CeMnNi$_4$: Impostor half metal

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Recent experiments show CeMnNi$_4$ 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 CeMnNi$_4$.

PACS number(s): 75.50.−y

Recently, Singh *et al.*[1] have measured the magnetic and transport properties of an unusual ferromagnetic material CeMnNi$_4$. The most striking observations are that the measured magnetic moment is 4.94μ_B/formula, remarkably close to an integer magnetization of 5μ_B, 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 CeMnNi$_4$ 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 $\mu\Omega$ 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 $\mu\Omega$ cm/K, a 1.5 order of magnitude change. These two facts could possibly be reconciled if in the magnetically saturated (half metallic?) state CeMnNi$_4$ had a much smaller carrier concentration and/or mobility than in the nonmagnetic state. However, in this case one would expect that slightly below T_C, where the magnetization rapidly disappears, the material would exhibit a negative temperature coefficient (as, for instance, in Fe$_x$Co$_{1-x}$S$_2$; see Ref. 2), which is not the case. Besides, while Fe$_x$Co$_{1-x}$S$_2$ is an itinerant ferromagnet, Mn magnetic moments in CeMnNi$_4$ are nearly certainly well localized and the Curie transition is most likely due to disordering of these moments. As discussed in more detail below, multiphase effects similar to those in colossal magnetoresistive materials may be responsible for such an odd behavior of the resistivity.

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

CeMnNi$_4$ crystallizes in the $F\bar{4}3m$ 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 linear augmented plane-wave (LAPW) calculations, using the WIEN package[3] and Perdew-Burke-Ernzerhof[4] gradient-corrected exchange-correlation potential. Muffin-tin (MT) radii of 2.5a_B for Ce and Mn and 2.23a_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 (21×21×21 mesh).[5]

The nonmagnetic density of states (DOS) of CeMnNi$_4$ 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 a Hubbard-type correction [e.g., within local density approximation (LDA)+*U*]. It is further seen that Mn forms a relatively narrow band
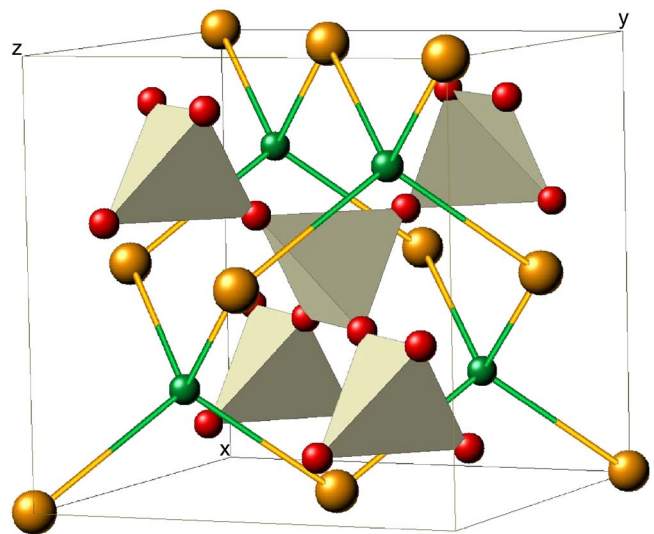

FIG. 1. (Color online) Crystal structure of CeMnNi$_4$. Large (brown) spheres denote the Ce atoms, the small (green) ones Mn, and the tetrahedra are formed by the Ni atoms, denoted by the small (red) spheres.
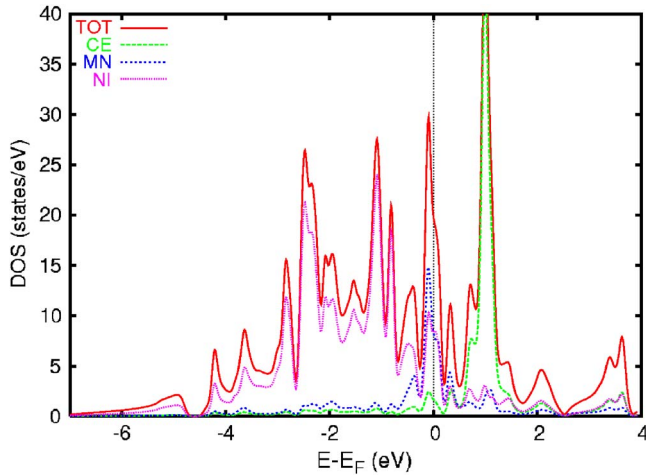
FIG. 2. (Color online) Density of states of nonmagnetic CeMnNi$_4$.

(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 per spin per formula, or 2 states/eV per 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 Figs. 3 and 4. 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 4.92μ_B/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 4μ_B, four Ni together about 1.2μ_B, and Ce is polarized antiferromagnetically with a moment of 0.2μ_B. Clearly the magnetic engine in this compound is Mn, whose d states are fully split by about 3 (!) eV.[6] 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 six d electrons, and full exchange splitting on the Mn site results in one spin-down and five spin-up electrons. Ce f (and d) states are above the Fermi level, so they hybridize more with the higher-lying 3d 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
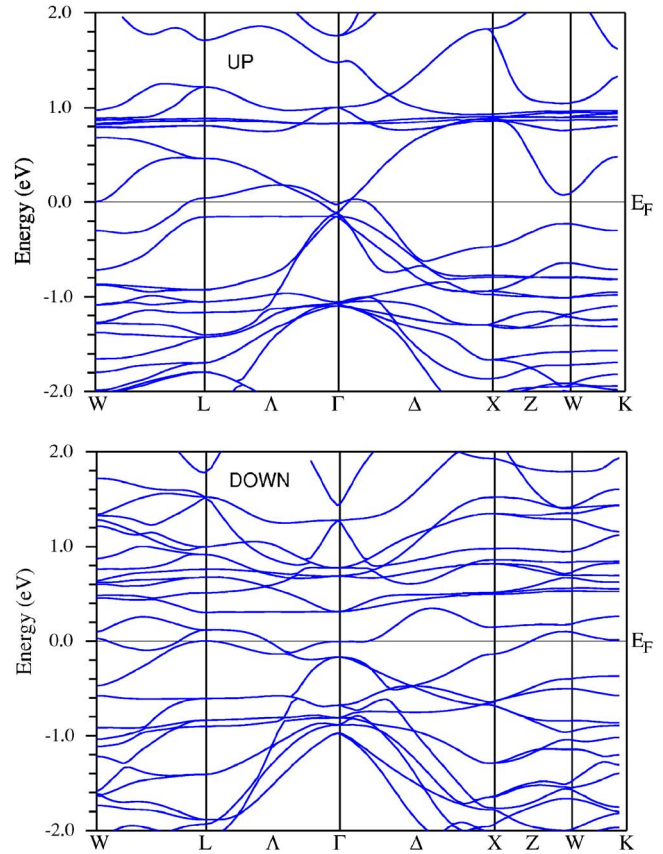

FIG. 3. (Color online) Band structuure of the ferromagnetic CeMnNi$_4$ in the optimized structure. Top panel: spin up. Bottom panel: spin down.

165 cm^{-1}, a very regular number for an intermetallic compound with 3d 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,[7] 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%
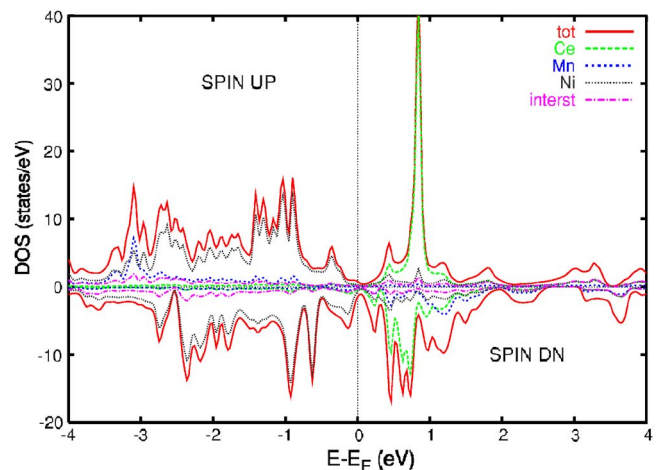

FIG. 4. (Color online) Density of states of the ferromagnetic CeMnNi$_4$ in the optimized structure.
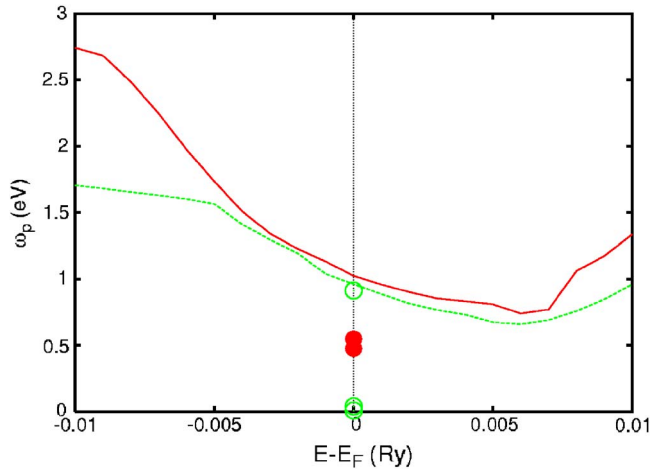
FIG. 5. (Color online) The plasma frequencies of ferromagnetic $CeMnNi_4$ in the optimized structure. Green dashed (red solid) lines show the spin-up (spin-down) components. Symbols show a band decomposition at the Fermi level: open, spin up; filled, spin down.
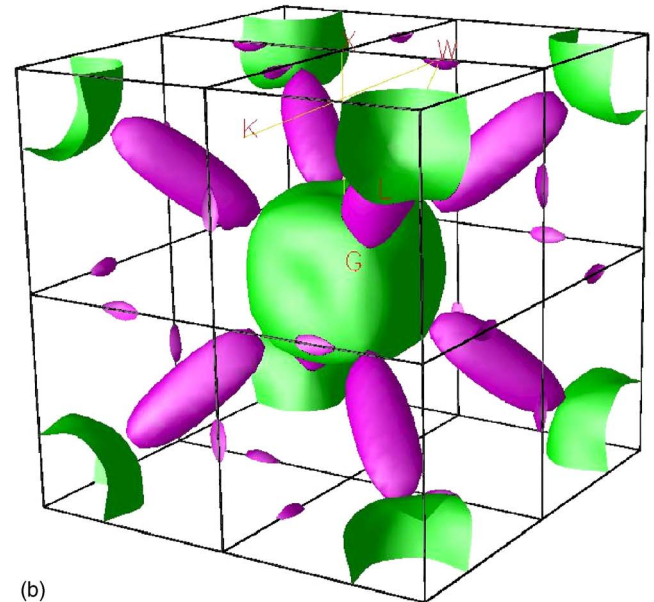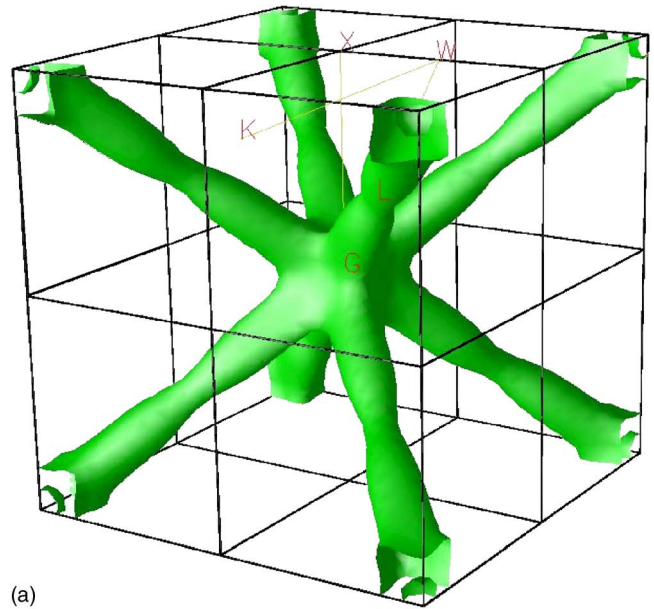

(a)

(b)

FIG. 6. (Color online) The Fermi surfaces of $CeMnNi_4$ for spin up (top) and spin down (bottom). Only one band is shown for the spin up and two for the spin down. Other bands create just barely noticeable Fermi surface pockets. In order to produce a large number of eigenvalues I used linear muffin tin orbital (LMTO) bands for this plot; I have verified that the difference beween LMTO and LAPW bands is too small to be visible on the scale of this figure.

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 Ni-Mn bonds of the order of $4.8a_B$, compared to nearly $5.5a_B$ 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 a 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 per formula, $N_\downarrow = 1.16$ states/eV per formula, corresponding to an electronic specific heat coefficient of 4.7 mJ/mol K^2, or 0.8 mJ/g -at. 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%.[1] 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.[8] 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: $v_{F\uparrow} = 2.1 \times 10^7$ cm/s, $v_{F\downarrow} = 1.9 \times 10^7$ cm/s. 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,[9] 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 that could scatter electrons. 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 near the transition temperature. Thus, the strong T dependence below T_C cannot be ascribed to a temperature-dependent scattering rate, therefore it must be due to a temperature dependence of the effective number of carriers $(n/m)_{eff}$, which is nothing but the plasma frequency expressed in different units. However, the plasma frequency is much larger in the paramagnetic state,[10] so if anything, the temperature dependence of $(n/m)_{eff}$, would have provided a resistivity minimum near T_C, as in $(Fe, Co)S_2$ alloys.[2]

The behavior below T_C is reminiscent of the colossal magnetoresistve manganates and some magnetic semiconductors, where large residual resistivity is also combined with a rapidly growing resistivity below T_C. Low effectve carrier density in $CeMnNi_4$ supports this analogy. However, in that case T_C coincides with a metal-insulator transition, resulting in a strong (orders of magnitude) maximum of resistivity near T_C, instead of rather flat behavior above T_C in $CeMnNi_4$. Nevertheless, spatial inhomogenuity 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 an accidentally near 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.

Note added in proof. Recently, a calculation addressing the phase stability of $CeMnNi_4$ was reported.[11] The authors found a hexagonal structure which is lower in energy than the cubic structure reported in the experiment. This strongly suggests that, as proposed above, the actual samples may have high concentration of defects and/or be nonstoichiometric.

[1] S. Singh, G. Sheet, P. Raychaudhuri, and S. K. Dhar, cond-mat/0509101 (unpublished).

[2] S. Ogawa, S. Waki, and T. Teranashi, Int. J. Magn. **5**, 349 (1974); B. Nadgorny and I. I. Mazin (unpublished).

[3] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, Computer code WIEN2K-05 (Techn. Universität Wien, Austria, 2005).

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[5] Since Ce f states are empty and removed from the Fermi level one can conjecture that spin-orbit effects are not important. Indeed, I have performed second-variational calculations with spin orbit and found the effect to be negligible. By the same token, one does not expect LDA$+U(f)$, calculations to any different from the regular LDA, and not even more relevant, given the delocalized nature of the f states in this compound. Out of curiosity, I have performed LDA$+U$ caculation in the around-mean-field approximation, appropriate for a metal like this, and using $U=1.25$ and $J=0.33$ eV for Ce f (as estimated from the

atomic loop in a LMTO program), and again found practically no change from straight LDA results.

[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.

[7] T. C. Shields, J. Mayers, and I. R. Harris, J. Magn. Magn. Mater. **63+64**, 587 (1987).

[8] I. I. Mazin, Phys. Rev. Lett. **83**, 1427 (1999).

[9] I. Zutic and S. Das Sarma, Phys. Rev. B **60**, R16322 (1999).

[10] In the hypothetical *nonmagnetic* state the plasma frequency is drastically larger than in the ferromagnetic state. The *paramagnetic* state of $CeMnNi_4$, is not nonmagnetic, but rather a disordered-local-moments states. Still, a rather accidental nature of the pseudogap in the ferromagnetic calculations strongly suggests that magnetic disorder should considerably increase ω_p.

[11] P. Murugan, A. K. Singh, G. P. Das, and Y. Kawazoe, cond-mat/0510748 (unpublished).