Over the past several years, two new major trends have emerged in research on superconductivity. One is the search for superconducting ground states near magnetic instabilities. Lonzarich et al., for example, have demonstrated that application of high pressure transforms the antiferromagnetic ground states of some heavy Fermion materials into superconductors [7]. The exotic superconductor Sr$_2$RuO$_4$ [8] exhibits more subtle signatures of magnetic correlations in the normal state above $T_c$ [9]. Another emerging trend is the search for superconductivity in intermetallic compounds with light elements. Recently Akimitsu et al. discovered superconductivity in MgB$_2$ [10]. High frequency phonons induced by the light element, B, are believed to be essential in yielding the high $T_c$.

A very recent addition to the list of new superconductors along these trends is MgCNi$_3$ [11-12]. MgCNi$_3$ forms a three-dimensional perovskite structure. Mg, C, and Ni replace Sr, Ti, and O in SrTiO$_3$, respectively. Six Ni atoms at the face-centered position of each cubic unit cell form a three-dimensional network of Ni$_6$-octahedra. Each C atom is located in the body-centered position surrounded by a Ni$_6$-octahedron cage. Ni 3d orbitals and C 2p orbitals form two electronic bands at the Fermi level, one being electron-like and the other hole-like [12]. The superconducting transition temperature is modestly high, $T_c = 7.0$K, for an intermetallic system. The discovery of a superconducting ground state in MgCNi$_3$ poses two interesting questions: Firstly, what is the role played by Ni 3d electrons? Unfilled Ni 3d orbitals usually form magnetically correlated bands, and recent band calculations indicate predominantly Ni 3d character at the Fermi level [13]. Furthermore, if C atoms are removed from MgCNi$_3$, MgNi$_3$ is expected to have a magnetic ground state [14]. These calculations imply that MgCNi$_3$ may also be on the verge of a magnetic instability. Unfortunately, the volatility of Mg in chemical reaction processes [14] makes growth of bulk samples difficult, and no details of possible electronic correlation effects have been addressed by conventional bulk measurement techniques.

Secondly, does the presence of C, a light element, imply that the phonon-mediated BCS mechanism is at work for stabilizing the superconducting ground state? Recent tunneling measurements by Mao et al. detected a zero bias conductance peak below $T_c$ suggesting otherwise. The tunneling result may be interpreted as an indication of the unconventional character of the superconducting pairing state.

In this Letter, we report the first $^{13}$C NMR investigation of MgCNi$_3$ both above and below $T_c$. Our sample was prepared in a manner similar to that previously reported [8], but with $^{13}$C enriched graphite as the starting material to enhance the intensity of the $^{13}$C NMR signal. This allowed us to follow the temperature dependence of the $^{13}$C NMR properties in a broad temperature range between 1.7K and 800K. We demonstrate that the normal state properties of MgCNi$_3$ show the signature of modest electronic correlation effects. Both the uniform spin susceptibility $\chi(q=0)$, as measured by the Knight shift $^{13}K$, and the spin fluctuations, as measured by the nuclear spin-lattice relaxation rate $1/13T_1$ divided by temperature $T$ $(1/13T_1T)^2$, increase monotonically below 800K down to $\sim 50$K and $\sim 20$K respectively, before saturating to a constant value. A single Korringa relation for a Fermi-liquid $1/T_1TK^2 = $const., can not account for the temperature dependences of $^{13}K$ and $1/13T_1T$ between 800K and $T_c$. The most likely scenario is that electronic correlation effects enhance both the static and dynamic magnetic susceptibility, and a modestly mass-enhanced Fermi-liquid-like state is realized somewhat above $T_c$. Over all, the normal state NMR properties of MgCNi$_3$ bear significant qualitative similarities with those of the exotic superconductor Sr$_2$RuO$_4$. However, we demonstrate that our NMR data below $T_c$ are consistent with conventional s-wave pairing.

In Fig.1(a), we present the Fourier transformed $^{13}$C NMR lineshape from MgCNi$_3$ powder. Above $T_c$, $^{13}$C in MgCNi$_3$ has a large, temperature dependent, positive NMR Knight shift $^{13}K$ with much narrower linewidth than the overall NMR shift. The narrow linewidth above
In Fig.2(a), we present the temperature dependence of the powder averaged NMR Knight shift $^{13}K$. According to band calculations [13-16], MgCNi$_3$ has two bands arising from Ni 3d and C 2p hybridization at the Fermi energy. In terms of the spin susceptibility $\chi_j^s(q=0)$ of the j-th band ($j = 1, 2$ is the band index), one can write $^{13}K$ as

$$^{13}K = \sum_j A_j \chi_j^s(q=0) + ^{13}K_{orb}. \quad (1)$$

where $A_j$ is the hyperfine coupling constant between the $^{13}$C nuclear spin ($I = \frac{1}{2}$) and the electrons in the j-th band. $^{13}K_{orb}$ is the orbital contribution in the nearly filled 2p orbitals of the C atoms and in various materials such as graphite, it is known to be as small as 0.01–0.02%. $A_j \chi_j^s(q=0)$ represents the spin contribution to the Knight shift from the j-th band. Since the hyperfine interaction is dominated by s-electrons, it is safe to assume that $A_1 \sim A_2$. Accordingly, the results in Fig.2(a) suggest that the total spin susceptibility $\sum_j \chi_j^s(q=0)$ increases by approximately 55-70% below 800K down to $T_c$, if we take $^{13}K_{orb} = 0.01 \sim 0.02%$. Needless to say, we cannot rule out the possibility that $\chi_1^s(q=0)$ and $\chi_2^s(q=0)$ exhibit somewhat different temperature dependences. The temperature dependence of $^{13}K$ changes curvature at about 120K from positive to negative, and saturates below about $T^* \sim 50K$. The electrical resistivity data also show a change of curvature in the same temperature range, and satisfy $\rho \sim T^n$ with $n \approx 1.8$ below $T^* \sim 50K$. These results suggest that an electronic crossover takes place near $T^* \sim 50K$ prior to the superconducting transition at $T_c = 7.0K$.

From standard K-\chi analysis [17], where we choose $^{13}K_{orb} = 0.014%$ from the insert to Fig.2(a), we obtained $A_1 = A_2 \sim 14 kOe/\mu_B$, the sum of the diamagnetic and Van-Vleck contribution as $\chi_{dia} + \chi_{v.v.} \sim -1.55 \times 10^{-4}[\text{e.m.u.}/\text{mol-f.u.}]$, and the saturated value of $\chi_{spin} \sim 4.77 \times 10^{-4}[\text{e.m.u.}/\text{mol-f.u.}]$ below 50K. Using $N(E_F) = 4.99[\text{states/eV f.u.}]$ [14] implies that the enhancement of the spin susceptibility $\chi_{spin}$ over the band value $\chi_{band} = 1.61 \times 10^{-4}[\text{e.m.u.}/\text{mol-f.u.}]$ is $\chi_{spin}/\chi_{band} \sim 3.0$. This is to be compared with the specific heat enhancement $\gamma/\gamma_{band} \sim 2.6$ [13]. These estimations give the Wilson ratio $R_W = \frac{\chi_{spin}/\chi_{band}}{\gamma/\gamma_{band}} \sim 1.15$ (see also [14]). $R_W = 2$ is expected in the strongly correlated limit, while $R_W = 1$ in the uncorrelated case, therefore $R_W = 1.15$ indicates that the electrons are in a mildly correlated state.

In Fig.2(b), we present the temperature dependence of the $^{13}$C nuclear spin-lattice relaxation rate $1/T_1T$ divided by temperature $T$, $1/T_1T$. See Fig.1(b) for an example of nuclear spin recovery after saturation. Theoretically, the spin contribution to $1/T_1T$ may be written as the wave vector $q$ summation of the imaginary part of the dynamical electron spin susceptibility $\chi''(q, \omega_n)$,

$$\frac{1}{T_1T} = \frac{\gamma_n^2 k_B}{\mu_B^2 \hbar} \sum_{i,j} \sum_q |A_{ij}(q)|^2 \frac{\chi''_{ij}(q, \omega_n)}{\omega_n} \quad (2)$$

where $\gamma_n = 10.7054 \text{ MHz/Tesla}$ is the nuclear gyromagnetic ratio of $^{13}$C, $\omega_n$ is the resonance frequency, and $i, j$ are band indices [13-16]. As emphasized earlier by Walstedt [20], cross terms between different bands can exist for the spin-lattice relaxation process, while such cross terms do not exist in NMR Knight shifts [13]. This makes separation of various contributions to $1/T_1T$ a non-trivial matter in multi-band systems such as MgCNi$_3$ and Sr$_2$RuO$_4$.

The most striking aspect of the $1/T_1T$ data is the continuous increase of its magnitude all the way from 800K to about 20K through $T^* \sim 50K$. Our results indicate that spin fluctuations are nearly a factor 3 enhanced with decreasing temperature. Within a simple Fermi liquid picture ignoring all the complications from the multi-band effects mentioned above (i.e. we assume that the two sets of d-p bands exhibit identical temperature dependences of spin susceptibility), a modified Korringa law, $1/T_{1,spin}TK_{spin}^2 = 1/S\beta$ should hold [13-16]. Here $1/T_{1,spin}$ and $K_{spin}$ are the spin contribution, and $S = (\frac{1}{\gamma_n^2}(\frac{\mu_B^2}{\hbar})^2 = 4.17 \times 10^{-6}$ sec K for $^{13}$C. $\beta$ is a quantity that signifies the effects of electronic correlations. In this scenario, the observed 50% to 70% increase in the spin contribution to the Knight shift $^{13}K$ between 800K and 120K implies that $1/^{13}T_1T$ would also increase by a factor $1.5^2(= 2.3)$ to $1.7^2(= 2.9)$ by the Korringa process from electron-hole pair excitations at the Fermi level. This is consistent with the factor 2.6 increase of $1/^{13}T_1T$ in the same temperature range. In fact, as shown in the inset to Fig.2(a), above 120K we can fit $1/^{13}T_1T$ and $^{13}K$ to the modified Korringa relation $1/^{13}T_1T = 1/^{13}T_{1,orb}T + (13K - ^{13}K_{orb})^2/S\beta$ with $\beta = 6.0$, the orbital contributions $1/^{13}T_{1,orb}T = 0.005$ sec$^{-1}$K$^{-1}$, and $^{13}K_{orb} = 0.014%$. When one is dealing with correlation effects in a three dimensional electron gas with a spherical Fermi surface, $\beta = 1$ for the uncorrelated case, and $\beta > 1$ for the ferromagnetically correlated case. On the other hand, the enhancement of low frequency spin fluctuations at non-zero wavevectors affects only $1/T_1T$, and hence tends to reduce $\beta$. The successful fit of $1/^{13}T_1T$ and $^{13}K$ by a modified Korringa law with $\beta = 6.0$ suggests that above 120K the d-p bands in MgCNi$_3$ form a Fermi-liquid state with relatively strong ferromagnetic correlation effects. This is consistent with the strong enhancement of the uniform spin susceptibility with decreasing temperature. We must caution, however, that $\beta = 6.0$ may be somewhat too large due to the fact that we have ignored the presence of two bands that would tend to overestimate $\beta$ by a factor $\sim 2$ [17]. Furthermore, as noted by Moriya [13], the precise magni-
tude of $\beta$ is sensitive to the deviation of the Fermi surface from spherical symmetry. We call for more sophisticated band theoretical analysis of our data to clarify the nature of the correlation effects at the quantitative level.

Even though the modified Korringa law describes our data reasonably well above 120K, it is important to notice that a single modified Korringa relation cannot account for the continuous increase of $1/^{13}T_1(T)$ below 20K through $T^* \sim 50$K down to $\sim 20$K. In this regime, $^{13}K$ shows a crossover to a low temperature constant regime. The fact that the overall spin fluctuations reflected in the wave vector integral of $\chi''(q,\omega_n)$ increase while the $q = 0$ component of the total static spin susceptibility $\sum_j \chi_j(q = 0)$ maintains a constant magnitude strongly suggests that spin fluctuations with finite wave vectors away from $q = 0$ continue to grow significantly below $T^* \sim 50$K.

Both $^{13}K$ and $1/^{13}T_1(T)$ are saturated below 20K. Using the same orbital contributions as before, the modified Korringa relation for the correlated Fermi-liquid gives $\beta = 4.7$ below 20K. This value is smaller than $\beta = 6.0$ observed above 120K by 20%, again signaling the importance of $20K$ of correlation effects with finite wave vectors. Putting all the pieces together, we obtain the following physical picture for the normal state of MgCNi$_3$: the electrons in the Ni-C d-p bands are modestly correlated; the primary channel of the correlation effects appear to be centered near $q = 0$ above 50K but spin fluctuations with finite wave vectors $q \neq 0$ show continuous growth down to 20K below which electron correlation effects are saturated with $R_W = 1.15$. Extensive efforts are underway to understand the electronic properties of MgCNi$_3$ based on band calculations[9,18], and our experimental data provides a good testing ground for those theories. It is worthwhile recalling that a similar situation is also encountered in Sr$_2$RuO$_4$. The $^{17}$O NMR Knight shifts in Sr$_2$RuO$_4$ increase with decreasing temperature and even begin to decrease below $T^* \sim 50$K. On the other hand, $1/^{17}T_1(T)$ continues to grow through 50K[1]. Subsequent inelastic neutron scattering measurements revealed that an anomalous enhancement of spin fluctuations corresponding to the nesting vectors of quasi-one dimensional 4d$_{yz,zx}$ bands is responsible for the continuous increase of $1/^{17}T_1(T)$ towards $T_c$[3].

Next, we turn our attention to the behaviour of $1/^{13}T_1$ in the superconducting state. As shown in Fig. 3a, a magnetic field of 9 Tesla destroys superconductivity down to $\sim 2.5$K above which $1/^{13}T_1$ maintains a Korringa behaviour $1/^{13}T_1(T) = 0.072$ sec$^{-1}$K$^{-1}$. However, at lower magnetic fields, $1/^{13}T_1$ is enhanced just below $T_c$, peaks at $\sim 0.9T_c(H)$, followed by an exponential decrease at lower temperatures. Moreover, the peak value of $1/^{13}T_1$ just below $T_c$ grows with decreasing magnetic field from 1 Telsa to 0.45 Tesla. For the lowest field at $H = 0.45$ Telsa, $1/^{13}T_1$ is enhanced by a factor $\sim 1.4$ just below $T_c(H = 0.45T) = 6.7$K. A similar robust enhancement is usually observed in conventional BCS superconductors due to the pile up of the density of quasi-particle excitations, and is known as the Hebel-Slichter coherence peak[23]. The temperature dependence of the coherence peak can be fit by incorporating a minor $k$-space anisotropy in the conventional s-wave gap[23].

$$\Delta(H, \Omega) = <\Delta(H) > (1 + a(\Omega)) \quad (3)$$

where $\Omega$ is the solid angle in $k$-space, $<\Delta(H) >$ is the mean gap value over all orientations in $k$-space and $a(\Omega)$ is the small anisotropy function with the condition $<a(\Omega) > = 0$. The best fit results, shown in Fig. 3, yield a mean gap magnitude of $<\Delta(H = 0.45T) > /k_B \sim 10.5$K and mean square anisotropy $<a^2(\Omega) > \sim 0.047$ in a magnetic field of 0.45 Tesla, or equivalently $<\Delta(H) > /k_B T_c(H = 0.45T) \sim 1.6$ which is consistent with the standard BCS value of $<\Delta(H=0) > /k_B T_c(H=0) = 1.75$[24]. $<\Delta(H) >$ may be somewhat underestimated by the influence of $H$, as $<\Delta(H = 1T) >$ is smaller than $<\Delta(H = 0.45T) >$ as shown in Fig. 3b.

We also noticed that the exponential decrease of $1/^{13}T_1$ saturates below $\sim 2.5$K and that the magnitude of $1/^{13}T_1$ itself is distributed below this temperature. It is known[18] that a large ‘flux avalanche’ effect occurs below 3K in MgCNi$_3$, and the saturation of $1/^{13}T_1$ is most likely due to the fluxoid contribution[25,26]. Unfortunately, the fluxoid effects prevented us from confirming the exponential decrease in $1/^{13}T_1$ down to the lowest temperature. We should caution that theoretically, a small peak in $1/^{13}T_1$ is known to arise even in non-s orbital pairing symmetries as long as singularities exist in the quasi-particle excitation spectrum. However, we are not aware of any materials with anisotropic pairing symmetry that shows such a robust coherence peak with the appropriate magnetic field dependence.

Given the qualitative similarities of the normal state NMR data between MgCNi$_3$ and the unconventional superconductor Sr$_2$RuO$_4$[8], the possible realization of conventional s-wave symmetry superconductivity in the former may be rather surprising. However, we point out that correlation effects in the three dimensional material MgCNi$_3$ are expected to be much weaker than in the quasi-two dimensional material Sr$_2$RuO$_4$[14,15]. Furthermore, the presence of the light C atom in the structure might create high frequency phonons and help open the s-wave channel at a higher temperature than the p- or d-wave channels. In fact, $T_c = 7$K of MgCNi$_3$ is several times higher than $T_c = 1.4$K of Sr$_2$RuO$_4$.

To summarize, we have reported the first $^{13}$C NMR measurements in MgCNi$_3$. The strong temperature dependence of $^{13}K$ and $1/^{13}T_1(T)$ and subsequent saturation
below $\sim 50$K and $\sim 20$K respectively are consistent with the presence of modest electronic correlation effects, possibly assisted by nesting effects. This suggests that the electronic state has reached a modestly mass-enhanced Fermi-liquid like state prior to the superconducting transition. The robust coherence peak and subsequent exponential decrease of $1/13T_1$ is consistent with s-wave pairing.

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[1] N.D. Mathur et al., Nature (London) 394, 39 (1998).
[2] Y. Maeno et al., Nature (London) 372, 532 (1994).
[3] K. Ishida et al., Phys. Rev. B 56, R505 (1997).
[4] T. Imai et al., Phys. Rev. Lett. 81, 3006 (1998).
[5] Y. Sidis et al., Phys. Rev. Lett. 83, 3320 (1999).
[6] J. Nagamatsu et al., Nature (London) 410, 63 (2001).
[7] T. He et al., Nature (London) 411, 54 (2001).
[8] M.A. Hayward et al., cond-mat/0104541.
[9] S.Y. Li et al., cond-mat/0104554.
[10] Q. Huang et al., cond-mat/0105240.
[11] Z.Q. Mao et al., cond-mat/0105349.
[12] B.D. Dugdale and T. Jarlborg, cond-mat/0105349.
[13] A. Narath and H.T. Weaver, Phys. Rev. 175, 373 (1968).
[14] L.C. Hebel and C.P. Slichter, Phys. Rev. 113, 1504 (1959).
[15] D.E. MacLaughlin, Solid State Physics 31, 1 (1976).
[16] Another conventional NMR approach to clarify the pairing symmetry of the superconducting state is to measure the Knight shift below $T_c$. Unfortunately, we found that the resonance linewidth becomes even broader than the magnitude of the normal state Knight shift due to fluxoid effects (see Fig. 1a).

[17] S.M. De Soto et al., Phys. Rev. Lett. 70, 2956 (1993).
[18] V.A. Stenger et al., Phys. Rev. Lett. 74, 1649 (1995).

FIG. 1. (a) A Fourier transformed $^{13}$C NMR spectrum (arb. units) in MgCNi$_3$ obtained at 4.6K, 7K, and 300K in 1 Tesla. (b) A typical $^{13}$C NMR spin echo recovery at 4.6K and 1 Tesla. A 180-degree saturation pulse was employed. The solid line is the best fit to a single exponential recovery with $T_1 = 3.3$ sec.
Figure 1: 
(a) The graph shows the relationship between $^{13}\text{K}$ (%) and temperature $T$(K). The inset shows the linear relationship between $\sqrt{\frac{1}{^{13}T_1T}}$ and $^{13}\text{K}$. 
(b) The graph illustrates the plot of $\frac{1}{^{13}T_1T}$ over temperature $T$(K). The inset depicts the linear correlation between $\frac{1}{^{13}T_1T}$ and $T$(sec$^{-1}$K$^{-1}$).
(a) \( \frac{1}{T_1} \text{(sec}^{-1}) \)

(b) \( \frac{R}{R_n} \)