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BCS-like superconductivity in $MgCNi_3$

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The low-temperature specific heat $C(T,H)$ of the superconductor $MgCNi_3$ has been measured in detail. $\Delta C/\gamma_n T_c = 1.97$ is estimated from the anomaly at T_c. At low temperatures, the electronic contribution in the superconducting state follows $C_{es}/\gamma_n T_c \approx 7.96\exp(-1.46T_c/T)$. The magnetic-field dependence of $\gamma(H)$ is found to be linear with respect to H. T_c estimated from the McMillan formula agrees well with the observed value. All the specific-heat data appear to be consistent with each other within the moderate-coupling BCS context. It is amazing that such a superconductor unstable to ferromagnetism behaves so conventionally. The Debye temperature $\Theta_D = 287$ K and the normal state $\gamma_n = 33.6$ mJ/mol K^2 are determined for the present sample.

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The recently discovered superconductivity in $MgCNi_3$ has been a surprise.[1] Though with $T_c \leqslant 8$ K which is lower than that of the other intermetallic superconductor MgB_2,[2] $MgCNi_3$ is interesting in many ways. Being a perovskite superconductor like $Ba_{1-x}K_xBiO_3$ and cuprate superconductors, $MgCNi_3$ is special in that it is neither an oxide nor does it contain any copper. Meanwhile, $MgCNi_3$ can be regarded as fcc Ni with only one quarter of Ni replaced by Mg and with C sitting on the octahedral sites. With the structure so similar to that of ferromagnetic Ni, the occurrence of superconductivity in $MgCNi_3$ is really surprising. Actually, there has been a theoretical prediction that $MgCNi_3$ is unstable to ferromagnetism upon doping with 12% Na or Li.[3] In this context, $MgCNi_3$ could be a superconductor near the ferromagnetic quantum critical point.[4,5] A possible magnetic coupling strength due to spin fluctuations was proposed.[6] Even more, a p-wave pairing in $MgCNi_3$ was suggested to be compatible with the strong ferromagnetic spin fluctuations.[3] If it were a p-wave superconductor, it would be the one with highest T_c (e.g., compared to Sr_2RuO_4 with $T_c \leqslant 1.5$ K). To examine these interesting scenarios, fundamental properties have to be experimentally established. Nevertheless, there has been no reliable report on fundamental parameters like the Debye temperature Θ_D. The values of the coupling strength from different experiments were inconsistent with each other.[7,8] Nor does there exist a consensus on the superconducting pairing symmetry. NMR experiments revealed an s-wave pairing in $MgCNi_3$,[7] while the tunneling spectra indicated an unconventional pairing state.[8] In this paper, we present detailed thermodynamic data and derivations of some fundamental parameters from them. *It is found that* $MgCNi_3$ *possesses a BCS-like* $C(T)$ *in the superconducting state*.

The $MgCNi_3$ sample was prepared based on the procedure described in Ref. 1. The starting materials were magnesium powder, glass carbon, and nickel fine powder. The raw materials were thoroughly mixed, then palletized and wrapped with Ta foil before sealed into an evacuated quartz tube. The sample was first sintered at 600 °C for a short time and ground before further treated in a similar way at 900 °C for 3 h. The x-ray diffraction pattern revealed the nearly single phase of $MgCNi_3$ structure. Details of the sample preparation and characterization will be published elsewhere.[9] Temperature dependence of resistivity $\rho(T)$ showed a similar curve as reported in the literatures.[1,10] For the present sample, $\rho = 217$ and 93 $\mu\Omega$ cm at $T = 300$ and 10 K, respectively. It is well known that T_c significantly depends on the real carbon content in the nominal $MgCNi_3$.[1,11] Magnetization, specific heat, and resistivity measurements all showed a superconducting onset at about 7 K in the present sample. The resistivity transition width is 0.5 K, while thermodynamic T_c determined from $C(T)$ is 6.4 K (see below). $C(T)$ was measured using a ^{3}He thermal relaxation calorimeter from 0.6 to 10 K with magnetic fields H up to 8 T. A detailed description of the measurements can be found in Ref. 12.

$C(T)$ of $MgCNi_3$ with $H = 0$ to 8 T is shown in Fig. 1 as C/T vs T^2. The superconducting anomaly at $H = 0$ is much sharper than that in Ref. 1, and clearly persists even with H up to 8 T. It is noted that C/T shows an upturn at very low temperatures. This upturn disappears in high H, which is a

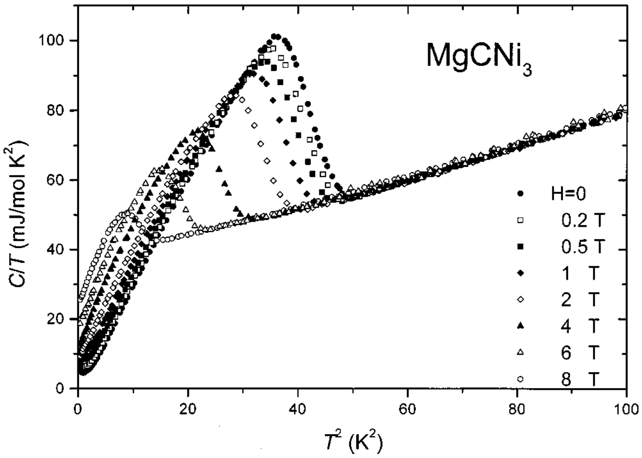

FIG. 1. $C(T,H)/T$ vs T^2 of $MgCNi_3$ for $H = 0-8$ T.

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manifestation of the paramagnetic contribution like the Schottky anomaly. The normal state $C_n(T)=\gamma_n T+C_{\rm lattice}(T)$ was extracted from $H=8$ T data between 4 and 10 K by $C(T,H=8\ {\rm T})=\gamma_n T+C_{\rm lattice}(T)+nC_{\rm Schottky}(g\mu H/k_B T)$, where the third term is a two-level Schottky anomaly. $C_{\rm lattice}(T)=\beta T^3+\delta T^5$ represents the phonon contribution. It is found that $\gamma_n=33.6$ mJ/mol K^2. This value of γ_n, with the electron-phonon coupling constant λ estimated below, requires a higher band $N(E_F)$ than most of those reported from calculations.[3,6,13,14] Θ_D derived from $C_{\rm lattice}$ is 287 K, impressively lower than that (450 K) of Ni. This low Θ_D, nevertheless, is close to the estimate based on the softening of the Ni lattice,[14] which could enhance the electron-phonon interaction. The concentration of paramagnetic centers can be estimated to be the order of 10^{-3}. With a dominant content of Ni in this compound, this number is understandable.

To elucidate superconductivity in MgCNi$_3$, it is of interest to derive $\Delta C(T)=C(T)-C_{\rm lattice}(T)-\gamma_n T$. The resultant $\Delta C(T)/T$ at $H=0$ is shown in Fig. 2(a). By the conservation of entropy around the transition, the dimensionless specific jump at T_c $\Delta C/\gamma_n T_c=1.97\pm0.10$ as shown in Fig. 2(b). This value of $\Delta C/\gamma_n T_c$ is very close to that in Ref. 1, though with a sharper transition in the present work. If the relation of $\Delta C/\gamma_n T_c=(1.43+0.942\lambda^2-0.195\lambda^3)$ (Ref. 15) is adapted as was in Ref. 1, λ is estimated to be 0.83. Both values of $\Delta C/\gamma_n T_c$ and λ suggest that MgCNi$_3$ is a moderate-coupling superconductor rather than weak coupling. To compare $\Delta C(T)$ of MgCNi$_3$ with a BCS one, $\Delta C(T)/T$ from the BCS model with $2\Delta/kT_c=4$ was plotted as the solid line in Fig. 2(a). There was no attempt to fit data with the BCS model. The choice of $2\Delta/kT_c=4$ instead of the weak-coupling value 3.53 was somewhat arbitrary and was to account for the larger $\Delta C/\gamma_n T_c=1.97$ than the weak-limit one 1.43. However, it is noted that the data can already be well described by the solid line, except for the low-temperature part of data which suffer contamination from the magnetic contribution. With this very magnetic contribution, it is difficult to check the thermodynamic consistency. Nevertheless, if the data below 3 K are replaced by the solid line in Fig. 2(a), entropy is conserved, as shown in the inset of Fig. 2(a). It is worth noting that $\Delta C(T)/T$ of MgCNi$_3$ is *qualitatively* different from that of Sr$_2$RuO$_4$, which is considered a *p*-wave superconductor.[16]

To further examine $C_{\rm es}\equiv C(T,H)-C_{\rm lattice}(T)$, $C_{\rm es}(T)/\gamma_n T_c$ vs. T_c/T for $H=0$ is plotted in Fig. 3. The fit of data between 2 and 4.5 K leads to $C_{\rm es}/\gamma_n T_c=7.96\times\exp(-1.46T_c/T)$. Both the values of the prefactor and the coefficient in the exponent are typical of BCS superconductors. Since the magnetic contribution would make $C_{\rm es}$ overestimated at low temperatures, the value of 1.46 in the exponent is probably slightly underestimated. This is in contrast to the case of MgB$_2$, in which $C_{\rm es}\propto\exp(-0.38T_c/T)$.[12,17] This small coefficient in the exponent for MgB$_2$ is usually attributed to a multigap order parameter.

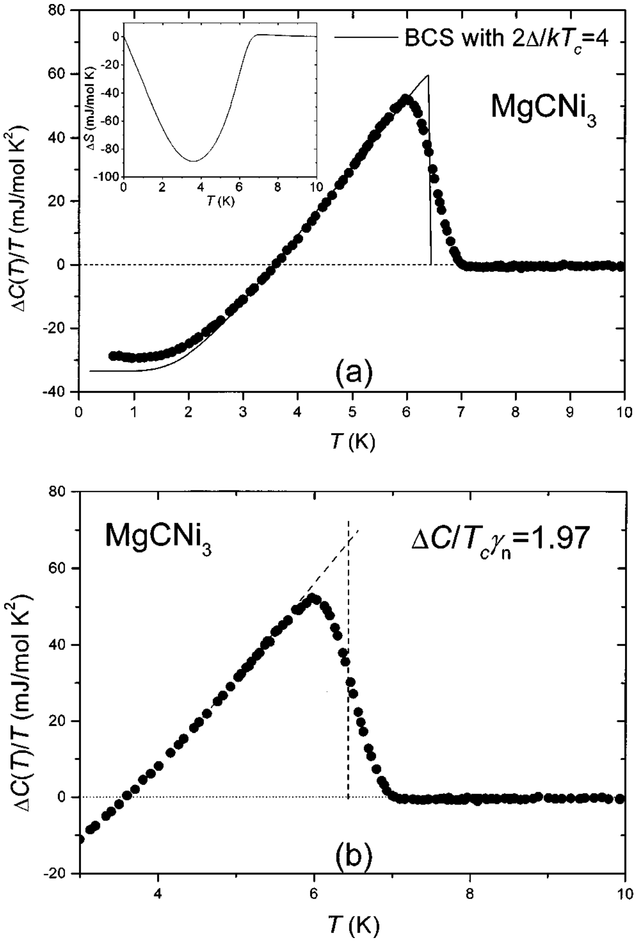

FIG. 2. (a) $\Delta C(T)/T$ vs T. The data are presented as the solid circles. The solid line is the BCS $\Delta C(T)/T$ with $2\Delta/kT_c=4$. The deviation at low temperatures from the solid line is due to the magnetic contribution of a small amount of the paramagnetic centers in the sample. Inset: entropy difference ΔS by integration of $\Delta C(T)/T$ according to the data above 3 K and the solid line below 3 K. (b) The dashed lines are determined by the conservation of entropy around the anomaly to estimate $\Delta C/T_c$ at T_c.

In magnetic fields, $C_{\rm es}(T,H)\approx C_{\rm es}(T,H=0)+\gamma(H)T$.[18,19] For a gapped superconductor, $\gamma(H)$ is expected to be proportional to H.[20] For nodal superconductivity, $\gamma(H)\propto H^{1/2}$ is predicted.[21] Actually, $\gamma(H)$ of cuprate superconductors has been intensively studied in this context.[22] To try to figure out $\gamma(H)$ in MgCNi$_3$, $C(T,H)/T$ vs H at $T=0.6$ K and $\delta C(T,H)/T(\equiv C(T,H)/T-C(T,0)/T)$ vs., H at 2 K are shown in Figs. 4(a) and 4(b), respectively. Data with $H\geqslant4$ T are presented as solid circles and shown in Fig. 4(a). The data clearly follow a straight line passing through the origin, which suggests $\delta\gamma\propto H$. The magnetic contribution is rather significant for low-field data at 0.6 K. The open circles represent data of C/T corrected with the Schottky term estimated from the previously mentioned fitting. (The correction is negligible at high fields.) Apparently, the Schottky anomaly is only an approximation and cannot totally account for the magnetic contribution at 0.6 K, especially for $H\leqslant0.5$ T. At $T=2$ K, the magnetic contribution is not so significant as at 0.6 K. Thus $\delta C/T$ in all magnetic fields are shown as the solid circles. As seen in Fig. 4(b), all high-field data can be well described by a straight line, again indicating a linear H dependence of γ. Data below $H=1$ T

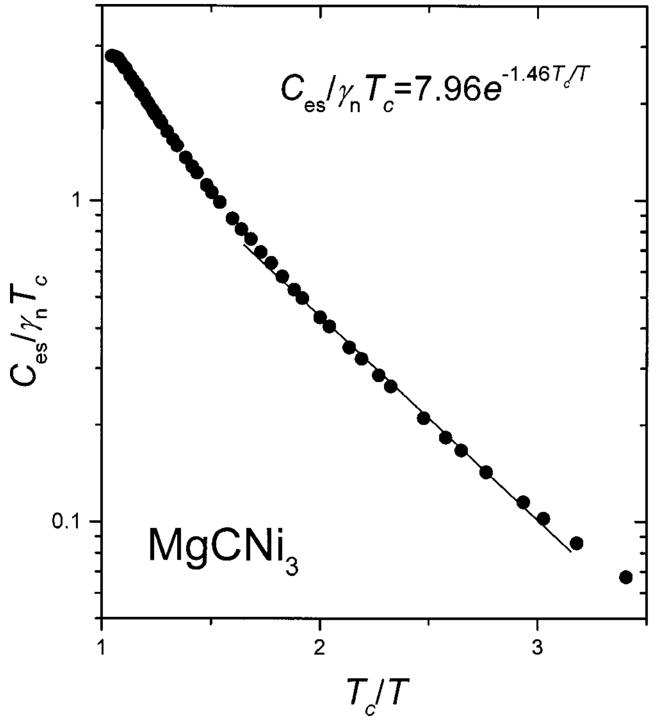

FIG. 3. C_{es} of MgCNi$_3$ in the superconducting state is plotted on a logarithmic scale vs. T_c/T. The straight line is the fit from 2 to 4.5 K.

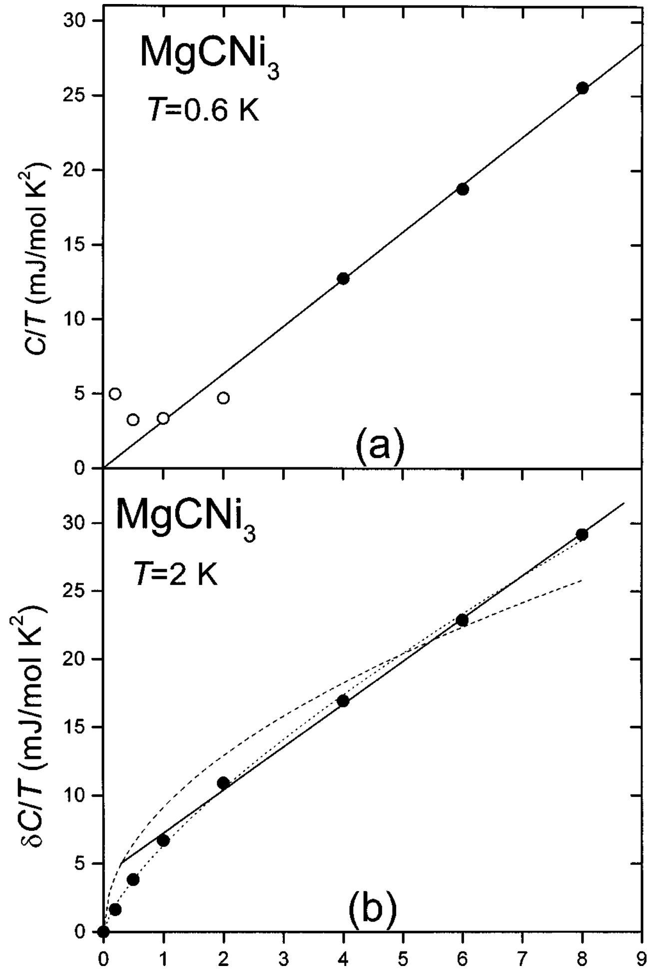

FIG. 4. Magnetic field dependence of (a) C/T at $T=0.6$ K and (b) $\delta C/T$ at $T=2$ K. The straight lines are linear fits of the data for $H\geqslant 4$ T implying $\delta\gamma\propto H$. The open circles in (a) represent data of C/T corrected with the Schottky term (see the text). In (b), the fitting range is from 1 to 8 T. Data below $H=1$ T deviate from the linear behavior due to flux line interactions at low H. The fits by $\delta\gamma(H)\propto H^{1/2}$ and by $\delta\gamma(H)\propto H^n$ are also shown by the dashed and dotted line, respectively, in (b) for comparison. The latter leads to $n=0.73$.

begin to deviate from a linear behavior due to flux line interactions at low H.[18] The straight line passes through the origin in Fig. 4(a), which implies that the flux line interactions are relatively insignificant compared to the core contribution at very low temperatures. This trend was also observed in Ref. 18. The slopes $d\gamma/dH$ in Figs. 4(a) and 4(b) are 3.17 ± 0.02 and 3.15 ± 0.08 mJ/mol K^2 T, respectively. These identical values at different temperatures suggest that the relation $\delta\gamma\propto H$ is genuine. Using $\gamma(H)=\gamma_n(H/H_{c2})$, $H_{c2}=10.6$ T for the present sample, which is close to that estimated from dH_{c2}/dT_c determined by both ρ and C measurements according to the Werthamer-Helfand-Hohenberg (WHH) formula.[23] This value is smaller than what was found in Ref. 10, probably due to different carbon contents, since T_c of the present sample is also lower than that in Ref. 10. On the other hand, one could try to fit the data in Fig. 4(b) by $\delta\gamma(H)\propto H^{1/2}$. The results are represented by the dashed line in Fig. 4(b). Apparently, the data cannot be well described in this manner, in contrast to the nice $\delta\gamma(H)\propto H^{1/2}$ relation found in cuprates.[24–32] A phenomenological fit of $\delta C/T(H)\propto H^n$ leads to $n=0.73$ [the dotted line in Fig. 4(b)], similar to that in the dirty limit Y(Ni$_{1-y}$Pt$_y$)B$_2$C.[33]

Due to the proximity of ferromagnetism, the superconducting order parameter in MgCNi$_3$ was expected to be a p-wave superconductor in Ref. 3 and others. However, it is noted that s-wave superconductivity in the weak ferromagnetism phase was once proposed.[4] Since there is no evidence for nodal lines of order parameter from the specific-heat data, nature must have chosen a gapped order parameter like $x+iy$ if there was p-wave superconductivity in MgCNi$_3$. To further investigate this issue, T_c can be estimated by the McMillan formula $T_c=(\hbar\omega_D/1.45)\times\exp\{-1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)]\}$, where μ^* characterizes the electron-electron repulsion.[34] Taking the Fermi energy $E_F\approx 6$ eV from the energy band calculations,[3,6] μ^* is estimated to be 0.15, and $T_c=8.5$ K is estimated by the above McMillan formula with $\lambda=0.83$. This impressive agreement with the observed T_c implies that the magnetic coupling strength λ_{spin}, if it existed, would be very small. This is consistent with the conclusion reported in Ref. 13. For comparison, $\lambda_{spin}=0.1$ would probably lower T_c to 3.7 K. Should such a small λ_{spin} have turned the order parameter into p-wave pairing, the physics would have been unusual. If one considers only the Ni d contribution, it would effectively make E_F smaller and thus lower T_c, leaving possible λ_{spin} even smaller. ($E_F=4$ eV leads to $T_c=7.6$ K which is even closer to that of the present sample.) It is instructive to compare the physical parameters of MgCNi$_3$ with those of

TABLE I. Comparison between $\mathrm{MgCNi_3}$, $\mathrm{Nb_{0.5}Ti_{0.5}}$, and Nb. Parameters of $\mathrm{MgCNi_3}$ are similar to those of $\mathrm{Nb_{0.5}Ti_{0.5}}$ and Nb. Parameters of $\mathrm{MgCNi_3}$ are from the present work, and those of $\mathrm{Nb_{0.5}Ti_{0.5}}$ and Nb are from Refs. 28–31.

	$\mathrm{MgCNi_3}$	$\mathrm{Nb_{0.5}Ti_{0.5}}$	Nb
T_c (K)	6.4	9.3	9.2
$\Delta C/\gamma_n T_c$	1.97	~1.9	1.87
$\ln(\theta_D/T_c)$	3.79	3.23	3.40
$2\Delta/kT_c$	⩾4	3.9	3.80
H_{c2} (T)	10.6	14.2	~0.2
Θ_D (K)	287	236	275
γ_n (mJ/mol $\mathrm{K^2}$)	33.6 (11.2/Ni)	10.7	7.79

$\mathrm{Nb_{0.5}Ti_{0.5}}$ and Nb, which are two *s*-wave superconductors. The results are listed in Table I. $\mathrm{MgCNi_3}$ appears ordinary among these superconductors. H_{c2} of Nb is much smaller than those of the others because $\mathrm{Nb_{0.5}Ti_{0.5}}$ and $\mathrm{MgCNi_3}$ are typical type-II superconductors while Nb is nearly type II. (The coherence length $\xi \approx 5.6$ nm in the present $\mathrm{MgCNi_3}$ sample, and the preliminary magnetization measurements suggest a penetration depth $\lambda_L = 128-180$ nm (Ref. 9).)

In conclusion, we have presented high quality data of $C(T,H)$ in $\mathrm{MgCNi_3}$. Parameters like $\Delta C/\gamma_n T_c$, Θ_D, and γ_n are well determined. Both the analysis of the data themselves and the comparative studies with other *s*-wave superconductors show that all the specific-heat data in $\mathrm{MgCNi_3}$ are consistent with each other within the moderate-coupling BCS context. It is amazing that such a superconductor unstable to ferromagnetism behaves so conventionally.

Another recent paper appeared with related issues.[35] The authors of Ref. 35 reached a similar conclusion concerning *s*-wave superconductivity in $\mathrm{MgCNi_3}$ in the framework of the two-band model.

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