CeMnNi₄: an impostor half-metal

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Recent experiments show CeMnNi₄ to have a nearly integer magnetic moment and a relatively large transport spin polarization, as probed by Andreev reflection, suggesting that the material is a half metal or close to it. However, the calculations reported here show that it is not a half metal at all, but rather a semimetal of an unusual nature. Phonon properties should also be quite unusual, with rattling low-frequency Mn modes. Nontrivial transport properties, including a large thermoelectric figure of merit, ZT, are predicted in the ferromagnetic state of the well ordered stoichiometric CeMnNi₄.

Recently, Singh et al. have measured the magnetic and transport properties of a novel ferromagnetic material, CeMnNi₄. The most striking observations are that the measured magnetic moment is 4.94 μB/formula, remarkably close to an integer magnetization of 5 μB, and at the same time Andreev reflection is suppressed in a way typical of highly polarized ferromagnets. The degree of spin polarization, deduced in the standard manner, was up to 65%, a relatively large number. These observations together suggest that CeMnNi₄ might be a half-metal. On the other hand, another, less obvious, observation cast doubt on such a simple interpretation: the resistivity as measured in Ref. 1 rapidly grows from zero temperature to T_C = 148 K, at a rate up to 2 μΩ·cm/K, characteristic of bad metals, with a very large residual resistivity of 0.24 mΩ·cm. At the same time, above T_C the temperature coefficient of the resistivity drops practically discontinuously to a value smaller than 0.06 μΩ·cm/K, a 1.5 order of magnitude change! Indeed, such large changes in the temperature coefficient resistivity at T_C have been previously encountered only near a metal-insulator transition (cf. colossal magnetoresistance, CMR). Some half metals may exhibit large changes of the resistivity slope near T_C without a metal-insulator transition, but the change is in the opposite direction.

Band structure calculations for this material can be expected to shed some light on the puzzling features described above. They do indeed, and in a rather unexpected way. In this paper I report such calculations and discuss their ramifications.

CeMnNi₄ crystallizes in the F43m group (#216). Its structure can be derived from the Heusler structure ABCD, where Ce and Mn occupy A and B positions, and Ni sits between C and D (plus three symmetry equivalent positions), Fig. 1. As one can see, Ni forms corner-sharing tetrahedra, similar to the spinel structure. The structure has one free parameter, the Ni position. If this position is exactly equal to (5/8, 5/8, 5/8) the lengths of the Ni-Ce and Ni-Mn bonds are exactly the same. As we will see, the optimized structure is very close to this, despite the fact that Ce has about 30% larger atomic radius than Mn. This is yet another hard to understand property of this compound. I have performed full-potential LAPW calculations, using the WIEN package and Perdew-Burke-

Ernzerho gradient-corrected exchange-correlation potential. Muffin-tin radii of 2.5 a_B for Ce and Mn and 2.23 a_B for Ni were used, the basis set included plane waves up to RK_max = 7 with APW local orbitals, and integration in k-space was performed using the tetrahedron method with 286 inequivalent points (21x21x21 mesh).

The nonmagnetic density of states (DOS) of CeMnNi₄ is shown in Fig. 2. One can clearly see that Ce f bands are about 1 eV above the Fermi level, indicating their delocalized character with no need of applying Hubbard-type correction (e.g., within LDA+U). It is further seen that Mn forms a relatively narrow band (0.25-0.30 eV), while the Ni bands are at least 4 eV wide (I will explain the origin of the Mn band narrowing later). Moreover, the Mn bands are pinned to the Fermi level, and are largely responsible for the very high DOS at the Fermi level (10 states/eV.spin.formula, or 2 states/eV.spin per 3d metal ion). Recalling that 3d transition metals have Stoner factors of the order of 1 eV, it is obvious that even after diluting with the less magnetic Ce the material should be very strongly magnetic. I thus proceed with magnetic calculations and find the band structure shown in Fig.
First, the ferromagnetic structure is found to be stabilized by a huge energy gain of 1.87 eV per formula. Second, the total calculated magnetization is 4.92 $\mu_B$ per formula, in nearly perfect agreement with the experiment, and indeed very close to an integer value. The moment is distributed like this: Mn carries approximately 4 $\mu_B$, four Ni together about 1.2 $\mu_B$ and Ce is polarized antiferromagnetically with a moment of 0.2 $\mu_B$. Clearly the magnetic engine in this compound is Mn, whose $d$ states are fully split by about 3 (!) eV. Ce plays the role of a cation in this compound, donating its one $f$-electron to Mn. This can be verified by taking the charges inside each MT sphere and distributing the interstitial charge proportionally to the MT sphere volumes, which yields $Q_{Ce} \approx 1.2e$, $Q_{Mn} \approx -0.6e$, $Q_{Ni} \approx -0.15e$. As a result, Mn has 6 $d$-electrons, and full exchange splitting on Mn site results in 5 spin-up and one spin-down electron. Ce $f$ (and $d$)-states are above the Fermi level, so they hybridize more with the higher-lying 3$d$ metal spin-down states (mostly Ni) than with the spin-up states, and the former acquire more of Ce character. This explains the antiferromagnetic polarization on Ce.

At this point it is worth mentioning that all calculations described above and below were performed in the structure obtained after optimizing the positions of Ni by minimizing the total energy in the ferromagnetic state. It appears that the optimal position of Ni in lattice coordinates is (0.624, 0.624, 0.624), and symmetry equivalent positions. This is spectacularly close to the “ideal” position of (5/8, 5/8, 5/8). Moreover, the corresponding $A_{1g}$ phonon of Ni does not appear to be particularly soft - the calculated frequency is about 165 cm$^{-1}$, a very regular number for an intermetallic compound with 3$d$ metals. If one substitutes Mn by Ce, the resulting structure, provided that Ni occupies the ideal position above, is the well known Laves phase. In fact, such a phase (CeNi$_2$) does form, with the lattice parameter practically identical (within 3%) to that of CeMnNi$_4$. This proves that the lattice parameter of the latter is defined by the Ce-Ni interaction. After one Ce is substituted by a Mn with its 30% smaller metal radius, Mn appears in a cage much larger than is needed for normal metallic bonding. Indeed, known Mn-Ni binaries (MnNi, MnNi$_3$) are characterized by the Ni-Mn bonds of the order of 4.8 $a_B$, compared to nearly 5.5 $a_B$ in CeMnNi$_4$. Thus, Mn in CeMnNi$_4$ is a “rattling” ion, similar, for example, to
La rattling in thermoelectric skutterudites. This anomalously large distance from Mn to its nearest neighbors explains why the Mn bands in CeMnNi$_4$ are so narrow.

Even a cursory glance at the density of states (Fig. 4) and especially at the band structure (Fig. 3) of the ferromagnetic CeMnNi$_4$ reveals that despite the nearly-integer magnetic moment it could not be farther from a half metal. What is actually happening is that in both spin channels the Fermi level, rather accidentally, falls inside a deep pseudogap (about 0.3 eV wide), thus making this material more a semimetal than half metal (except that in a classical semimetal, like Bi, there is at least a direct gap, although the valence band and the conductivity bands have a small indirect overlap, whereas in CeMnNi$_4$ there is no gap at all). The DOS at the Fermi level is $N_{\uparrow} = 0.85$ states/eV.formula, $N_{\downarrow} = 1.16$ states/eV.formula, corresponding to an electronic specific heat coefficient of 4.7 mJ/mol.K$^2$, or 0.8 mJ/g-atom.K$^2$. This is a very small DOS, characteristic rather of doped semiconductors than of metals.

Note that the corresponding spin polarization of the DOS is $-16\%$, far from the observed $66\%$. Of course, one has to keep in mind that the Andreev reflection is sensitive only to the transport spin polarization, and likely, given the high resistivity of current samples, to the diffusive transport spin polarization. Let me remind the reader that the latter can be expressed in terms of the spin-dependent contribution to the plasma frequency, $P_{diff} = (\omega_{p\uparrow}^2 - \omega_{p\downarrow}^2)/(\omega_{p\uparrow}^2 + \omega_{p\downarrow}^2)$. Should the Fermi velocities for the two spin channels be drastically different, that could explain the observed high transport spin polarization. However, direct calculations yield the opposite result (Fig 5): $\omega_{p\uparrow} = 1.07$ eV, $\omega_{p\downarrow} = 1.10$ eV, corresponding to $3\%$ spin polarization. This means that the Fermi velocities are very close for both spins and actually relatively small for a typical transition metal:

$$\nu_{F\uparrow} = 2.1 \times 10^7 \text{ cm/sec}, \nu_{F\downarrow} = 1.9 \times 10^7 \text{ cm/sec}.$$ The message here is that the low DOS occurs not because of light electrons, but because of the small Fermi surfaces. Indeed, only three bands, one for the spin-up and two for the spin-down channel form noticeable Fermi surface pockets, shown in Fig. 6. This emphasizes again the analogy with semimetals.

While the calculations definitely do not agree with the measured spin polarization, this does not necessarily mean that either are wrong. The accepted technique for analyzing Andreev reflection data assumes an equal barrier strength for both spin channels. As has been pointed out previously, this assumption is not always justified and may change the results substantially.

One cannot exclude sample problems either; the temperature dependence reported in Ref. 1 hints at that. Indeed, the extremely weak temperature dependence of the resistivity above $T_C$ implies that there are no low-energy excitations (phonons or magnons) that could scat-
ter electrons (otherwise one would have a linear $T$ dependence, as in the Bloch-Grüneisen formula). On the other hand, if such excitations were present below $T_C$ but disappeared at the phase transition, a negative temperature coefficient would be expected just near the transition temperature, since the electron-scattering will be not present above $T_C$. On the other hand, if the resistivity were mainly due to static defects, the temperature dependence of the resistivity could be explained by a gradual decrease of the carrier concentration with temperature in the ferromagnetic phase, from $T = 0$ to $T_C$, which would have then to remain constant above $T_C$. However, the effective carrier concentration, $(n/m)_{\text{eff}}$, is nothing but the plasma frequency expressed in different units, and, as discussed above, the plasma frequency in CeMnNi$_4$ is much larger in the paramagnetic state 10, which would yield a decrease, not increase of $\rho$ with the temperature, with a resistivity minimum near $T_C$ (as, for instance, in Fe$_2$Co$_{1-x}$S$_2$, see Ref. 2).

On the other hand, the behavior below $T_C$ is reminiscent of the CMR manganates and some magnetic semiconductors, where large residual resistivity is also combined with a rapidly growing resistivity below $T_C$. The low effective carrier density in CeMnNi$_4$ supports this analogy. However, in CMR materials $T_C$ coincides with a metal-insulator transition, in most cases resulting in a strong (orders of magnitude) maximum of resistivity near $T_C$, instead of rather flat behavior above $T_C$ in CeMnNi$_4$, or in even more complicated temperature dependences driven by various structural transformations. Nevertheless, spatial inhomogeneity and percolation effects, known to be operative in manganates, may play an important role in CeMnNi$_4$ too. All this emphasizes again the unusual character of this material and calls for further experimental studies.

Let me now summarize the results of the calculations. First, despite the apparent resemblance to a half metal, CeMnNi$_4$ is not one. Its magnetic moment is simply accidentally nearly integer. Second, CeMnNi$_4$ exhibits a very deep pseudogap at the Fermi level, with the DOS dropping to a uniquely low value for an intermetallic compound. Third, despite the small DOS, the Fermi velocity is also rather low, which makes CeMnNi$_4$ electronically similar to semimetals. Intriguingly, the calculated electronic structure and transport properties offer no obvious explanation of the observed temperature dependence of the resistivity, which, unless one is willing to write this off as a sample problem, represent a very interesting challenge to the theory. Finally, the crystal structure is essentially set by the Ce-Ni cage, with Mn rattling in a cavity much larger than what is appropriate for this ion. These rather unusual characteristics should lead to interesting transport and optical properties. In particular, last but not least, the similarity to semimetals and presence of rattling phonon modes should make CeMnNi$_4$ a very promising low-temperature thermoelectric, provided it can be synthesized in a stoichiometric and defect-free form. On the other hand, by intentionally introducing defects one can create a material with a very high equilibrium magnetization and very low resistivity, making it a better soft magnetic material than the ferrites. Obviously, practical applications in this direction would require optimizing the material to raise its Curie temperature to room temperature.

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6 Although Mn d-bands are narrow and very likely correlated, such a large exchange splitting makes applying LDA+U correction to Mn an unnecessary complication: it would just increase the splitting between the occupied and unoccupied Mn states without any interesting effects at the Fermi level.
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$U = 1.25$ and $J = 0.33$ eV for Ce $f$ (as estimated from the atomic loop in an LMTO program), and again found practically no change from straight LDA.