Itinerant electrons and magnetism in the Co–C chain compound YCoC

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Density-functional studies of the electronic structure of the Co–C linear-chain compound, YCoC are reported. The band structure near the Fermi energy shows a mixture of rather heavy Co-*d*-derived bands, and near-one-dimensional dispersive bands associated with the bonding of the Co–C chains. The resulting density of states is high, yielding an extremely weak ferromagnetic instability via the Stoner mechanism. However, the Fermi surfaces are strongly nested, suggesting competing antiferromagnetic spin fluctuations. An interesting possibility is that in clean samples a renormalized paramagnetic ground state may emerge, due to the combination of the weak competing ground states, the near one dimensionality of the bands, and quantum fluctuations.

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YCoC is the prototypical example of a family of carbide and nitride metals. The compounds, which were first reported by Gerss and Jeitschko,[1] have structures dominated by the presence of orthogonal straight linear metal—C (or N) chains.[1–3] These chains are well separated. The Co–C distance along the chains in YCoC is 1.825 Å, while the closest Co–Co distance (and Y–Y distance) is 3.432 Å; the Co–Y nearest-neighbor distance is 3.099 Å. This is a most unusual structural motif, as was emphasized by Hoffmann and co-workers.[4,5] Despite this, YCoC has a surprisingly simple high-symmetry crystal structure. It occurs in the primitive tetragonal space group $P4_2/mmc$, with two formula units per cell.[1] The lattice parameters were determined as $a=b=3.65$ Å and $c=6.8636$ Å. The existing samples are reported to be C deficient, but it is thought that the stoichiometric compound is stable.[1] The unit cell contains two Co–C chains running along the (equivalent) tetragonal *a* and *b* directions separated by $c/2$ in the *z* direction. The Co atoms are arranged on top of each other with intervening Y layers at $c/4$ and $3c/4$. Assuming that Y states do not participate in the bands near the Fermi energy E_F and noting the large Co–Co separation, one is led to the expectation of a Fermiology dominated by one-dimension features, i.e., from weakly interacting chains. Hoffmann and co-workers[4] calculated the electronic structure of such chains within an extended Huckel approach. They identified a substantial *d*-*p* π bonding character. These features are also present in our band structure as shown below.

Carbides with the YCoC structure also form with a variety of rare earths in place of Y. In addition, CaNiN occurs in this structure. Interestingly, these compounds are metallic and in several cases the rare earth moments are reported to order ferromagnetically with Curie temperatures T_C up to 22 K.[3] CaNiN and YCoC are both reported to be paramagnetic metals at low temperature.[2,3] This metallic behavior is somewhat surprising in compounds with such a one-dimensional structural motif, especially for CaNiN, which has an odd number of valence electrons per chain. Massidda and co-workers,[6] and Mattheiss[7] performed band-structure calculations for CaNiN, confirming the *d*-*p* π antibonding character of the states around E_F as well as finding some three dimensionality due to interchain coupling, presumably underlying the metallic character.[6] The reported band structure of CaNiN (Refs. 6 and 7) shows a rather large peak in the density of states (DOS) below E_F. The implication is that the value at E_F, $N(E_F)$, may be considerably higher in YCoC, which has a lower valence electron count. Here, calculations of the electronic structure of YCoC are reported to address some of these issues.

The calculations were done using the experimental crystal structure.[1] They were performed within the local-density approximation (LDA) using the general potential linearized augmented plane-wave (LAPW) method[8] with local orbitals[9] to relax linearization errors and include the semicore states of Y. Core states were treated relativistically, while a scalar relativistic approximation was used for the valence states. LAPW sphere radii of 1.90 and 1.45 bohrs were used for the metal and C atoms, respectively. Basis sets consisting of approximately 1200 LAPW functions plus local orbitals were employed, yielding good convergence. The zone samplings during the self-consistent iterations were done with 144 special **k** points in the irreducible 1/16 wedge of the tetragonal zone, while a denser mesh of 637 points was used for determining the electronic DOS and Fermi-surface averages. The fixed spin moment calculations were done using 468 special **k** points in the wedge, while a denser mesh of 1088 special **k** points in the wedge was used for the self-consistent ferromagnetic calculation to obtain a reliable local spin-density approximation (LSDA) value for moment.

The calculated non-spin-polarized LDA band structure is shown in Fig. 1. The corresponding density of states is given along with Co *d* and C *p* projections in Fig. 2, while the Fermi surfaces are displayed in Fig. 3. The first 16 bands, which extend from approximately -6 eV to $+1$ eV relative to E_F, are derived from the Co $3d$ and C $2p$ states, with little Y participation. Four bands cross E_F—two dispersive bands, which are associated with antibonding *d*-*p* combinations and two rather weakly dispersive Co-*d*-derived bands. As may be seen from the weak dispersions along Γ-*Z* and the reflection symmetry of the band plot about its center, the electronic structure is quite two dimensional, though not perfectly so. This is also evident in the Fermi surfaces. Interestingly, it is the heavy bands that show the greatest three-dimensional character. The Fermi surfaces consist of very

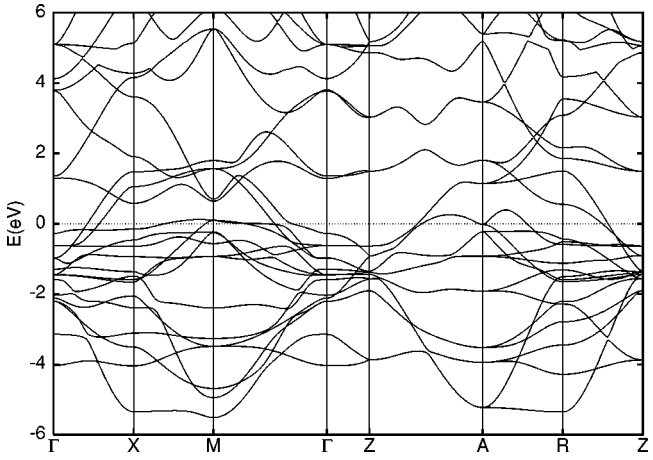

FIG. 1. Valence-band structure of YCoC. The C $2s$ derived bands lie at ~ -10 eV and are not shown.

one-dimensional sheets from the light bands. The two light bands (one from each chain, with a symmetric-antisymmetric splitting at $k_x=0$), after reconnection, yield the two Γ-Z centered electron cylinders and the two large holelike barrels around the zone center. These bands are near half filled, and highly nested, which of course is favorable for Fermi-surface instabilities, but also are highly dispersive, which disfavors instabilities. Also, the nesting vectors of the two sheets are significantly different. Based on a comparison with the band structure of CaNiN and the arguments of Massidda and coworkers, the instability is most likely not reached in YCoC. The two Co-d-derived heavy bands are most dispersive along the diagonal directions in the x-y plane. These dispersions come from hopping via the intermediate, nominally unoccupied Y $5p$ and $4d$ orbitals, as is confirmed by projections of these states onto the Y LAPW spheres. This also explains the relatively greater k_z dispersion of these bands, as the Y atoms lie in the $c/4$ and $3c/4$ planes between the Co–C chains. These lead to flatish sheets of Fermi surface along the (1,1,0) directions, largest in the $k_z=0$ plane, and

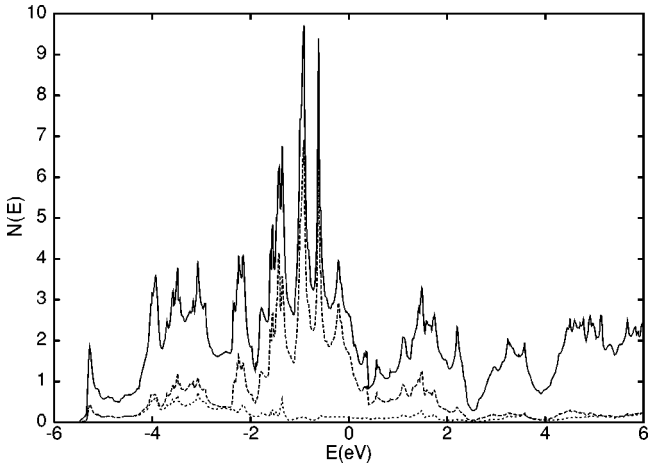

FIG. 2. Calculated electronic DOS on a per formula unit (1/2 unit cell) basis for non-spin-polarized YCoC. The dashed (dotted) lines are the d-like (p-like) projections onto the LAPW spheres of Co (C).

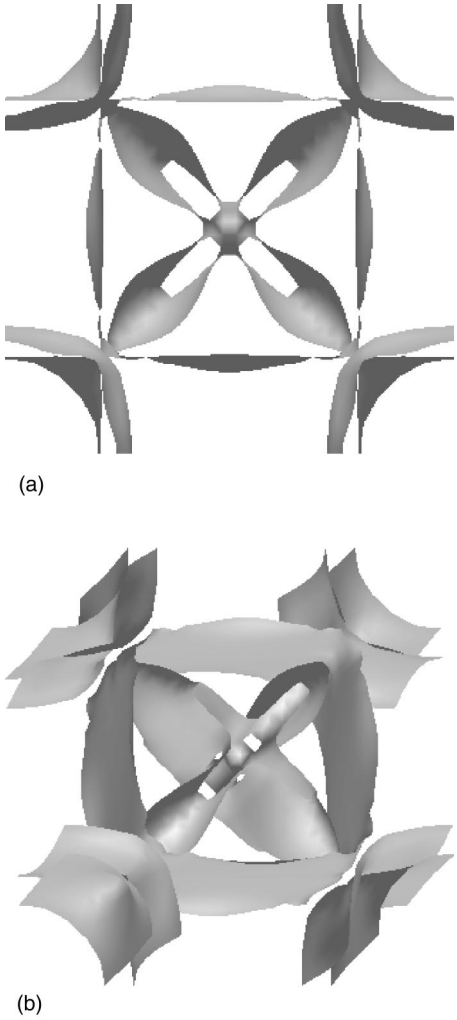

FIG. 3. LDA Fermi surfaces of non-spin-polarized YCoC viewed along the c axis (top) and at an angle (bottom). Γ points are at the corners.

with nesting vectors close to the zone center (the nesting is not as pronounced as for the light bands, but note that these are much heavier bands). These heavy sheets are more three dimensional than the light sheets. The heavy holelike sheets may be expected to favor a ferromagnetic instability, if the density of states is high enough. Furthermore, this may well underlie the ferromagnetism observed in some of the rare earth compounds, RCoC.

The rigid-band approximation based on CaNiN can be seen to be a crude approximation for YCoC, presumably reflecting mostly chemical differences between C and N. Nonetheless, E_F does lie on the upper edge of a rather large peak in the DOS, as expected from that picture. A rather large value, $N(E_F)=2.65$ eV^{-1} on a per formula unit basis results (cf. 1.45 eV^{-1} for CaNiN as reported in Ref. 6). The Fermi velocities, which are dominated by the light bands, are $v_{Fx}=2.1\times10^7$ and $v_{Fz}=0.5\times10^7$ cm/s, yielding a transport anisotropy ρ_c/ρ_a in lowest-order Boltzmann theory of ~ 20—somewhat lower than that found in CaNiN.[6]

Fixed spin moment calculations were done to determine how close YCoC is to a ferromagnetic instability. The calcu-

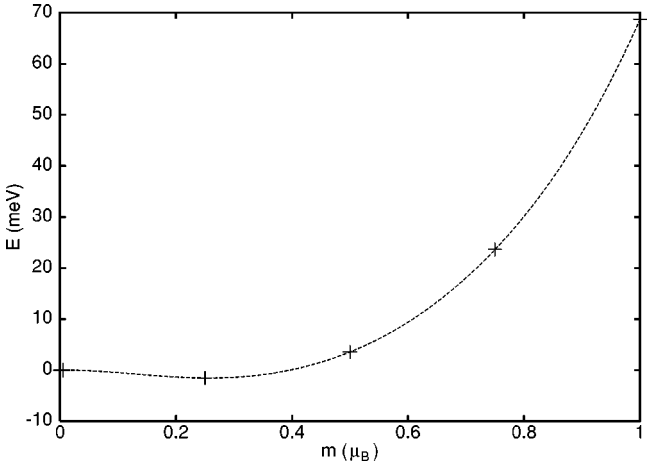

FIG. 4. Fixed spin moment energy as a function of the constrained ferromagnetic spin polarization on a per formula unit (1/2 unit cell) basis. The self-consistent spin magnetization is $0.27\mu_B$/Co with an energy 2 meV/Co lower than the non-spin-polarized case.

lated LSDA energy as a function of constrained spin moment is shown in Fig. 4. The compound is found to be on the borderline of a ferromagnetic instability within the LSDA, and in fact is slightly on the magnetic side. The calculated spin moment is slightly less than $0.3\mu_B$ per Co with a magnetic energy of 2 meV relative to the non-spin-polarized case, also on a per Co basis. The magnetization resides almost entirely on the Co sites, as it is associated with the heavy bands (these are not significantly hybridized with C *p* states). Calculations were done to check for an antiferromagnetic state consisting of ferromagnetic chains, stacked antiferromagnetically in the *c* direction, but this state was found not to be stable. Possibly the LSDA ferromagnetic ground state could be reconciled with the experimental observation of a paramagnetic metallic state by noting that the compound is reported to be C deficient as synthesized[1] and that there is some upturn in the susceptibility at low temperature.[3] However, there is a more interesting possibility that quantum spin fluctuations suppress the magnetic ordering.

Density-functional theory is in principle an exact ground-state theory. It should, therefore, correctly describe the spin density of magnetic systems. However, common approximations to the exact density-functional theory, such as the LSDA and the generalized gradient approximations (GGA), neglect Hubbard correlations beyond the mean-field level, with the well-known result that the magnetic tendency of strongly Hubbard correlated systems is often *underestimated*. *Overestimates* of magnetic tendencies, especially in the LSDA are very much less common. However, another type of correlations that are missed in these approximations, are quantum spin fluctuations. This is because the LSDA and GGA are parameterized based on electron gases with densities typical for atoms and solids. However, the uniform electron gas is very far from magnetism in this density range. The result for noncollinear magnetism in molecules is well known—a so-called ''spin-contamination'' in which the LSDA predicts classical magnetism, with, e.g., nonquantized magnetic moments and singlets described with nonzero, static, but canceling, spin densities on various sites. In solids near quantum critical points, the result is an overestimate of the magnetic moments and tendency toward magnetism (i.e., misplacement of the position of the critical point) due to the neglect of the quantum critical fluctuations.[10–13]

One may note that in YCoC the LSDA ferromagnetism is extremely weak and that the electronic structure has strong one-dimensional and two-dimensional character, as well as a potential competition between fluctuations associated with the light sheets (at the zone boundary) and zone-center fluctuations associated with the heavy sheets. These features favor such a quantum suppression of the phase transition, as they imply soft longitudinal fluctuations (see Fig. 4) and a large phase space (reduced dimensionality and competition). In this scenario, YCoC would be a rather interesting metal, especially if clean, low residual resistivity samples can be made and studied. Some signatures of strong quantum spin fluctuations would be non-Fermi-liquid behavior (down to some crossover temperature), a low-temperature maximum in the susceptibility without the onset of magnetic ordering, and possibly a metamagnetic transition. Since the LSDA places YCoC on the borderline of ferromagnetism, one might expect that the experiment will show a renormalized paramagnet. Also, since Y provides electrons for the band filling, but otherwise contributes little to the electronic structure near the E_F, and since E_F lies on the edge of a DOS peak, it may be expected that alloying with a divalent ion, e.g., Ca, on the Y site will bring the system closer to the magnetic instability.

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