Superconductivity near Ferromagnetism in $MgCNi_3$

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An unusual quasi-two-dimensional heavy band mass van Hove singularity (vHs) lies very near the Fermi energy in $MgCNi_3$, recently reported to superconduct at 8.5 K. This compound is strongly exchange enhanced and unstable to ferromagnetism upon hole doping with ~12% Mg → Na or Li (i.e., 0.04 hole/Ni). We identify an essentially infinite mass along the M-Γ line, which accounts for the two dimensionality of this vHs. This compound provides new opportunities to probe the ferromagnetic critical point as well as introducing the novelties of 2D behavior into a 3D system.

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The discovery of ~40 K superconductivity in MgB_2 [1] has spurred interest in searching for superconductivity in unlikely materials, and other discoveries are uncovering previously unanticipated relationships between ferromagnetism (FM) and superconducting states. Of this latter category, there are now several examples, such as the magnetic organometallic $(BETS)_2FeCl_4$, where superconductivity is actually *induced* [2] by a strong applied magnetic field rather than being destroyed by it, and the intermetallic UGe_2, where superconductivity emerges [3,4] in spite of strong ferromagnetism and coexists with it to the lowest temperatures, and is almost certainly triplet paired. The possibility of FM on the surface of the exotic superconducting oxide Sr_2RuO_4 [5,6] is yet another aspect of the strong relationship between FM and superconductivity that is yet to be understood.

A new compound that would not be considered a likely candidate for superconductivity is $MgCNi_3$, whose conduction electrons are derived predominantly from Ni which is itself a ferromagnet, yet it superconducts at 8.5 K [7]. This perovskite compound can be regarded as fcc Ni that is expanded by 8%, one-quarter of the Ni replaced by Mg, then C atoms put into the octahedral sites. Partial replacement of Ni by Co or Cu reduces (or destroys) T_c [8], while other substitutions have not been reported. The Hall coefficient is strongly dependent on temperature, unlike a conventional metal (Fermi liquid), while the measured critical field H_{c2} has a conventional shape [9]. Tunneling spectra show a strong zero bias anomaly that has been interpreted as evidence of strong coupling superconductivity of an unconventional type [10].

Previous workers have explored the possibility of conventional phonon-coupled pairing. Dugdale and Jarlborg [11] use a rigid atom model and the Debye frequency of Ni to suggest a coupling strength $\lambda \approx 0.7$, which could be consistent with $T_c = 8$ K; spin fluctuations that oppose such conventional pairing were neglected. Shim *et al.* employed the same rigid atom model but emphasized the large uncertainty [12] due to the lack of knowledge of the phonon spectrum, and Singh and Mazin have noted [13] that the rigid atom model as used is unjustified in materials such as $MgCNi_3$.

In this paper it is shown that this compound, in addition to being superconducting, is also an incipient ferromagnet, which can be driven to ferromagnetism by partial (≈12%) replacement of Mg with a monovalent metal such as Li or Na. This close proximity of superconductivity to magnetism itself invites consideration of unconventional pairing, and our identification of three symmetry-equivalent van Hove singularities (vHs's), each with quasi-two-dimensional (quasi–2D) character, provides further support for unconventional pairing and possible coexistence of FM and superconductivity, two types of collective order that are usually antagonistic.

The perovskite structure ABX_3 itself is unusual for such an intermetallic compound, since perovskites much more commonly have a strongly negative ion (O^{2-} or a negatively charged halide) on the site occupied by Ni in this compound. The electronic structure is entirely different when a metal atom is on the X sublattice, because hopping occurs directly between metal (Ni) atoms rather than through an intermediate (oxygen, say) atom. Likewise, the important phonon modes are different from those in oxide perovskites or Ni metal, as Singh and Mazin have discussed [13]. Thus it is essential first to understand the character of the charge carriers, for which purpose we have carried out full potential, all-electron density functional based calculations [14]. The resulting spectral distribution of the electronic states (for the experimental lattice constant $a = 3.812$ Å) is shown in Fig. 1, and is much like the results obtained elsewhere [11–13,15]. The states at the Fermi level are predominantly Ni d_{xz}, d_{yz} in the local coordinate system in which the $\hat{z}$ axis is directed toward the two neighboring C atoms. Besides the superconductivity, the remarkable feature of this compound is the sharp and narrow peak in the density of states (DOS) just 45 meV

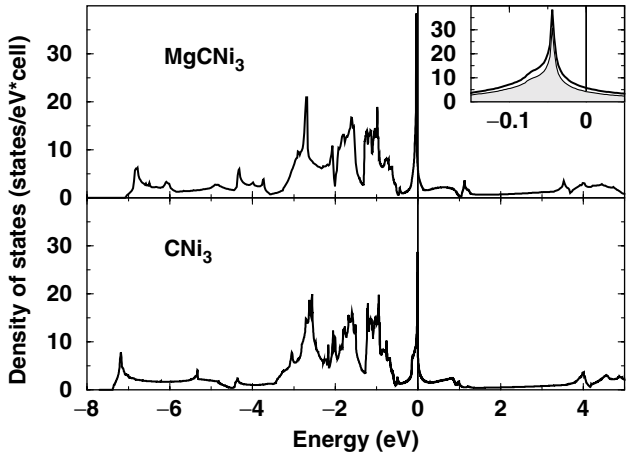

FIG. 1. The density of states of $MgCNi_3$ (top panel), showing the nearly filled Ni d states and the extremely sharp and narrow peak just below E_F arising from a van Hove singularity. The inset gives a blowup of the peak, with the shaded portion indicating the dominant Ni $3d$ contribution. The lower panel shows the density of states for $\square^{2+}CNi_3$ (see text).

below the Fermi level [11]. This peak results from a vHs arising from a remarkably flat, primarily Ni $3d$ derived (but C is crucial), band at and around the three M points [$(1,1,0)\pi/a$ and equivalent points] in the simple cubic Brillouin zone. Thus it is high mass Ni $3d$ holes that form the superconducting pairs, and Ni-Ni hopping is important for their transport. For this M point, only the Ni atoms in the same x-y plane as the C atom contribute to the vHs, i.e., the wave functions at the vHs are layered.

To understand more clearly the origin of this peak, a fictitious material $\square^{2+}CNi_3$ was studied, in which Mg was removed but its two valence electrons were retained. While the C atom does have an important effect on the bonding and the resulting density of states (not pictured), for practical purposes the Mg simply gives up its two valence electrons to the bands (formed mainly by Ni) and has almost no other effect, as can be seen in Fig. 1. We utilize this important point below. If there were 0.5 electron less per cell, E_F would lie just at the peak in the DOS where $N(E)$ is a factor of 8 larger.

In addition to promoting superconductivity, a large value of $N(E_F)$ (equal to 2.4 states/eV-spin here) leads to spin fluctuations and an exchange-enhanced magnetic susceptibility χ that strongly opposes singlet superconductivity, and potentially leads to a ferromagnetic instability (where $\chi \rightarrow \infty$) which is incompatible with singlet superconductivity. This latter scenario applies to Sr_2RuO_4 [16], which is a nearly ferromagnetic superconductor ($T_c = 1.5$ K) and is now understood to be a parallel-spin-paired (triplet) superconductor. Density functional calculations are very reliable in calculating this tendency toward magnetism, and indeed the instability to FM, particularly in intermetallic compounds such as $MgCNi_3$. The enhanced (observed) susceptibility [17] is given by

$$\chi = \chi_0/[1 - N(E_F)I] \equiv S\chi_0\,, \qquad (1)$$

where $\chi_0 = 2\mu_B^2 N(E_F)$ is the bare susceptibility obtained directly from the band structure and I is the exchange interaction.

We have calculated $I \approx 0.29 \pm 0.01$ eV in two ways. One, which demonstrates directly our main thesis that $MgCNi_3$ is close to ferromagnetism, was a calculation for ordered $Mg_{1/2}Li_{1/2}CNi_3$. This material is predicted to be ferromagnetic, and the exchange splitting Δ_{ex} between majority and minority bands (Fig. 2) gives $I = 0.30$ eV from the relation $\Delta_{ex} = Im$, where m is the ferromagnetic moment in units of μ_B. The other calculation of I resulted from fixed spin moment calculations [18], in which the energy $E(m)$ is calculated subject to the moment being constrained to be m. The behavior at small m is $E(m) = (1/2)\chi^{-1}m^2$ from which $I = 0.28$ eV can be extracted from Eq. (1). Singh and Mazin [13] obtained a similar value for the Stoner parameter. Thus $S = 3.3$, and it is certainly unexpected for a conventional (singlet) superconducting state to survive so near a ferromagnetic instability, especially when the superconducting carriers are heavy and are the same ones that will become magnetic.

To quantify how near this system is to being ferromagnetic, we have carried out (i) a series of virtual crystal calculations for $Mg_{1-\delta}Na_\delta CNi_3$ (justified by the results shown in Fig. 2) to find the concentration δ_{cr} of the ferromagnetic critical point, and (ii) an extended Stoner analysis [19]. The two results are consistent in predicting the onset of FM at $\delta_{cr} \simeq 0.12$. The ordered magnetic moment $m(\delta)$ versus hole-doping level is shown in the inset of Fig. 3, where it is evident that, in the absence of superconductivity, a moment grows as $m(\delta) = \mathcal{G}(\delta - \delta_{cr})^{1/2}$ for small $\delta - \delta_{cr}$ beyond the critical concentration. The behavior of $m(\delta)$ in the small m limit can be obtained analytically from an expansion of $\bar{N}(m)$ (the DOS averaged over a region centered at E_F and containing m electrons):

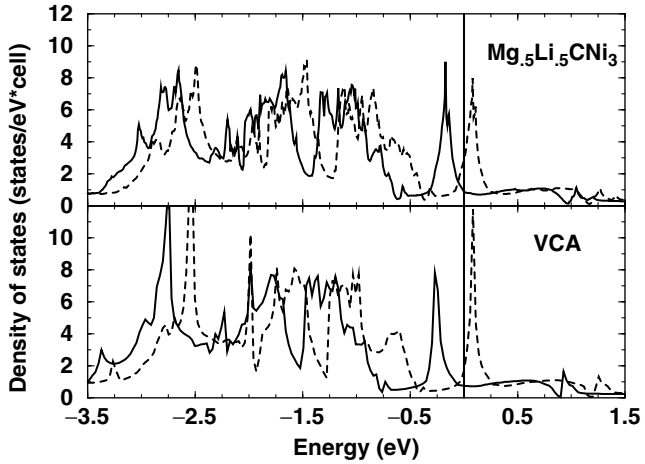

FIG. 2. Density of states of ferromagnetic $\delta = 0.5$ materials. Top panel: the ordered compound $Mg_{0.5}Li_{0.5}CNi_3$. Bottom panel: a virtual crystal result for $Mg_{0.5}Na_{0.5}CNi_3$. This level of doping results in a filled majority van Hove peak and a nearly empty minority van Hove peak. The calculated magnetic moments are $0.83\mu_B$ and $0.95\mu_B$, respectively.

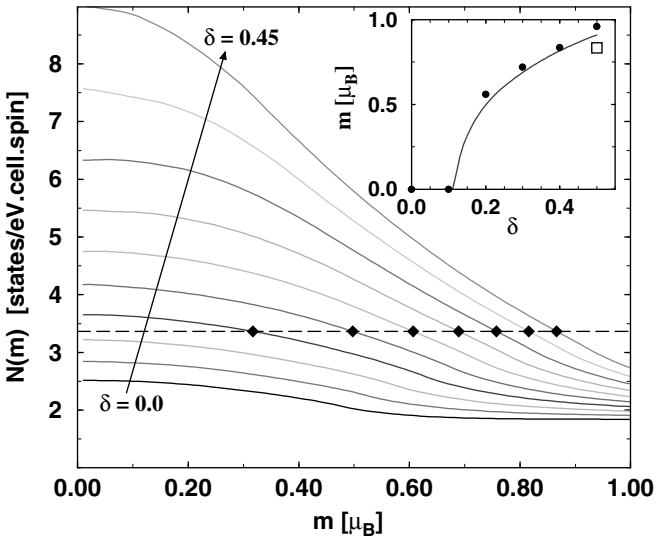

FIG. 3. The mean value $N(m)$ (defined in the text) versus m. Hole-doping concentrations $0 \le \delta \le 0.45$ are shown. The dashed line indicates $1/I$ ($I = 0.29$ eV). The solid curves give results from a rigid band treatment based on the $MgCNi_3$ ($\delta = 0$) DOS. The inset gives the predicted value of the ferromagnetic moment versus the hole concentration from the Stoner model (solid line) and from specific self-consistent virtual crystal calculations (dots) for $Mg_{1-\delta}Na_\delta CNi_3$, which indicates the consistency. The square gives the moment for the ordered compound $Mg_{1/2}Li_{1/2}CNi_3$ discussed in the text and in Fig. 2.

$$\bar{N}(m,\delta) \approx \bar{N}(0,\delta_{\rm cr}) + \frac{d\bar{N}(0,\delta_{\rm cr})}{d\delta}(\delta - \delta_{\rm cr}) + \frac{1}{2}\frac{d^2\bar{N}(0,\delta_{\rm cr})}{d^2m}m^2 = I^{-1}, \quad (2)$$

and using $\bar{N}(0,\delta_{\rm cr}) = 1/I$ to obtain the square root law, with

$$\mathcal{G} = \left| 2\frac{d\bar{N}(0,\delta_{\rm cr})}{d\delta} \Big/ \frac{d^2\bar{N}(0,\delta_{\rm cr})}{d^2m} \right|^{1/2} \approx 1.7\mu_B . \quad (3)$$

There are experimental indications from tunneling [10] that the superconductivity in $MgCNi_3$ may arise from triplet pairing [20], in which case the magnetic correlations themselves provide the coupling (as recently argued for heavy fermion superconductors [21]). In that case T_c would initially be enhanced as the critical point is approached ($\delta \to \delta_{\rm cr}$). We return to a discussion of the critical point below. Our results show that hole doping with Na or Li will be an excellent way to probe this possibility; Mg vacancies will also dope holes but we have not evaluated the accompanying change in the electronic structure or the lattice relaxation. Although pressure might have been expected to be a useful tool in this regard, we have found the position of the vHs to be remarkably *insensitive* to the reduction of the lattice constant, at least up to 5%.

We now consider in more detail the electronic structure and its implications, especially in the critical region $\delta \approx 0.12$. In this region E_F is still 35 meV from the vHs, so (near) divergence of $N(\varepsilon)$ *per se* is not a crucial consideration. Various pairing susceptibilities (see below) must be considered, and they will involve energy denominators $\delta\varepsilon = \varepsilon_{\vec{k},n} - \varepsilon_{\vec{k}+\vec{q},m}$, where n, m label the three M points where the vHs's occur. For $n = m$, $\delta\varepsilon$ will be small for small $\vec{q}$, which relates to the ferromagnetic instability we have considered above. Since there are vHs's at three inequivalent M points, there will also be a potential antiferromagnetic (AFM) instability near vectors $\vec{Q}$ that span two inequivalent vHs's. These values of $\vec{Q}$ are in fact equal to M, so AFM tendencies in $\chi(Q)$ are peaked at or near the M points. AFM order is frustrated on the Ni sublattice.

The dominant instability is determined largely by phase space availability. The band giving the vHs, shown in detail in Fig. 4, is quite flat (to within 50 meV) in a roughly cubic region of side π/a centered on each M point, which totals 3/8 of the Brillouin zone volume. Band masses at the vHs are quite large: $m^* \approx 12$–13 along M-X, and $m^* \approx -8$ along M-R. Along M-Γ, however, this band is amazingly constant (to within 0.2 meV) for a distance of $\approx \frac{1}{3}\frac{\pi}{a}$, i.e., it has a practically infinite effective mass along this line. Because of this lack of dispersion along one direction, the shape of the $N(E)$ peak in Fig. 1 has the logarithmic divergence characteristic of 2D models. Since this dispersionless line is oriented differently for each M point, there is no pronounced nesting of the vHs. We note that this lack of dispersion is of entirely different origin than dispersionless bands in conventional perovskites, which occur due to negligible $dd\delta$ hopping between neighboring metal atoms. [22]

A 2D vHs promotes charge density wave formation [23] as well as an enhanced tendency to superconducting pairing [24]. The $MgCNi_3$ vHs shown in Fig. 1 introduces

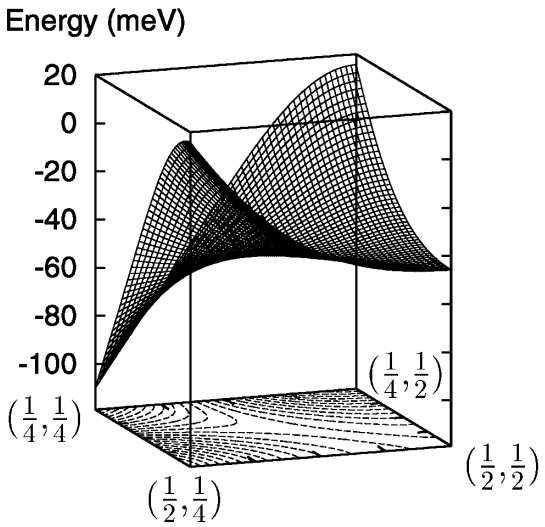

FIG. 4. Surface plot (and contour plot below) of the van Hove singularity in ε_k (relative to E_F) in the Γ-M-X plane, with M at the right-hand corner (planar coordinates are given in units of $2\pi/a$). Note the extreme flatness of the dispersion along the diagonal $M \to \Gamma$. The negative effective mass sheet of the vHs lies in the third direction.

2D character, and the accompanying tendency to 2D instabilities, into a 3D system. These phenomena are not directly applicable in $MgCNi_3$, but will become more so upon hole doping, as E_F approaches the vHs. As δ increases, the ferromagnetic instability is reached before the "vHs physics" becomes active. Beyond $\delta = \delta_{cr}$, however, the exchange splitting of the bands will drive the minority spin vHs through the Fermi level (see Fig. 1, where it is already above E_F), and density waves and superconducting pairing *in the minority channel alone* will be favored. In general, the strong exchange enhancement and the proximity to a ferromagnetic instability is most consistent with triplet pairing, appropriate forms of which can coexist with FM as in UGe_2 [3,4,25], or with incipient FM as in Sr_2RuO_4. There are numerous possibilities of triplet order parameters for a cubic system [26], some of which have gaps but many of which have nodes and therefore are gapless. Also, some order parameters are nonunitary [27] leading to magnetism in the superconducting phase. Because of the Meissner effect, the magnetic character is not trivial to detect, and distinguishing a gapless state requires high quality thermodynamic and spectroscopic data, most of which are not yet available.

Our results indicate that hole-doped $MgCNi_3$ presents a promising case for (triplet) superconductivity that coexists with ferromagnetism. Fay and Appel [28] contended that triplet pairing via longitudinal spin fluctuations would cause T_c to peak *near* $\delta = \delta_{cr}$ (on either side) but vanish *at* the critical point, but this has recently become controversial. Blagoev *et al.* [29] and Kirkpatrick *et al.* [30] also expect $T_c(\delta_{cr})$ to vanish, but the former obtain singlet superconductivity within the (weakly) ferromagnetic phase, while the latter obtain triplet pairing with an enhanced T_c due to coupling to magnons within the ferromagnetic phase. Roussev and Millis, using expansions around the critical point, obtain instead a *maximum* of T_c at the critical point [31]. Hole-doped $MgCNi_3$ is an excellent system for helping to clarify this issue.

To summarize, we have shown that the superconductor $MgCNi_3$ is near a ferromagnetic instability that can be reached by hole doping on the Mg site. The effective carriers are Ni-derived holes of very high band mass (likely enhanced by dynamic spin fluctuations and phonons). The ferromagnetic instability is related to an unusual quasi-2D heavy mass van Hove singularity less than 50 meV below E_F. This quasi-2D character supports earlier suggestions that its superconductivity is unconventional in nature, and we suggest that hole doping is an ideal way to probe the onset of ferromagnetism in the superconducting state.

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