation $\Theta_\text{D} = (12\pi^4 nR)^{1/3}$, where $R = 8.314$ J (mol K)$^{-1}$ and $n = 5$ is the number of atoms in one unit cell, we get the Debye temperature $\Theta_\text{D} = 291$ K.

The electron–phonon coupling constant ($\lambda_{\text{ep}}$) can be estimated from the McMillan formula [24]

$$T_c = \frac{\Theta_\text{D}}{1.45 \exp \left[ - \frac{1.04(1 + \lambda_{\text{ep}})}{\lambda_{\text{ep}} - \mu^*(1 + 0.62\lambda_{\text{ep}})} \right]}$$

(1)

where $\mu^*$ is the Coulomb pseudopotential taking a value of about 0.11. Using $\Theta_\text{D} = 291$ K and $T_c = 3.2$ K, we obtain $\lambda_{\text{ep}} = 0.53$. Therefore, we can say that CuNNi$_3$ is a weak coupling superconductor.

Figure 4 shows the electronic specific heat ($C_\text{e}$) below $T_c$, obtained from the zero field data. Three models were used to fit the data, $C \propto T^2$, $T^3$, and $\exp(-b/\beta T)$, expected for line nodes, point nodes, and a fully gapped model, respectively. The small residual linear term $\gamma_0T$ of 0.75 $T$ (mJ mol$^{-1}$ K$^{-1}$) was held constant throughout the fits. The best fit is provided by a fully gapped model. An s-wave BCS model of the entire $C_\text{e}$ data gives an isotropic gap value $\Delta_0 = 0.42$ meV. The ratio $2\Delta_0/k_B T_c = 3.05$ obtained here is close to the prediction for the weak coupling limit ($2\Delta_0/k_B T_c = 3.53$), indicating a weak coupling strength. The inset of figure 4 shows the superconducting part of the electronic specific heat $\Delta C(T) = C(T) - \beta T^2 - \gamma_0 T$, obtained from the zero field data. The superconducting transition temperature $T_c = 3.1$ K has been estimated by an entropy conserving construction (solid line in the inset of figure 4). This value agrees well with the transition temperature $T_c = 3.2$ K derived from resistivity and dc susceptibility data. The normalized specific heat jump at $T_c = 3.1$ K is $\Delta C/\gamma_0 T_c = 1.21$. This is close to the BCS value (1.43), indicating that CuNNi$_3$ is a weak electron–phonon coupling superconductor.

Dominance of an s-wave channel is supported by measurements of the magnetic field dependence of the Sommerfeld parameter $\gamma_\text{c}(H)$ [25]. It is known that the electronic specific heat in a magnetic field can be expressed
The magnetic field dependence of $\Delta \gamma_e$ as a function of the magnetic field $H$ below 0.6 T. The solid line corresponds to a linear ($\sim H$) relation and the dotted line represents the nonlinear ($\sim H^{1/2}$) relation.

by $C_e(T, H) = C_e(T, H = 0) + \gamma_e(H)T$. The magnetic field dependence of $\gamma_e(H)$ is associated with the form of the gap function of the superconductor. For a highly anisotropic gap or a gap with nodes, $\gamma_e(H) \propto H^{1/2}$ is predicted [26]. In contrast, for a fully gapped superconductor, $\gamma_e(H)$ is expected to be proportional to $H$ [27]. Figure 5 shows the magnetic field dependence of $\Delta \gamma_e = \gamma_e(H) - \gamma_e(0)$ as a function of the magnetic field $H$ at $T = 0.4$ and 0.8 K. As shown in figure 5, the field-linear increase in $\Delta \gamma_e(H)$ suggests that most electronic states near the Fermi energy are gapped in CuNNi3 and clearly is at odds with a $\Delta \gamma_e(H) \propto H^{1/2}$ dependence. This linear relation is demonstrated well by the data below 0.6 T, providing more evidence for the s-wave pairing.

Figure 6 shows the temperature dependence of the resistivity under different dc magnetic fields.

Figure 7. The temperature dependence of the upper critical field obtained by resistivity (open squares) and specific-heat (red circles) measurements. The solid line is a fit of the Ginzburg–Landau (GL) formula.

The extrapolation yielded $\mu_0H_{c2}(0) = 1.21$ T, which is close to the WHH estimate.

The low critical field values, $\mu_0H_{c1}(T)$, were determined from the low-field magnetization curves. The inset of figure 8 shows the initial part of the magnetization curves over the temperature range from 2.0 to 3.0 K. The low-field parts of these magnetization curves almost overlap on a common Meissner line (as shown by a solid line in figure 8) due to the Meissner effect. Therefore, $\mu_0H_{c1}(T)$ could be determined at the point where the magnetization curve starts to deviate from the ‘Meissner line’. Figure 8 shows the temperature dependence of $\mu_0H_{c1}(T)$. The data for $\mu_0H_{c1}(T)$ could be fitted with the empirical formula $\mu_0H_{c1}(T) = \mu_0H_{c1}(0)[1 - (T/T_c)^2]^{2/3}$ [29] and $\mu_0H_{c1}(0)$ was determined to be 4.0 mT.

With these results for $\mu_0H_{c1}(0)$ and $\mu_0H_{c2}(0)$, we can estimate several superconducting parameters for CuNNi3. The superconducting coherence length $\xi(0)$ and penetration depth $\lambda(0)$ can be estimated by using the relations $\xi(0) = [\phi_0/(2\pi H_{c2}(0))]^{1/2}$ and $\lambda(0) = [\phi_0/(2\pi H_{c1}(0))]^{1/2}$, where $\phi_0$ is the quantum of flux. The values of $\xi(0)$ and $\lambda(0)$ come out to be 165 Å and 4058 Å, respectively. Consequently, the
The temperature dependence of $\mu_0 H_{c1}$. The inset shows magnetization curves at several temperatures used for determining $H_{c1}$.

Ginzburg–Landau parameter $\kappa = \lambda(0)/\xi(0)$ is 24.6, showing that this system is a type II superconductor. Using these parameters, the thermodynamic critical field $\mu_0 H_c(0)$ could be obtained from the following relation [25]:

$$H_{c1} H_{c2} = H_c^2(0) \ln \kappa.$$  

We find that the thermodynamic critical field $\mu_0 H_c(0)$ is 38.9 mT.

The superconducting condensation energy ($E_c$) provides a stringent self-consistency check on the derived parameters [25]. Therefore, we calculate $E_c$ with the specific-heat data as follows. The entropy difference between the normal state and the superconducting state is obtained by

$$\Delta S(T) = \int_0^T (\Delta C/T) dT,$$

and $E_c$ is determined through

$$E_c = \int_{T_c}^{T_f} \Delta S(T) dT.$$  

Figure 9 shows the temperature dependence of the condensation energy $E_c$, which is about 76.6 mJ mol$^{-1}$ at 0 K. The inset shows the entropy difference between the normal state and the superconducting state. Actually, $E_c$ can also be calculated by the following equation [30]:

$$E_c = \alpha N(E_F) \Delta \gamma / 2 = \alpha \frac{3}{4 \pi^2 k_B^2} \gamma_\alpha \Delta_0^2.$$  

For a BCS s-wave superconductor, $\alpha = 1$, using $\gamma_\alpha = 38.52$ mJ (mol K$^2$)$^{-1}$ and $\Delta_0 = 0.42$ meV, we obtain a value of $E_c = 71.1$ mJ mol$^{-1}$, which is close to the value of 76.6 mJ mol$^{-1}$ obtained above. The consistency between the $E_c$ values obtained by two different methods verifies the validity of the determined $\gamma_\alpha$ and $\Delta_0$. The thermodynamic critical field $\mu_0 H_c(0)$ can also be obtained by the relation $\mu_0 H_c^2(0)/2 = F_N - F_S = \int_{0}^{1} (\Delta C/T) dT$. This gives the value of $\mu_0 H_c(0)$ as 38.7 mT, which is in excellent agreement with that derived from the critical fields.

Table 2 summarizes the superconducting- and normal-state parameters that we obtained for CuNNi$_3$ and, for comparison, those of ZnNNi$_3$ [7] are also shown.

### Table 2. Superconducting- and normal-state properties for CuNNi$_3$ and ZnNNi$_3$.

| Parameter   | ZnNNi$_3$ | CuNNi$_3$ |
|-------------|-----------|-----------|
| $T_c$ (K)   | 3.0       | 3.2       |
| $\mu_0 H_{c1}$ (mT) | 6.9       | 4.0       |
| $\mu_0 H_{c2}$ (T) | 0.96      | 1.21      |
| $\mu_0 H_c(0)$ (mT) | —        | 38.7      |
| $\xi(0)$ (Å) | 185       | 165       |
| $\lambda(0)$ (Å) | 3089      | 4058      |
| $\kappa(0)$ | 17        | 24.6      |
| $2\Delta(0)/k_B T_c$ | —        | 3.05      |
| $\Delta C/\gamma_\alpha T_c$ | —        | 1.21      |
| $\gamma$ (mJ (mol K$^2$)$^{-1}$) | 13        | 39.27     |
| $\beta$ (mJ (mol K$^2$)$^{-1}$) | 0.26      | 0.392     |
| $\Theta_B$ (K) | 336       | 291       |

4. Conclusion

In summary, we succeeded in synthesizing a new nitride superconductor, CuNNi$_3$, with antiperovskite structure. The nitrogen content in the CuNNi$_3$ sample was determined to be close to stoichiometric by elemental analysis and Rietveld refinement. The superconducting- and normal-state properties of CuNNi$_3$ were determined by means of magnetic susceptibility, electrical resistivity, and specific-heat measurements. An analysis of the temperature dependence of the specific heat shows that the superconducting properties of CuNNi$_3$ can be interpreted to be close to stoichiometric by elemental analysis and Rietveld refinement. The superconducting properties of CuNNi$_3$ and ZnNNi$_3$ have been investigated using first-principle calculations [21], no theoretical calculation results
on the superconductivity of CuNNi$_3$ have been reported. Recently, some theorists in our institute have studied the superconducting properties of CuNNi$_3$ using first-principle calculations, and obtained a superconducting transition temperature which is close to our experimental value. Their research results will be published soon.

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