Competition between the BCS superconductivity and ferromagnetic spin fluctuations in MgCNi$_3$

L. Shan, Z.Y. Liu, Z.A. Ren, G.C. Che, and H.H. Wen

1National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China

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The low temperature specific heat of the superconductor MgCNi$_3$ and a non-superconductor MgCo$_{0.85}$Ni$_3$ is investigated in detail. An additional contribution is observed from the data of MgCNi$_3$ but absent in MgCo$_{0.85}$Ni$_3$, which is demonstrated to be insensitive to the applied magnetic field even up to 12 Tesla. A detailed discussion on its origin is then presented. By subtracting this additional contribution, the zero field specific heat of MgCNi$_3$ can be well described by the BCS theory with the gap ratio ($\Delta/k_B T_c$) determined by the previous tunneling measurements. The conventional $s$-wave pairing state is further proved by the magnetic field dependence of the specific heat at low temperatures and the behavior of the upper critical field.

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Since the discovery of the new intermetallic perovskite superconductor MgCNi$_3$ [1], plenty of efforts have been focused on the superconducting pairing symmetry in this material because its conduction electrons are derived predominantly from Ni which is itself a ferromagnet [2,3,4,5]. However, up to now, there is still not a consensus on this issue. The measured penetration depth [6], critical current behavior [7] and earlier tunneling spectra [8] suggested an unconventional superconductivity, the later tunneling data [9] supported the $s$-wave pairing symmetry and gave a reasonable interpretation on the contradiction to the result in Ref[8]. The $s$-wave pairing has also been demonstrated by the $^{13}$C NMR experiments [10] and the specific heat measurements [1,8,11,12,13,14]. To our knowledge, all the previous reports on the specific heat of MgCNi$_3$ [1,8,11,12,13,14] were characterized in the framework of a conventional phonon-mediated pairing. However, there is an obvious deviation of the experimental data from the prediction of BCS theory in the low temperature regime [8,13], i.e., the entropy conservation rule is not satisfied. Such deviation has been interpreted by the presence of unreacted Ni impurities in Refs[8,12], whereas it is still prominent in the samples without Ni impurities [14]. On the other hand, strong spin fluctuations have been observed in MgCNi$_3$ by NMR experiment [10], which is suggested to be able to severely affect the superconductivity in MgCNi$_3$ [2,5,17,11,16] or even induce some exotic pairing mechanism [2]. Consequently, the behavior of the specific heat will inevitably be changed by the spin fluctuations. Therefore, before a real pairing mechanism being concluded from the specific heat data, we have to carefully investigate how the ferromagnetic spin fluctuations contribute to the specific heat of MgCNi$_3$.

In this work, we elaborate on the specific heat ($C$) of MgC$_x$Ni$_3$ system both in normal state and superconducting state. A low temperature upturn is clearly distinguished in the $C/T$ vs $T^2$ curves and found to be insensitive to the applied magnetic field. By doing some quantitative analysis, we present the evidence of most possible mechanisms responsible for this upturn. After subtracting this additional contribution, a well defined BCS-type electronic specific heat is extracted. The temperature dependence of the upper critical field and the field dependence of the low temperature specific heat also supports such conventional BCS superconductivity in MgCNi$_3$. These analyses indicate that although the spin fluctuations may suppress the pairing strength in MgCNi$_3$, the superconductivity is certainly not induced by any exotic mechanism.

Poly-crystalline samples of MgC$_x$Ni$_3$ were prepared by powder metallurgy method. Details of the preparation were published previously [17]. The superconductor MgCNi$_3$ has a $T_c$ of 6.7K and the non-superconductor MgCo$_{0.85}$Ni$_3$ was synthesized by continually reducing the carbon component until the diamagnetism was completely suppressed. The heat capacity data presented here were taken with the relaxation method [18] based on an Oxford cryogenic system Maglab in which the magnetic field can be achieved up to 12 Tesla. Details of the sample information and the measurements can be found in recent report [11]. It should be emphasized here that the Cernox thermometer used for calorimetry has been calibrated at 0, 1, 2, 4, 8 and 12 Tesla, and the calibration for the intermediate fields is performed by an interpolation using the result of the adjacent fields. Therefore, any prominent field dependence of the specific data should reflect the intrinsic properties of the measured sample.

In general, the low temperature specific heat $C(T,H)$ of a superconductor consists four main contributions by neglecting the component of the nuclear moments [20,21], each has a different dependence on $T$ and two of which depend on $H$, also in different ways,

$$C(H,T) = C_{mag}(H,T) + C_{DOS}(H,T) + \gamma_0 T + C_{ph}(T)$$ (1)
The obvious upturn in the low temperature $C(T)/T$ vs $T^2$ curves of MgCNi$_3$ can not be associated with Ni impurities since the X-ray diffraction pattern shows no indication for Ni impurities \cite{11}. To say the least, if there is still extreme small content of Ni impurities leading to the prominent low temperature upturn of $C/T$, the field dependence of its specific heat should also be obvious, which is clearly inconsistent with our experimental results. Moreover, if this upturn is due to the excess free Ni in MgCNi$_3$, it should also be observed in MgC$_{0.85}$Ni$_3$ because of the similar process of synthesizing these two samples. Quantitatively, taking the data from references \cite{21, 22} yields for 10% of superfluous Ni an upturn which is at least two orders of magnitude smaller than the observed one. Therefore, the contribution of the excessive Ni can be neglected compared with the whole specific heat. Furthermore, the possible Schottky anomaly is presented in Fig. \ref{fig:3}; its field dependence is obviously too strong to compare with our experimental result ( nearly field independent ).

It is found that this upturn can be well fitted if the above mentioned $T^5$ term is considered ( see the upper solid line in Fig. \ref{fig:2} ). In other words, the departure from the $T^5$ behavior may be due to the non-Debye phonon DOS, which is consistent with the notable difference of the Debye temperature between MgCNi$_3$ and MgC$_{0.85}$Ni$_3$ \cite{11}. If the electron-phonon coupling is indeed the origin of superconductivity in MgCNi$_3$, it is reasonable to associate the disappearance of superconductivity in MgC$_{0.85}$Ni$_3$ with the remarkable difference of its phonon DOS from that of MgCNi$_3$. However, some careful work is needed to understand such obvious difference of phonon structure between these two samples, since they have similar crystal lattices and chemical components.
Another possible explanation of the above mentioned low temperature upturn is the existence of strong spin fluctuations due to the higher DOS at fermi energy (N(E_F)) of MgCNi_3 than that of MgC_{0.85}Ni_3 [11], consequently, the coupling between the electrons and spin fluctuations in MgCNi_3 should also be stronger. The ferromagnetic spin fluctuations have been demonstrated by NMR experiments [10]. Doniach and Engelsberg [23] and Berk and Schrieffer [24] showed that the absorption and re-emission of spin fluctuations renormalizes the electronic self-energy, leading to an enhanced effective mass at low temperatures. This effect manifests itself as a low-temperature enhancement of the electronic specific-heat coefficient, \( \lambda_{sf} \), which depends on temperature as \( T^2 \ln(T/T_{sf}) \) (here \( T_{sf} \) is the characteristic spin-fluctuation temperature) at low temperature. Considering the presence of ferromagnetic spin fluctuations, the normal state specific heat of MgC_{x}Ni_3 is expressed as follows,

\[
C_n(H=0,T) = A[1+\lambda_{ph} + \lambda_{sf}(T)]T + \gamma_0 T + \beta T^3
\]

where \( \beta T^3 \) are the contributions of phonon excitations, \( \lambda_{sf} T \) and \( \lambda_{ph} T \) represent the contributions of effective mass renormalization due to the electron-spin fluctuation coupling and the electron-phonon coupling, respectively, and \( A \) is a constant correlated with \( N(E_F) \). It can be seen from Eq. (2) that the deviation from the linear dependence of \( C(T)/T \) on \( T^2 \) is due to the temperature dependence of \( \lambda_{sf} \). Moreover, Béal-Monod, Ma, and Fredkin [27] have estimated the shift \( \delta C/T \) caused by an applied field \( H \) to be

\[
\delta C/T \approx 0.1 \frac{\mu H}{k_B T_{sf}} T^2 \ln S
\]

where \( S \) is Stoner factor. Eqs. (2) and (3) indicate that the possible magnetic field dependence of the normal state specific heat is completely determined by the spin fluctuations. For simplicity, Eq. (2) can be rewritten as \( C_n(H=0,T) = \gamma_n(T) T + \beta T^3 \), in which \( \gamma_n(T) = A[1+\lambda_{ph} + \lambda_{sf}(T) + \gamma_0/A] \). Therefore, the \( \gamma_n \sim T \) relation directly reflects the temperature dependence of \( \lambda_{sf} \). In Fig. 4 we present the determined \( \gamma_n(T) \) by selecting various \( \beta \)-values. Fitting the \( \gamma_n(T) \) relations to the formula of \( A(1+B T^2 \ln(T/T_{sf})) \) yields \( T_{sf} \), varying from 13 to 16K. By inserting the determined \( T_{sf} \), calculated Stoner factor \( S \) [2] and the highest field value in our measurements into Eq. (3), we can estimate the shift \( \delta C/T \) caused by the applied field to be less than 2%, which is in agreement with our experimental results. However, if this explanation is correct, we must understand the collapse of the entropy conservation around \( T_c \) caused by considering such additional electronic specific heat, as discussed below. Therefore, the specific-heat contributions of the spin fluctuations themselves may be another candidate responsible for the low temperature upturn in specific heat of MgCNi_3.

Despite the true mechanism of the low-temperature upturn of \( C/T \), this additional specific heat contribution should be regarded as a part of the normal-state background of the superconducting specific heat below the upper critical field \( H_{c2}(T) \). In earlier analysis to the specific heat data [8, 11, 12], this additional part of background has been neglected more or less below \( H_{c2}(T) \). We point out here that neglecting this additional contribution will lead to the collapse of the entropy conservation as reported in references [8, 16]. This opinion is motivated by the subsequent analysis. As shown in Fig. 4a), the normal state background ( as shown in Fig. 2) has been subtracted from the zero-field specific heat data, the entropy difference \( \Delta S(T) = \int_0^T dT \Delta C/T \) is presented in the inset of Fig. 4a), here \( \Delta C = C_{H=0} - C_n \). It is found that the entropy conservation is then well satisfied, indicating that the remainder is the contribution of superconducting state. Such analysis has also been ap-
served downward curving 

\( C(T, H) \) of conventional s-wave superconductors with line nodes in the gap function, Volovik et al. 28 pointed out that in the mixed state, supercurrents around a vortex core cause a Doppler shift of the quasi-particle excitation spectrum. This shift has important effects upon the low energy excitation around the nodes, where its value is comparable to the width of the superconducting gap. For \( H \gg H_c \), it is predicted that 
\[ N(E_F) \propto |E - E_F| \]
and the possible expansion of the quasi-particles in the vortex cores. From the Bogoliubov equations assuming noninteracting vortices, the DOS associated with the bound excitations is derived as 
\[ \text{DOS} \propto |E - E_F| \] at low temperatures 28. This prediction has been well proved for hole doped cuprates 29. Whereas in a conventional s-wave superconductor, the specific heat in the vortex state is dominated by the contribution from the localized quasi-particles in the vortex cores. From the above discussions, we can conclude that the coexistence and competition of spin fluctuations and phonons does not change the phonon-mediated pairing mechanism of MgCNi3.

In order to further verify this picture, we investigate the field dependence of the low temperature specific heat of MgCNi3. It is known that the electronic specific heat in magnetic fields can be expressed by 
\[ C_{el}(T, H) = C_{el}(T, H = 0) + \gamma(H) T \]
The magnetic field dependence of \( \gamma(H) \) is associated with the form of the gap function of the superconductor. For example, in a superconductor with line nodes in the gap function, the quasiparticle DOS ( \( N(E) \) ) rises linearly with energy at the Fermi level in zero field, \( N(E) \propto |E - E_F| \), which results in a contribution to the specific heat \( C_{DOS} = \alpha T^2 \) will disappear and be substituted by the excitations from both inside the vortex core and the de-localized excitations outside the core. For d-wave superconductors with line nodes in the gap function, Volovik et al. 28 pointed out in that the mixed state, supercurrents around a vortex core cause a Doppler shift of the quasi-particle excitation spectrum. This shift has important effects upon the low energy excitation around the nodes, where its value is comparable to the width of the superconducting gap. For \( H \gg H_c \), it is predicted that 
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\[ \text{DOS} \propto |E - E_F| \] at low temperatures 28. This prediction has been well proved for hole doped cuprates 29. Whereas in a conventional s-wave superconductor, the specific heat coefficient \( \gamma(H) \) of conventional s-wave superconductor should linearly depend on the magnetic field well above \( H_c \).

Fig. 6 shows the field dependence of \( \gamma(H) - \gamma(0) \) of MgCNi3 below 3K. The data reported by different groups 11, 14, 15 merge into each other by timing a prefactor \( A \) close to unity. It is found that \( \gamma \) linearly depends on
above mentioned behaviors of conventional conductors. It may be argued that the low temperature 
\[ \gamma \] \( T = 0 \) is nearly universal at low temperatures below upper 
critical field \( H_c \). Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, 
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Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, 
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FIG. 6: The magnetic field dependence of the specific heat 
coefficient \( \gamma (H) - \gamma (0) \) at low temperatures.

FIG. 7: The comparison of the temperature dependence of 
the upper critical field \( H_c(T) \) with the BCS-like descriptions 
in lower and higher temperature limits.

\( H \) above 0.5T and persists up to 8T which is close to the 
upper critical field of MgCNi\(_3\). The legible linearity of \( \Delta \gamma \sim H \) relation at higher field and its negative 
curvature below 0.5T are in good agreement with the 
above mentioned behaviors of conventional \( s \)-wave superconductors. It may be argued that the low temperature 
limit of about 2K in our measurements is not low enough 
to distinguish the \( d \)-wave’s \( \Delta \gamma \sim H^{1/2} \)-law. However, it 
should be emphasized that the observed \( \Delta \gamma \sim H \) relation 
is nearly universal at low temperatures below upper 
critical field, which is very similar to the behavior of \( V_3Si \) 
\[ 32 \], a typical conventional \( s \)-wave superconductor.

Finally, we compare the temperature dependence of 
the upper critical field \( H_c(T) \) with the prediction of BCS 
theory in which the \( H_c(T) \) can be expressed as follows,

\[ H_c(T) \approx 1.74H_c(0)(1 - T/T_c) \quad (T_c - T \ll T_c) \quad (4a) \]

\[ H_c(T) \approx H_c(0)[1 - 1.06(T/T_c)^2] \quad (At low T) \quad (4b) \]

As shown in Fig. 7, the best fitting to BCS model is 
denoted by solid lines. At lower temperature, the 
experimental data can be well described by Eq. (4b). 
For the higher temperature near \( T_c \), a prefect of 1.65 is 
obtained instead of the theoretical prediction of 1.74 as 
expressed in Eq. (4a). Nonetheless, the BCS model is still 
a preferred description for \( H_c(T) \) of MgCNi\(_3\) considering 
the stronger electron-phonon coupling and the presence 
of ferromagnetic spin fluctuations.

In summary, we have investigated the specific heat 
data of MgC\(_2\)Ni\(_3\) system. A remarkable field independent 
contribution is found in MgCNi\(_3\), reflecting the departure 
of normal-state specific heat from \( T^3 \)-law. By removing 
this contribution, the zero-field data is well described by 
the \( \alpha \)-model ( a slightly revised BCS model ). The 
conventional \( s \)-wave superconductivity is further supported 
by the linear field dependence of specific heat coefficient 
\( \gamma (H) \) and the BCS-like temperature dependence of up-
per critical field \( H_c(T) \). It is then concluded that, al-
though electron-magnon ( spin fluctuations ) coupling 
coexists and competes with electron-phonon coupling ef-
effect in MgCNi\(_3\), it only acts as pair breakers while does 
not induce a new exotic superconductivity.

Note added: Most recently, the carbon isotope effect in 
superconducting MgCNi\(_3\) observed by T. Klimeczuk and 
R.J. Cava indicates that carbon-based phonons play a 
critical role in the presence of superconductivity in this 
compound \[ 33 \].

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