Normal state resistivity, upper critical field and Hall effect of superconducting perovskite $MgCNi_3$

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Abstract

The normal state resistivity, upper critical field $H_{c2}$ and Hall coefficient $R_H$ in superconducting perovskite $MgCNi_3$ ($T_c \approx 8K$) have been studied. Above 70 K, $\rho(T)$ fits well curve predicted by Bloch-Grüneisen theory consistently with electron-phonon scattering. $H_{c2}(0)$ was estimated to be about 15.0 Tesla within the weak-coupling BCS theory, and the superconducting coherence length $\xi(0)$ is approximately 47 Å. $R_H$ of $MgCNi_3$ is negative for the whole temperature range which definitely indicates that the carrier in $MgCNi_3$ is electron-type. $R_H$ is temperature independent between $T_c$ and $\sim 140$ K. Above $\sim 140$ K, the magnitude of $R_H$ decreases as temperature rises. At $T = 100$ K, the carrier density is $1.0 \times 10^{22}/cm^3$, which is comparable with that in perovskite $(Ba, K)BiO_3$, and less than that of the metallic binary $MgB_2$.

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INTRODUCTION

The recent discovery of superconductivity in the simple intermetallic compound $MgB_2$ has attracted great attention because of its relatively high transition temperature ($T_c = 39$ K) and the highly promising potential application. It suggests that intermetallic compounds with simple structure types are worth serious reconsideration as sources of new superconducting materials. More recently, the observation of superconductivity at 8 K in the perovskite structure intermetallic compound $MgCNi_3$ indicates that $MgB_2$ will not be the only one of its kind within the chemical paradigm for new superconducting materials.

The variable stoichiometry compound $MgC_xNi_3$, for $0.5 < x < 1.25$, has been reported and assigned to the perovskite structure type by analogy in 1950's, but neither its crystal structure nor its physical properties had been determined. By using powder neutron diffraction, He et al. has found that the superconducting phase in nominal composition $MgC_{1.25}Ni_3$ is $MgC_{0.96}Ni_3$ with the classical cubic perovskite structure, space group $Pm − 3m$. They also determined the electron-phonon coupling constant $\lambda_{ph} \sim 0.77$ by specific heat measurements. Although this value of $\lambda_{ph}$ is in the range of conventional phonon, more properties of both normal state and superconducting state need to be clarified to determine the microscopic mechanism of superconductivity in this compound. A complete structural and electronic equivalence of the superconducting oxide perovskites like $(Ba, K)BiO_3$ (BKBO) and intermetallic perovskite superconductor $MgCNi_3$ has been considered. For the oxide perovskites, an important characteristic of the superconductivity is that the electronic states at the Fermi energy involve holes in the oxygen electronic orbitals. Preliminary band structure calculations have shown that the electron states at the Fermi surface of $MgCNi_3$ are dominated by the $3d$ orbitals of Ni, so the conduction may also involve holes in Ni $d$-states. Although it is expected that the carriers should be holes as monovalent potassium replaces divalent barium in BKBO, the Hall coefficient measurement on BKBO thin films indicates that the charge carriers are electrons. Therefore the measurement of the Hall effect in $MgCNi_3$ should be very interesting.
In this paper, we report the study of the normal state resistivity and the first measurements of the upper critical field $H_{c2}$ and Hall coefficient $R_H$ for superconducting perovskite $MgCNi_3$. It is found that at high temperature (above 70 K) $\rho(T)$ can be fitted well by Bloch-Grüneisen theory. $H_{c2}-T$ phase diagram was obtained. The sign and temperature dependence of $R_H$ were determined by Hall effect measurement, which definitely indicates that the carrier in $MgCNi_3$ is electron-type.

**EXPERIMENT**

To obtain perfectly stoichiometric composition $MgCNi_3$ with highest $T_c$, excess carbon is required. Due to the volatility of Mg during the synthesis of this compound, excess Mg is needed. In this study, sample with nominal formula $Mg_{1.2}C_{1.4}Ni_3$ was prepared. Starting materials were bright Mg flakes, fine powders of Ni, and the powders of amorphous carbon with high purity. Starting materials were mixed, ground for a few minutes, and pressed into pellet. The pellet was loaded in a Ta foil, which was in turn sealed in a stainless steel reactor. The above operations were carried out in a glove box with an Ar environment, in which the content of oxygen and water is less than a few ppm. The reactor was fired in a tube furnace under high-pure Ar atmosphere for half an hour at 600°C, followed by an hour at 900°C. After cooling, the sample was reground, pressed into pellet, and sintered for another one hour at 900°C under the same environment. The resulting sample was dense with a length of 7 mm and a width of 2 mm. The structure was characterized by powder x-ray diffraction (XRD) analysis using Rigaku D/max-γA x-ray diffractometer (XRD) with graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). The data were collected over $2\theta$ range from 15° to 75° with a 0.02° step.

In order to obtain a good Hall voltage signal, the sample was mechanically polished until it was very thin (360 µm). The longitudinal and Hall voltages were measured by using the standard dc 6-probe method. The magnetic field was applied perpendicular to the sample surface by using a superconducting magnet system (Oxford Instruments) and
The applied current is 15 mA. The Hall voltage was extracted from the antisymmetric parts of the transverse voltages measured under opposite directions to remove the longitudinal component due to the misalignment of the Hall voltage pads. The Hall voltage was found to be linear in the magnetic field.

RESULTS AND DISCUSSION

Fig. 1 shows temperature dependence of resistivity under zero field and the XRD pattern (inset) for the sample with nominal composition \(Mg_{1.2}C_{1.4}Ni_3\). XRD pattern indicates that the sample is nearly single phase. By the least-square fitting to the positions of 7 Bragg reflection peaks between 2\(\theta\) values of 15\(^\circ\) and 75\(^\circ\), the cubic cell parameter \(a = 3.81154(5) \text{ Å}\) is obtained, being consistent with previous reports. The resistive superconducting transition is very sharp. The midpoint of the resistive transition is 8.0 K, the 90-10% transition width is less than 0.3 K, and the resistive onset temperature is 8.2 K. \(T_c\) of the sample is nearly the same as that reported in Ref. 2. The resistivity ratio \(\rho_{300K}/\rho_{9K}\) is 2.5 which is larger than that in Ref. 2. Also the normal state resistivity is about 3 times larger than that in Ref. 2. It is important to note that the shape of \(\rho(T)\) curve is almost identical to that reported by He et al. One can observe an upward curvature of \(\rho(T)\) curve at low temperature followed by a downward one for higher temperature. It looks like that of conventional metals and different from the simply linear-T dependence observed in copper oxide superconductors. The similar shape of \(\rho(T)\) curve has been observed in BKBO thin film and single crystal in which \(\rho(T)\) fits well curve predicted by Bloch-Grüneisen theory consistently with electron-phonon scattering.

In order to investigate to what extent the resistive behavior is consistent with electron-phonon scattering mechanism, we fit the resistivity data with an explicit form of the Bloch-Grüneisen expression which is valid in the case of an Einstein phonon distribution \(\epsilon = k_B\Theta_E\) as in Ref. 9:

\[
\rho^{-1} = \rho_p^{-1} + (\rho_0 + \rho_{ph})^{-1}
\]  

(1)
\[ \rho_{\text{ph}} = \rho_{t} \coth(\Theta_{E}/2T)[1 + (2/3)\sinh^{2}(\Theta_{E}/2T)]^{-1} \]  

\( \rho_{0} \) and \( \rho_{p} \) are respectively a residual and a parallel resistivity, respectively. \( \rho_{t} \) is a constant. It is found that between 70 K and 300 K \( \rho(T) \) fits well curve by the Bloch-Grüneisen expression. The solid line in Fig.2 represents the result of the best fit to the experimental data. The best fit result gives \( \Theta_{E} = 206(1) \text{ K} \), \( \rho_{0} = 202(1) \mu\Omega\text{cm} \), \( \rho_{p} = 574(1) \mu\Omega\text{cm} \), and \( \rho_{t} = 177(1) \mu\Omega\text{cm} \). The Einstein temperature \( \Theta_{E} \) is comparable with that of BKBO\textsuperscript{4}. Below 70 K, the fitting is not well and gives very low \( \Theta_{E} \). We speculate it that the Einstein phonon distribution is not proper and continuous phonon spectra, such as Debye spectrum, should be adopted at low temperature. We simply fit the low temperature resistivity data using a power law, \( \rho = \rho_{0} + aT^{n} \). The fit result gives \( \rho_{0} = 120.7(1) \mu\Omega\text{cm} \), \( n = 1.46(1) \). The fit curve is also shown as an unbroken line in Fig.2.

Fig. 3 shows the \( \rho(T) \) curves under magnetic fields up to 14 T. The resistive superconducting transition shifts to low temperature with increase of the magnetic field. The onset temperature decreases and the broadening of the superconducting transition is almost absent with the increasing magnetic field. This result is in contrast to the high-\( T_{c} \) cuprate superconductors and similar to A15 intermetallic compounds such as \( \text{Nb}_{3}\text{Sn} \). Fig. 4 shows the \( H_{c2} - T \) phase diagram obtained from the \( \rho \) vs. \( T \) curves at different fields. Here \( T_{c} \) is defined as the intersection of the linear extrapolation of the most rapidly changing part of \( \rho(T) \) and that of the normal state resistivity, as shown in the upper inset of Fig. 4. The lower inset of Fig. 4 is the magnetic field dependence of the resistance of the sample at 2.3 K. Defining \( H_{c2} \) as the intersection of the linear extrapolation of the most rapidly changing part of \( \rho(H) \) and that of the normal state resistivity, one can get \( H_{c2}(2.3K) = 12.5 \text{ T} \), which is in good agreement with the result from temperature dependence \( \rho(T) \). Within the weak-coupling BCS theory, \( H_{c2}(T = 0) \) can be estimated using the Werthamer-Halfand-Hohenberg(WHH) formula\textsuperscript{4},

\[ \mu_{0}H_{c2} = -0.693(dH_{c2}/dT)_{T=T_{c}}T_{c} \]  

which leads to a \( \mu_{0}H_{c2} \) value of 15.0 T. Meanwhile the Pauli-limiting field
\[ \mu_0 H^{Pauli} = 1.24K_BT_c/\mu_B \] (4)

expected within the same weak-coupling BCS theory\textsuperscript{13} is also 15.0 Tesla for \( T_c = 8.12 \) K, inferred from Fig. 4. One can see that \( \mu_0 H^{WHH} \) and \( \mu_0 H^{Pauli} \) agree perfectly with each other. The superconducting coherence \( \xi(0) \) is estimated to be approximately 47 Å, using the Ginzburg-Landau formula for an isotropic three-dimensional superconductor, \( \mu_0 H_{c2} = \Phi_0/2\pi\xi^2(0) \).

Fig. 5 shows the Hall coefficient \( R_H \) from room temperature down to \( T_c \) under 10 T. The two curves in the inset represent the Hall voltage measured at 100 K for opposite magnetic fields up to 10 T. Clearly, the field dependent Hall voltage is symmetric and linear. The \( R_H \) is negative for the whole temperature range. We found that \( R_H \) is essentially temperature independent between \( T_c \) and \( \sim 140 \) K, at least within our experimental accuracy. Above \( \sim 140 \) K, the magnitude of \( R_H \) decreases as temperature increases. It is found that \( R_H(140K)/R_H(295K) \) is about 1.3. At \( T = 100 \) K, \( R_H = -6.1 \times 10^{-10} \) m\(^3\)/C, and the calculated carrier density is \( 1.0 \times 10^{22}/cm^3 \). The main feature of the Hall effect is the negative \( R_H \). It definitely indicates that the carrier in MgCNi\(_3\) is electron-type, which is strongly supported by the negative thermoelectrical power observed from room temperature to 10 K\textsuperscript{14}. The carrier density is comparable with that of BKBO\textsuperscript{7}, and less than that of metallic binary MgB\(_2\)\textsuperscript{15} and larger than that in copper oxide superconductors\textsuperscript{16}. Another feature of the Hall coefficient is the fact that it depends on temperature. For conventional isotropic metal with ordinary electron-phonon scattering mechanism, the Hall coefficient is expected to be temperature-independent. We note that \( R_H \) temperature behavior of MgCNi\(_3\) is very similar to that of \( Ba_{1-x}K_xBiO_3 \) single crystal\textsuperscript{3}. A good example of temperature dependent \( R_H \) is copper based superconducting oxides, in which \( R_H(T) \) is explained by exotic magnetic excitation\textsuperscript{17}. Preliminary band structure calculations have shown that the electron states at the Fermi surface of MgCNi\(_3\) are dominated by the 3\( d \) orbitals of Ni\textsuperscript{6}. The itinerant electrons arise from the partial filling of the nickel \( d \)-states, which generally leads to ferromagnetism as is the case in metallic. The temperature dependence of \( R_H \) may also be ascribed to
magnetic excitations as copper based superconducting oxides. However, $Ba_{1-x}K_xBiO_3$ has no magnetic ion and manifests similar temperature dependence of $R_H$ as $MgCNi_3$, so the temperature behavior of $R_H$ remains an open question.

CONCLUSION

In summary, we have measured the temperature dependence of resistivity, upper critical field and Hall effect for superconducting perovskite $MgCNi_3$. Above 70 K, the normal state $\rho(T)$ behavior follows Bloch-Grüneisen theory consistently with electron-phonon scattering, being similar to that of the three-dimensional BKBO with the same structure. From $H_{c2}-T$ phase diagram, $H_{c2}(0)$ was estimated about 15.0 Tesla within the weak-coupling BCS theory, the superconducting coherence length $\xi(0)$ was found to be approximately 47 Å. Negative $R_H$ definitly suggests that the carrier is electron character, is the same as that in BKBO and different from that in $MgB_2$. At $T = 100$ K, $R_H = -6.1 \times 10^{-10} m^3/C$, and the calculated carrier density is $1.0 \times 10^{22}/cm^3$, which is comparable with that in BKBO, and less than that of $MgB_2$ and larger than that in copper oxide superconductors. $R_H$ is temperature independent between $T_c$ and $\sim 140$ K. Above $\sim 140$ K, the magnitude of $R_H$ decreases as temperature increases. The temperature behavior of $R_H$ remains an open question.

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FIGURE CAPTIONS

FIG 1:
The temperature dependence of resistivity for MgCNi$_3$ sample. Inset: the XRD pattern.

FIG 2:
The temperature dependence of normal state resistivity for MgCNi$_3$ sample. The solid lines are fit of $\rho(T)$ to Bloch-Grüneisen expression and power law, respectively.

FIG 3:
The $\rho(T)$ curves under magnetic fields up to 14 Tesla for MgCNi$_3$.

FIG 4:
Upper critical field $H_{c2}$ as a function of temperature for MgCNi$_3$. The upper inset shows the temperature dependence of sample resistivity under zero magnetic field. The lower inset shows the magnetic field dependence of resistance at $T = 2.3$ K.

FIG 5:
Temperature dependence of Hall coefficient measured under 10 Tesla for MgCNi$_3$. The two lines in the inset represent the Hall voltage measured at 100 K for opposite two directions of the applied field up to 10 T.
FIG. 1

ρ (µΩcm)

T (K)

FIG. 1
FIG. 2

$\rho$ ($\mu\Omega\text{cm}$) vs. $T$ (K)
FIG. 3

$\rho$ ($\mu\Omega\text{cm}$) vs $T$ (K)

$H = 0$ T
$H_{c2}(T)$

$H_{c2} = 12.5 \, T$

$T_c = 8.12 \, K$

$\rho (\mu \Omega \, cm)$

FIG. 4
