Superconductivity near Ferromagnetism in MgCNi$_3$

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(Received 25 June 2001; published 26 December 2001)

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 $\sim$12% Mg $\rightarrow$ Na or Li (i.e., 0.04 hole/Ni). We identify an essentially infinite mass along the $M$–$\Gamma$ 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.

DOI: 10.1103/PhysRevLett.88.027001 PACS numbers: 74.70.Ad, 71.20.Lp, 74.20.–z, 74.25.Ha

The discovery of $\sim$40 K superconductivity in MgB$_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)$_2$FeCl$_4$, 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$_2$RuO$_4$ [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 $\lambda = 0.7$, 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 $z$ 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...
compounds such as MgCNi$_3$, indeed the instability to FM, particularly in intermetallic superconductors. Density functional calculations are very reliable in calculating this tendency toward magnetism, and is now understood to be a parallel-spin-paired (triplet) susceptibility. This latter scenario applies to Sr$_2$RuO$_4$. The two results are consistent in predicting the onset of FM at $\delta_{cr} = 0.12$. 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 $m(\delta) = G(\delta - \delta_{cr})^{1/2}$ 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):

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

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 $I = 0.29 \pm 0.01$ 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 $\Delta_{ex}$ between majority and minority bands (Fig. 2) gives $I = 0.30$ eV from the relation $\Delta_{ex} = \text{Im}$, where $m$ is the ferromagnetic moment in units of $\mu_B$. 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 $\delta_{cr}$ of the ferromagnetic critical point, and (ii) an extended Stoner analysis [19]. The two results are consistent in predicting the onset of FM at $\delta_{cr} = 0.12$. 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 $m(\delta) = G(\delta - \delta_{cr})^{1/2}$ 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):

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We now consider in more detail the electronic structure or the lattice relaxation. Although pressure might have been expected to be a useful tool in this regard, we have not evaluated the accompanying change in the electronic structure. 

Mg vacancies will also dope holes but we have argued for heavy fermion superconductors [21]). In that case, there is no pronounced nesting of the vHs. We return to a discussion of the critical point below. Our results show that hole doping may arise from triplet pairing [20], in which case the magnetic instability near vectors \( \tilde{Q} \) that span two inequivalent vHs. These values of \( \tilde{Q} \) 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(149,1000),(196,1439), is quite flat (to within 50 meV) in a roughly cubic region of side \( \pi/a \) centered on each M point, which totals 3/8 of the Brillouin zone volume. Band masses at the vHs are quite large: \( m^* = 12-13 \) along \( M-X \), and \( m^* = -8 \) along \( M-R \). Along \( M-\Gamma \), however, this band is amazingly constant (to within 0.2 meV) for a distance of \( = \pi/a \), 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 so (near) divergence of \( N(e) \) per se is not a crucial consideration. Various pairing susceptibilities (see below) must be considered, and they will involve energy denominators \( \delta e = e_{L,n} - e_{L+\tilde{Q},m} \), where \( n, m \) label the three M points where the vHs’s occur. For \( n = m \), \( \delta e \) will be small for small \( \tilde{Q} \), 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 \( \tilde{Q} \) that span two inequivalent vHs’s. These values of \( \tilde{Q} \) 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.
2D character, and the accompanying tendency to 2D instabilities, into a 3D system. These phenomena are not directly applicable in MgCNi₃, but will become more so upon hole doping, as $E_F$ approaches the vHs. As $\delta$ 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 UGe₂ [3,4,25], or with incipient FM as in Sr₂RuO₄. 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 MgCNi₃ 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, obtained instead a maximum of $T_c$ at the critical point [31]. Hole-doped MgCNi₃ is an excellent system for helping to clarify this issue. To summarize, we have shown that the superconductor MgCNi₃ 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.

W.E.P. and E.T. are grateful to R. Cava for conversations and for early communication of research results. This work was supported by the Italian MURST COFIN, by European Union TMR Contract No. ERBFMRXCT970155, by U.S. Office of Naval Research Grant No. N00017-97-1-0956, by National Science Foundation Grant No. DMR-9802076, and by the Deutscher Akademischer Austauschdienst. R.W. acknowledges support from Fundación Antorchas Grant No. 13661-27.

[20] Since doping simply due to the presence of an interface may occur at a tunnel junction, and it requires only a small amount of hole doping to introduce Ni moments, the possibility of magnetic moments at the interface should not be overlooked.