Electronic structure, magnetism and superconductivity of MgCNi₃

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The electronic structure of the newly discovered superconducting perovskite MgCNi₃ is calculated using the LMTO and KKR methods. 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 0.7, which suggests that the material is a conventional type of superconductor where Tc 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 non-stoichiometry of the compound, has consequences for the stability of the results.

The perovskite oxides have hosted a wide variety of exotic phenomena, including high-temperature superconductivity, colossal magnetoresistance and ferroelectricity. However, the recent report of superconductivity below 8K in the intermetallic compound MgCNi₃ by He et al. is the first in a material which has the perovskite structure without any oxygen. Presented as a three-dimensional analog of the borocarbide superconductors, MgCNi₃ (where there has recently been suggestion of non-s-wave pairing), He et al. speculated that the favoring of a superconducting ground state over a ferromagnetic one in MgCNi₃ (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. Huang et al., however, report no magnetic or structural transitions for MgCNi₃ in the range 2—295K. Recent tunneling measurements by Mao et al. have indicated that MgCNi₃ 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 MgCNi₃, focusing on the central issues of magnetism and superconductivity.

The structure of MgCNi₃ has been reported to be that of a classic perovskite, 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 MgCNi₃ was calculated using both the LMTO and, as a cross-check and comparison, with the KKR method. The lattice parameter was fixed at the experimental low-temperature value of 7.2 a.u. (3.81Å). For the KKR calculations, made within the atomic sphere approximation (ASA), self-consistency was reached using 286 k-points within the irreducible wedge of the simple cubic Brillouin zone (BZ). The KKR code used non-overlapping muffin-tin potentials, and the mesh of k-points was adaptive and determined principally by the required integration tolerances.

The bands, density of states (DOS) and Fermi surface (FS) from the LMTO results are shown in Figs. 1, 2 and 3 respectively. In Fig. 2, the dashed line represents the contribution of Ni to the total (solid line) DOS. It should be noted that near the Fermi energy, E_F, the DOS is almost completely due to Ni (see Table I). The KKR results were very similar to those from the LMTO, but the Ni d-bands were flatter, generating a larger DOS at the Fermi level (86.4 compared to 47.6 states (Ry cell)⁻¹ from the LMTO). 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.

Henceforth, we will focus on the LMTO results. These 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 spheroid-like 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. 3) are quite dispersive near E_F, with a Fermi velocity of 2.0 × 10⁵ m/s, 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. As the 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 fer-
romagnetic ground state can be expressed in terms of the Stoner factor, $S = 1/(1 - \bar{S})$, this being the exchange enhancement, which diverges at a ferromagnetic transition [3]. The DOS per Ni atom is considerably smaller than in fcc Ni, and the calculated value of the Stoner factor $\bar{S}$=0.43 is far from the ferromagnetic limit. This suggests that, in contrast to common expectations of Ni-rich compounds, magnetism will not be present in this compound 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.

The electron-phonon coupling constant, $\lambda$, can be expressed as

$$\lambda = \sum_i \frac{\eta_i}{M_i \omega_i^2}$$

where the sum runs over all atoms, $i$, with masses, $M_i$, and phonon frequencies, $\omega_i$, while the numerator, $\eta_i$, is the electronic contribution. Here, $\eta$ was calculated in the rigid muffin-tin approximation. This implies that only dipole terms without screening are included. The large Ni-d DOS is such that the contribution to $\eta$ is dominated by Ni d to f scattering. In order to get an idea of how large $\lambda$ could be, we estimate the phonon contribution by using the Debye temperature of fcc Ni (450 K). In this case, we obtain 0.67 for $\lambda$, which, with the bare DOS, gives an electronic specific heat coefficient of 4.7 mJ per mole Ni K$^{-2}$. This is smaller than the experimental value (about 10 mJ per mole Ni K$^{-2}$), which leaves room for additional enhancements due to spin- or valence-fluctuations. From their specific heat measurements, He et al. [12] infer $\lambda = 0.77$ (with errors of +0.17 and -0.09). We should like to point out that with the bare Fermi energy DOS from the KKR calculations, the agreement with the electronic specific heat constant would be much closer. On the other hand, the LMTO-derived $\lambda$ would give a superconducting critical temperature, $T_c$, of the order of 10K (using the McMillan formula with $\mu^* = 0.13$ [11]), in line with the experimental observations, whereas that derived from the KKR DOS would be much larger. It should also be noted that this calculation of $\lambda$ is strongly dependent on the phonon frequencies, which are not calculated here.

Since there is a large peak in the DOS close to $E_F$, and if doping (the occupancy of the C-site is 0.96 rather than unity, in the measured material), 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 $S$ 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 electronic structure of the newly discovered perovskite superconductor, MgCNi$_2$ 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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FIG. 1. Electronic band structure of MgCNi₃ along the high-symmetry directions of the simple cubic BZ.

FIG. 2. Density of states (DOS) for MgCNi₃. The total DOS (solid line) and the partial Ni DOS (dashed line) are shown.

FIG. 3. The Fermi surface sheets of MgCNi₃.

TABLE I. Site decomposition of the density of states at $E_F$ [(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|
| Ni₃  | 1.0| 2.8| 36.3| 0.3|