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Superconductivity Near Ferromagnetism in $MgCNi_3$

H. Rosner,[1] R. Weht,[2,3] M. Johannes,[1] W. E. Pickett[1] and E. Tosatti[3,4]
[1]Department of Physics, University of California, Davis CA 95616
[2]Departamento de Física, CNEA, Avda. General Paz y Constituyentes, 1650 - San Martín, Argentina
[3]ICTP, P.O. Box 586 34014 Trieste, Italy
[4]SISSA and INFM/SISSA, Via Beirut 2-4, 34014 Trieste, Italy

ABSTRACT

Superconductivity and ferromagnetism have been believed to be incompatible over any extended temperature range until certain specific examples – $RuSr_2GdCu_2O_8$ and UGe_2 – have arisen in the past 2-3 years. The discovery of superconductivity above 8 K in $MgCNi_3$, which is primarily the ferromagnetic element Ni and is strongly exchange-enhanced, provides a probable new and different example. This compound is shown here to be near ferromagnetism, requiring only hole-doping by 12% substitution of Mg by Na or Li. This system will provide the means to probe coupling, and possible coexistence, of these two forms of collective behavior without the requirement of pressure.

The discovery [1] of ∼40 K superconductivity in MgB_2 has spurred interest in searching for superconductivity in materials that would not be expected, based on the "old rules" to be likely candidates, and for unconventional (non singlet) pairing states. There have been other examples of various kinds, 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 occurs [3,4] in spite of strong ferromagnetism and coexists with it to the lowest temperatures, and the problem of ferromagnetism [5,6] on the surface of the exotic superconducting oxide Sr_2RuO_4. A new compound that would not be considered a likely candidate is $MgCNi_3$, whose conduction electrons are primarily derived from Ni which is itself a ferromagnet, and yet $MgCNi_3$ superconducts at 8.5 K [7]. Here it is shown that this compound is itself an incipient ferromagnet, which should be driven to ferromagnetism by partial (≈12%) replacement of Mg with a monovalent metal such as Li or Na. This proximity of superconductivity to magnetism strongly suggests unconventional pairing, and the crossover region between these phases will provide a novel playground in which to observe the competition, and possibly the coexistence, of these two intrinsically quantum mechanical – and usually antagonistic – collective phases.

The compound $MgCNi_3$ was shown recently to be superconducting by He *et al.* [7]. The perovskite structure itself is rather 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. 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 [8]. The resulting spectral distribution of the electronic states (all calculations are for the experimental lattice constant a=3.812 Å) are shown in Fig. 1. The conducting states at the Fermi level are dominated by Ni d_{xz}, d_{yz} and also $d_{x^2-y^2}$ character, in the local coordinate system in which the $\hat{z}$ axis is directed toward

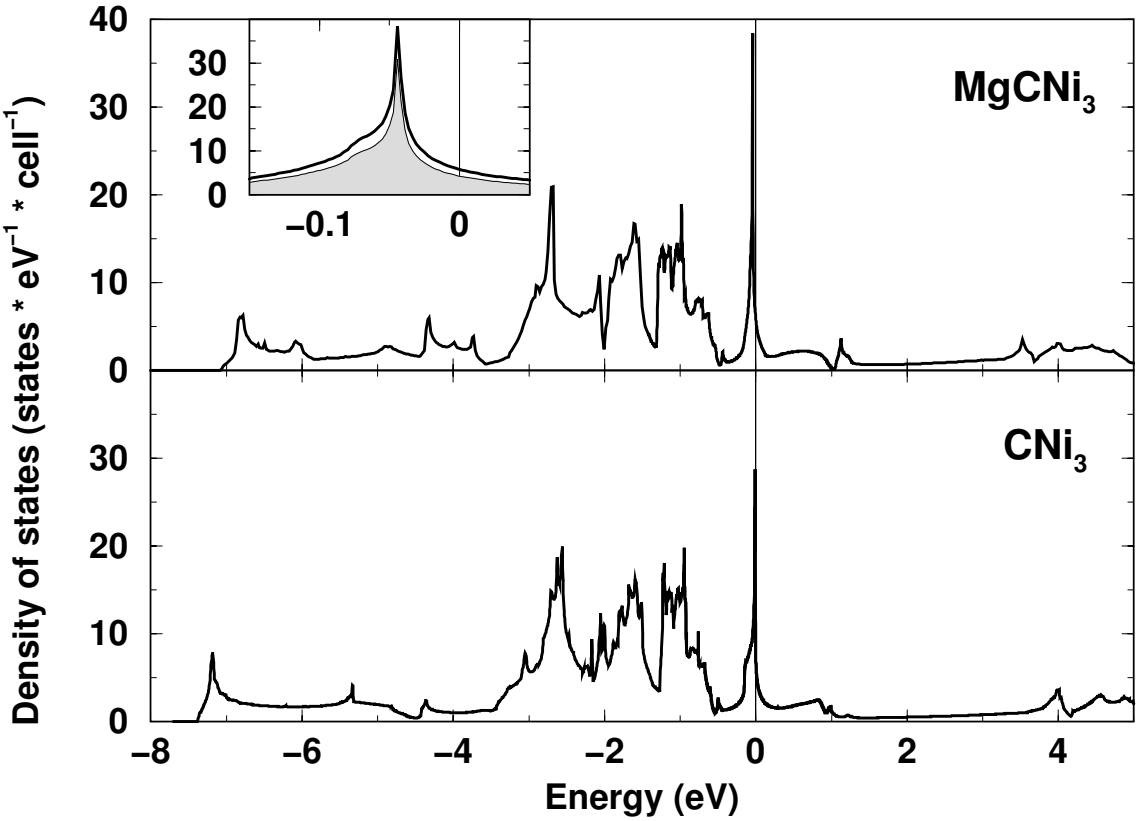

FIG. 1. **The extended van Hove singularity.** The density of states of $MgCNi_3$ (top panel), showing the nearly filled Ni d states and the extremely sharp and narrow peak just below E_F arising from a van Hove singularity (flat bands in the electronic band structure). The inset gives a blowup of the peak, with the shaded portion indicating the dominant Ni $3d$ contribution. The lower panel shows the density of states for $\square^{2+}CNi_3$ (Mg is removed but its two valence electrons are retained to give the same band filling). The very strong similarity, including the peak, reveals that Mg gives its electrons to the CNi_3 bands with little other influence and validates the rigid band and virtual crystal calculations of magnetism. A calculation for Ni_3 (*i.e.* both Mg and C removed; not shown here) reveals that C plays a significant role in forming the flat band and resulting van Hove peak.

the two neighboring C atoms. The remarkable feature of this compound is the sharp peak in the density of states (DOS) just 45 meV below the Fermi level [9]. This peak results from a van Hove singularity arising from a remarkably flat, primarily Ni $3d$ derived, band at and around the $M = (1, 1, 0)\pi/a$ point in the simple cubic Brillouin zone.

Thus the first result we obtain is that it is Ni $3d$ holes that form the superconducting pairs, and that bonding of these holes states is primarily Ni-Ni. (These states are not directed toward the C atom, and the Ni-Ni distance is only 8% larger than in Ni metal.) Because the DOS peak is so high and narrow, specific numerical values of the type that we will quote can be dependent on the method and quality of calculation (we find our methods give almost equivalent results but require at least 800 independent k-points in the irreducible Brillouin zone). The general predictions, within specified limits, are the same, however, for two different methods of calculation [8], and the results indicate that $MgCNi_3$ is quite unlike conventional intermetallic superconductors.

To understand more clearly the origin of this peak, the fictitious material $\square^{2+}CNi_3$ was

studied, *i.e.* Mg was removed but its two valence electrons were retained. While the C atom does have an appreciable 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 return to this important point below. If there were 0.5 electron less per cell, however, E_F would lie just at the peak in the DOS where N(E) is a factor of 6-8 larger. A large value of $N(E_F)$, which is 2.4 states/eV-spin for $MgCNi_3$, is known to promote conventional superconductivity where electrons are coupled by phonon exchange and are paired in antiparallel spin ("singlet") fashion.

A large value of $N(E_F)$ also suggests the likelihood of an exchange-enhanced magnetic susceptibility χ, which strongly opposes singlet superconductivity, or possibly even an instability to ferromagnetism (where $\chi \to \infty$) which is incompatible with singlet superconductivity. This latter scenario applies to Sr_2RuO_4 [10], which is a nearly ferromagnetic superconductor (but only below 1.5 K) and is now understood to be a parallel-spin-paired superconductor ("triplet" or p-wave). Density functional calculations are very reliable in calculating this tendency toward magnetism, and indeed the instability to ferromagnetism, especially in intermetallic compounds such as $MgCNi_3$. The enhanced susceptibility (which is what is observed in experiment) is given by

$$\chi = \frac{\chi_o}{1 - N(E_F)I} \equiv S\chi_o, \tag{1}$$

where χ_o is the bare susceptibility obtained directly from the band structure and is $2N(E_F)$ (in units of μ_B^2) 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 $Mg_{1/2}Li_{1/2}CNi_3$, which effectly simply removes 0.5 valence electron from the cell. This material is predicted to be ferromagnetic, and the exchange splitting Δ between majority and minority bands (Fig. 2) gives I= 0.30 eV from the relation $\Delta = Im$ where m is the ferromagnetic moment in units of μ_B. The other calculation of I resulted from fixed spin moment calculations [11], in which the energy $E(m)$ is calculated subject to the moment being constrained to be m. The behavior at small m is

$$E(m) = (1/2)\chi^{-1}m^2 \tag{2}$$

where χ is the enhanced susceptibility defined above, from which $I = 0.28$ eV can be extracted. The susceptibility is enhanced by a factor of 3.3; it is certainly unexpected for a conventional (singlet) superconducting state to survive so near a ferromagnetic instability, especially when the superconducting carriers are the same ones that will become magnetic.

To quantify how near this system is to ferromagnetism, we have carried out (i) a series of virtual crystal calculations for $Mg_{1-\delta}Na_\delta CNi_3$ to find the critical concentration δ_{cr}, and (ii) an extended Stoner analysis [12], which is essentially a rigid band study for the same instability, but is much less demanding computationally. The two results are consistent in predicting the onset of ferromagnetism at $\delta_{cr} = 0.12$. The ordered magnetic moment $m(\delta)$ versus hole doping level is shown in the inset in 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 the DOS $\bar{N}(m)$ averaged over the states within $\pm m$ of E_F:

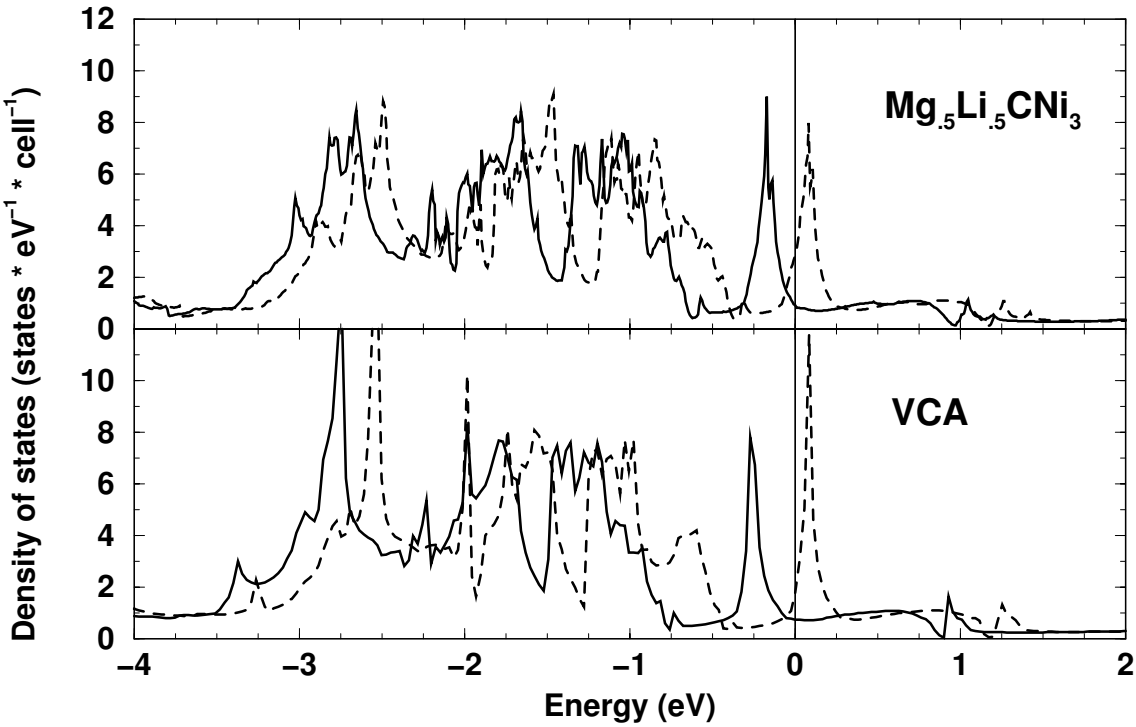

FIG. 2. **Ferromagnetic states obtained from self-consistent calculation.** Density of states of ferromagnetic $\delta = 0.5$ materials. Top panel: the ordered compound $Mg_{0.5}Li_{0.5}CNi_3$. Bottom panel: a virtual crystal result for $Mg_{0.5}Na_{0.5}CNi_3$. Note that this level of doping results in a filled majority van Hove peak and an empty minority van Hove peak. The very similar results indicate the small difference between Li and Na for hole doping, and the small and unimportant difference between distinct but ordered cations and averaged (hence perfectly ordered) cations. The magnetic moments are 0.83 μ_B and 0.95 μ_B, respectively.

$$\bar{N}(m,\delta) \approx \bar{N}(0,\delta_{cr}) + \frac{d\bar{N}(0,\delta_{cr})}{d\delta}(\delta - \delta_{cr}) + \frac{1}{2}\frac{d^2\bar{N}(0,\delta_{cr})}{d^2m}m^2 = I^{-1} \tag{3}$$

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

$$\mathcal{G} = \left|2\frac{d\bar{N}(0,\delta_{cr})}{d\delta}/\frac{d^2\bar{N}(0,\delta_{cr})}{d^2m}\right|^{1/2} \approx 1.75\mu_B. \tag{4}$$

There are experimental indications from tunneling [13] that the superconductivity in $MgCNi_3$ may arise from triplet pairing [14]. We have shown that hole doping with Na or Li will be an excellent way to probe this possibility. While it is unexpected that singlet superconductivity would occur at all in a Ni compound that is as strongly exchange enhanced as $MgCNi_3$ is (the increasing enhancement that diverges as $\delta \to \delta_{cr}$ should kill singlet superconductivity very quickly), for triplet pairing the increasing magnetic correlations may provide the coupling (as recently argued for heavy fermion superconductors [15]) and enhance T_c as $\delta \to \delta_{cr}$.

The exciting possibility is that (triplet) superconductivity might coexist with ferromagnetism, as reported recently for UGe_2 [3,4,16]. $Mg_{1-\delta}(Na,Li)_\delta CNi_3$ provides the new possibility, if indeed coexistence occurs due to triplet pairing, of studying the emergence of ferromagnetism (as δ crosses δ_{cr}) within an existing superconducting phase. The phenomenological

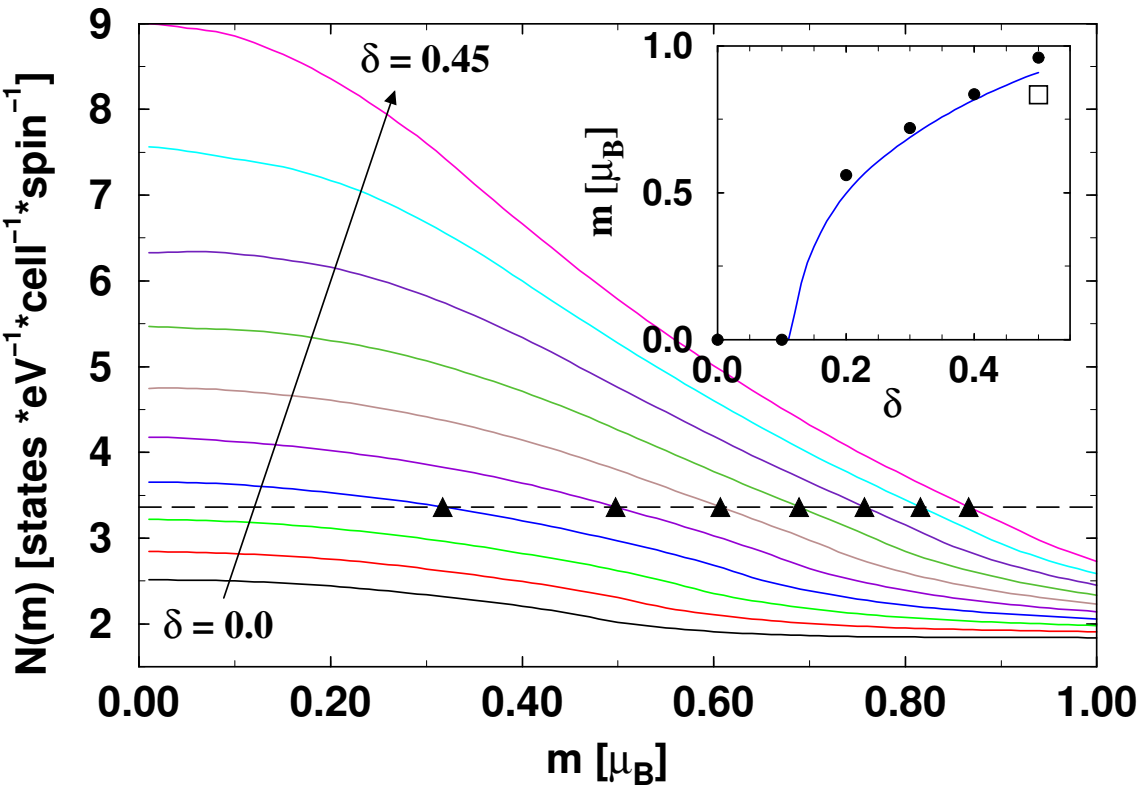

FIG. 3. **Instability of the system to ferromagnetism.** The mean value N(m) of the density of states around E_F necessary to create a magnetic moment m, versus m. Hole-doping concentrations $0 \leq \delta \leq 0.45$ are shown. The dashed line indicates $1/I$ (I=0.29 eV is the exchange interaction strength) above which the paramagnetic system is unstable to ferromagnetism. 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.

theory of coexistence in just such a case has been put forward recently [17], concluding that the heat capacity has a linear-in-T term that is strongly dependent on the magnetization. Solutions of the Eliashberg equations for a spin fluctuation system near the quantum critical point [18] suggest that triplet superconductivity might not be as strongly favored near the critical point as might have been suggested. Hole-doped $MgCNi_3$ appears to be an excellent system to use as a probe of these fundamental questions.

The theoretical case for superconductivity arising from magnetic fluctuations was laid out by Fay and Appel [19], who found that T_c should peak at $\delta = \delta_{cr}$. Machida and Ohmi [20] emphasize that a non-unitary triplet state is most likely in a case that is likely to apply to $MgCNi_3$, since it intrinsically breaks time-reversal symmetry as does ferromagnetism. In such non-unitary phases, a magnetic field may enhance T_c [20],

There are other factors that bear consideration. The triplet pairing that is suggested by the proximity to ferromagnetism is much more sensitive to disorder effects than is singlet pairing, so effort must be given to making stoichiometric samples (which is not easy even in the undoped compound [7]). In addition, the sharp, narrow peak in N(E) could favor a band

Jahn-Teller structural instability that would compete with the ferromagnetic tendencies if the electron-lattice coupling is strong. These possibilities must be given attention in future experimental and theoretical study.

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