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Electronic structure, magnetism, and superconductivity of MgC_xNi_3

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The electronic structure of the newly discovered superconducting perovskite $MgCNi_3$ is calculated using the LMTO method. The states near the Fermi energy are found to be dominated by Ni-d. The Stoner factor is low while the electron-phonon coupling constant is estimated to be about 0.5, which suggests that the material is a conventional type of superconductor where T_c is not affected by magnetic interactions. However, the proximity of the Fermi energy to a large peak in the density of states in conjunction with the reported nonstoichiometry of the compound has consequences for the stability of the results.

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The recent report of superconductivity below 8 K in the intermetallic compound $MgCNi_3$ by He *et al.*[1] is the first in a material which has the perovskite structure without any oxygen. The perovskite oxides have hosted a wide variety of exotic phenomena, including high-temperature superconductivity,[2] colossal magnetoresistance,[3] and ferroelectricity.[4] Presented as a three-dimensional analog of the borocarbide superconductors[5] (where there has recently been suggestion of non-s-wave pairing[6]), He *et al.* speculated that the favoring of a superconducting ground state over a ferromagnetic one in $MgCNi_3$ (with its high Ni content), makes it a potential candidate for unconventional superconductivity. In the rare-earth nickel borocarbides, the presence of moment-bearing rare-earth atoms and high Ni content makes the very existence of superconductivity surprising, and some of the phenomena associated with its interplay with magnetism have not been observed in any other superconducting material.[7,8] Huang *et al.*,[9] however, report no magnetic or structural transitions for $MgCNi_3$ in the range 2–295 K. Recent tunneling measurements by Mao *et al.*[10] have indicated that $MgCNi_3$ is a strong-coupling superconductor, and moreover that the pairing symmetry could be non-s-wave. Here we present calculations of the electronic structure of $MgCNi_3$, focusing on the central issues of magnetism and superconductivity as a function of doping.

The structure of $MgCNi_3$ has been reported to be that of a classic perovskite,[9] comprising a C atom at the body-center position, surrounded by a cage of Ni atoms at the face-center positions, with the Mg occupying the cube corners. The electronic structure of $MgCNi_3$ was calculated using the LMTO method.[11] The lattice parameter was fixed at the experimental low-temperature value of 7.2 a.u. (3.81 Å).[9] The calculations were made within the atomic sphere approximation (ASA) and self-consistency was reached using 286 k points within the irreducible wedge of the simple cubic Brillouin zone (BZ).

The density of states (DOS), bands and Fermi surface (FS) are shown in Figs. 1, 2, and 3, respectively. In Fig. 1, the dashed line represents the contribution of Ni to the total (solid line) DOS. These results agree well with the calculations of Hayward *et al.*[12] and Shim and Min.[13] It should be noted that near the Fermi energy, E_F, the DOS is almost completely due to Ni (see Table I). Clearly, with the Fermi level lying in such close proximity to a large peak in the DOS, there will be a sensitivity in the derived quantities. Should single crystal samples become available, a determination of the FS topology would be a stringent check on the location of the Fermi energy on the DOS peak, since the low dispersion of the Ni-d bands would make the topology very sensitive to small shifts in E_F.

The calculations include s, p, d, and f states for all atoms because the partial f-DOS is required in the evaluation of the electron-phonon coupling. Some bands were found to be sensitive to the choice of linearization energies, but a separate LMTO calculation using only s, p, and d states for Ni, and s and p states for Mg and C, gave the same FS topology and a very similar total DOS at E_F. Two bands cross E_F, making one jungle-gym-like FS sheet around the BZ edge, with a spheroidlike sheet around Γ. The second FS plot shows some X-centered shell-like features at the BZ faces and small, delicate "cigars" along Γ-R.

The bands (Fig. 2) are quite dispersive near E_F, with a Fermi velocity of 2.0×10^5 m s^{-1}, which in combination with the large DOS, would give the material a good metallic conductivity. The temperature dependence of the resistivity is reported as having the signature of a poor metal;[1] as the

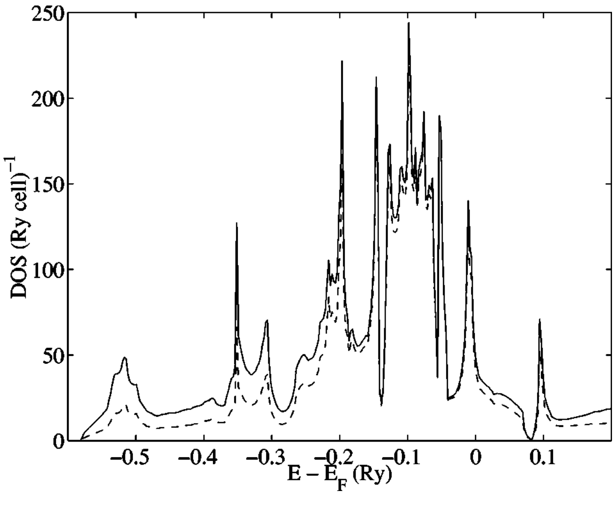

FIG. 1. Density of states (DOS) for $MgCNi_3$. The total DOS (solid line) and the partial Ni DOS (dashed line) are shown.

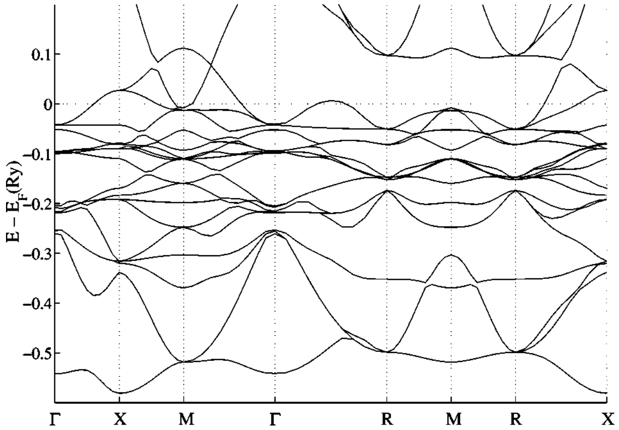

FIG. 2. Electronic band structure of $MgCNi_3$ along the high-symmetry directions of the simple cubic BZ.

calculated DOS is strongly varying near E_F, it is expected that unusual T dependencies could occur.

The propensity for a metallic system to adopt a ferromagnetic ground state can be expressed in terms of the Stoner factor, $S=1/(1-\overline{S})$, this being the exchange enhancement, which diverges at a ferromagnetic transition.[14,15] The DOS per Ni atom is considerably smaller than in fcc Ni, and the calculated value of the Stoner factor, $\overline{S}=0.43$, is far from the ferromagnetic limit. This suggests that in contrast with common expectations for Ni-rich compounds,[1] magnetism will not be present here and should not interfere much with superconductivity. Antiferromagnetic ordering would also seem unlikely, since the three-dimensional structure makes the FS topology quite complicated with no obvious nesting features. Shim and Min,[13] however, found a subtly different FS topology from that presented by us,[16] and suggested that there might be nesting across the Γ-centered electron sheet which, in their calculation, is more octahedral in shape.

The electron-phonon coupling constant, λ, can be expressed as $\lambda=\Sigma_i(\eta_i/M_i\langle\omega_i^2\rangle)$, where the sum runs over all atoms, i, with masses, M_i, and phonon frequencies, ω_i, while the numerator, η_i, is the electronic contribution.[17] Here, η was calculated in the rigid muffin-tin approximation;[17] this implies that only dipole terms without screening are included. The large Ni-d DOS is such that the contribution to η is dominated by Ni d to f scattering. In order to get an idea of how large λ could be, we estimate the phonon contribution by using a scaling of the Debye temperature (Θ_D) of fcc Ni [450 K (Ref. 20)] via the bulk modulus, B. When the atomic mass is constant, we can use that $\Theta_D=c(a\cdot B)^{1/2}$, where c is a constant and a is the lattice constant.[18]

It is worth noting that the structure of $MgCNi_3$ is like that of fcc Ni except for three things: first, the C atom goes into an interstitial site, unoccupied in the fcc structure; secondly, one Ni site is replaced by a Mg atom; thirdly, the lattice constant is increased from 3.52 Å in fcc Ni to 3.81 Å by the presence of Mg and C. Thus the similarity with fcc Ni is already significant for the structure, and this is confirmed in the general DOS properties near E_F. The calculated bulk moduli are about 1.9 Mbar and 0.5 Mbar for fcc Ni and $MgCNi_3$, respectively (both evaluated at their experimental volumes). The bulk modulus seems to be determined by the Ni sublattice, since the calculated value for $MgNi_3$ at the two volumes are very similar, namely 1.8 and 0.5 Mbar. Hence, one can conclude that the lattice expansion, caused by the alloying with Mg and C, leads to an important softening of the Ni lattice. As the electronic states at E_F are dominated by Ni, it is mainly the phonon properties of the Ni lattice that should enter the calculation of λ.

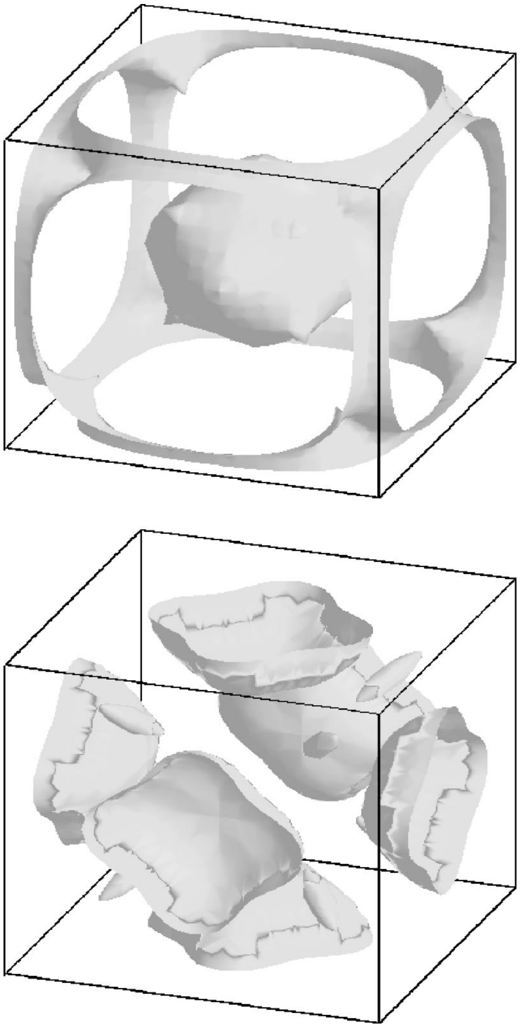

FIG. 3. The Fermi surface sheets of $MgCNi_3$.

In this case, we obtain $\Theta_D=240$ K and $\lambda=0.89$, which, with the bare DOS, gives an electronic specific heat coefficient of 5.3 mJ per mole Ni K^{-2}. This is smaller than the experimental value[1] (about 10 mJ per mole Ni K^{-2}), which

TABLE I. Site decomposition of the density of states at E_F $[(\mathrm{Ry\ cell})^{-1}]$.

Site	s	p	d	f
Mg	0.1	2.0	0.5	0.1
C	0.2	3.6	0.1	0.2
Ni_3	1.0	2.8	36.3	0.3

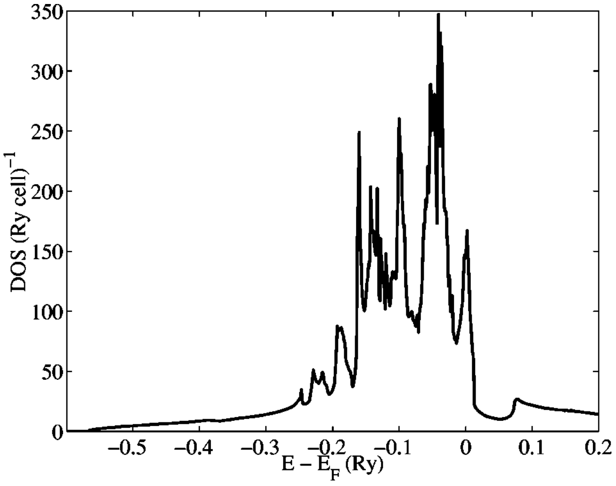

FIG. 4. Density of states (DOS) for (hypothetical) $MgNi_3$ at $a = 7.2$ a.u.

leaves room for additional enhancements due to spin or valence fluctuations. From their specific heat measurements, He *et al.*[1] infer $\lambda = 0.77$ (with errors of $+0.17$ and -0.09). We should like to point out that with a somewhat larger DOS, λ would be larger as well and both would contribute to give better agreement with the specific heat coefficient.

This LMTO-derived λ would give a superconducting critical temperature, T_c, of the order of 9 K [using the McMillan formula with $\mu^* = 0.13$ (Ref. 19)], in line with the experimental observations.[1] We would like to emphasize that this calculation of λ is strongly dependent on the phonon frequencies, and in our evaluation of the average phonon frequency it is not possible to detect possible softening or hardening of specific phonon branches.

There is a large peak in the DOS close to E_F, and if doping were to add 0.5 holes per unit cell, E_F would reach that peak. In this case, the DOS at E_F would be more than twice as large, reaching 130 states per cell per Ry, which would mean that $\overline{S}$ would become close to unity. However, this is unlikely for the measured material, since the specific heat coefficient would become too large, both due to the bare DOS and from the additional enhancements.

The occupation of the C site is reported to be slightly smaller than one (0.96) for the sample with a T_c of 8 K, with a rapid suppression of superconductivity as the C content is reduced further.[1] A rigid-band shift to account for $x = 0.96$ implies less than a 5% increase of the DOS and λ, having only minor effects on our calculated results. It was noted that in the absence of the C site, the structure would be like that of fcc Ni, but with one out of four Ni replaced by a Mg atom. A calculation of the band structure of $MgNi_3$ with the same lattice constant as for the superconducting material confirms the similarity with the electronic structure of pure fcc Ni (cf. Fig. 4). (A calculation with the C site replaced with a vacancy muffin tin shows this too.) The Fermi level is now lower, falling at the peak and making $N(E_F)$ very large with 151 states/Ry cell, or 49 states/(Ry Ni) compared to 55 states/(Ry Ni) in fcc Ni. The Stoner factor increases to 1.54, and magnetic order appears in spin-polarized calculations. The matrix element for electron-phonon coupling, however, does not increase in proportion with the total DOS. The Ni-*d* becomes more dominant which reduces, in part, the dipolar coupling. Using the same phonon frequency as before, we find $\lambda = 0.41$; this is still larger than in fcc Ni.

By making a crude interpolation between our results for $MgCNi_3$ and $MgNi_3$, it is possible to propose the following scenario for superconductivity and magnetism as a function of a further reduction of the C occupation, *x*. For $x = 1$, the material is a rather conventional strong-coupling superconductor. The quite substantial λ is largely due to an unusual lattice softening of the Ni sublattice. As *x* decreases, $N(E_F)$ will increase, since the Fermi level moves lower towards the large peak in the DOS, leading to a gradual increase of the Stoner factor. In this region of doping, it is possible that T_c would increase since the Stoner factor is not yet very large. At about 0.4 holes per cell, the Stoner factor would be about 0.9, making spin fluctuations probable with a consequent pair-breaking effect and a suppression of T_c. The increase of the DOS and specific-heat enhancements due to spin fluctuations would make it worthwhile to also measure precise values of γ for smaller *C*-site occupation, *x*, when T_c is suppressed, since it should increase according to these predictions. If the material remains stable with even smaller *C* concentrations, it should be possible to observe ferromagnetism.

These results indicate that a large DOS at E_F is not always beneficial for superconductivity. A very large DOS tends to induce spin fluctuations or magnetic order, which quickly destroy the superconducting pairing. The situation for Ni is that the *d*-like part of the DOS is so dominant that despite a large total DOS, the coupling is not as large as expected. Long-range monopolar coupling may become more important, as in some oxides. It has been pointed out that the essentially filled *d*-band in Ni is similar to the filled O *p* bands in perovskite oxides, which may also be the stabilizing factor for this particular structure.[1] However, the band structure of oxides like WO_3, ruthenates, manganites, and titanates with the same structure is quite different, with the presence of a large band gap. Furthermore, our results indicate that the phonon softening is important for λ in this material. Without knowledge of the experimental difficulties in producing other related Ni-based systems, we suggest that the possibility of lattice softening should be exploited in order to find a higher superconducting T_c. By substituting Ca for Mg, or Si for C, one should expand the Ni-lattice further and decrease the phonon frequencies. With no large differences in the electronic structure near E_F, one can expect an increased λ from the Ni lattice.

The electronic structure of the newly discovered perovskite superconductor, $MgCNi_3$ is reported. In summary, we find that although the DOS at the Fermi level is dominated by the Ni *d* states, it is not large enough to induce magnetic instabilities. However, the DOS is sufficiently large to produce strong electron-phonon coupling.

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