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Electronic structure of $NaCo_2O_4$

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First principles density functional calculations of the electronic and magnetic properties of the layered oxide $NaCo_2O_4$ have been performed using the general potential linearized augmented plane wave method. The electronic transport properties are discussed in terms of the calculated paramagnetic band structure. It is found that the thermopower and specific heat data above 10 K are well accounted for with only moderate renormalization in spite of the fact that this is a strongly correlated system characterized by $W \ll U$. Weak instabilities of itinerant magnetic character are found. The low temperature properties (T below 10 K) are discussed in terms of these.

I. INTRODUCTION

The unexpected discovery[1] of heavy fermion (HF) behavior in the spinel structure transition metal oxide LiV_2O_4 has led to considerable activity aimed at further elucidating the properties of this unique compound and the underlying origin of its HF ground state.[2–13] Nonetheless, a proper understanding remains to be achieved. HF materials are typically intermetallic compounds containing Ce, U, or Yb atoms. They are characterized by the usual Landau Fermi liquid scaling properties, but only at very low temperature (beginning as low as 0.3 K, depending on the material) and with extraordinarily strongly renormalized effective masses, $m^* \approx (100\text{–}1000) m_e$. They show apparent local moment paramagnetic behavior with strongly increasing spin susceptibility χ and specific heat coefficient γ with decreasing temperature, but do not order magnetically and eventually settle at low T into a state with constant γ and χ and Wilson ratio near unity. Following extensive investigation over many years, a basic understanding of the phenomena has been established. The origin is a many body effect associated with the interaction of itinerant conduction electrons with strongly correlated f electrons on local moment rare earth ions.

From an experimental perspective, LiV_2O_4 behaves very much like a typical HF material. In addition, electronic structure calculations[8–10,12] indicate that the active V t_{2g} manifold consists of two types of states. These are narrow a_{1g} states, which form local moments and are subject to strong correlations ($W \ll U$), and itinerant bands derived from the remainder of the t_{2g} manifold, again reminiscent of the usual HF's. (The V t_{2g} manifold is well separated from all other bands; the ionic configuration is $d^{1.5}$, of which presumably one electron occupies the a_{1g} state providing the local moment.) However, from an electronic structure point of view the similarity with the f-band HF's stops here. Both the ''localized'' and ''conduction'' bands originate from the same transition metal d shell, and as a result both Hund's coupling and coupling via off-diagonal Coulomb interactions are expected to be very strong. While certainly a candidate, it is unclear whether Kondo singlet formation will occur under these circumstances. LiV_2O_4 also offers some new features that may be of relevance to its HF-like behavior, most notably the strong geometric frustration of the antiferromagnetic exchange couplings in this spinel structure compound.

Terasaki and co-workers[14] have reported that another transition metal oxide, $NaCo_2O_4$, shows some similarity to LiV_2O_4, though it is still not nearly as well characterized. As in LiV_2O_4, the transition metal atoms have half-integer valence (formally, $Co^{3.5+}$) and sit on a geometrically frustrated lattice [in $NaCo_2O_4$ this is a two-dimensional (2D) triangular lattice]. Both materials are metallic[15] and apparently strongly renormalized at low temperature, though the renormalization in $NaCo_2O_4$ is apparently smaller ($\gamma \sim 80$ mJ/mol K^2 and still rising with decreasing T at 4 K).[17] KCo_2O_4 forms in the same structure, and is also metallic, although less is known about this material.[16]

Unlike cubic spinel LiV_2O_4, $NaCo_2O_4$ occurs in a layered hexagonal structure.[18] This consists of 2D triangular lattice Co sheets, octahedrally coordinated with O above and below the Co planes. The resulting CoO_2 layers are stacked along the hexagonal c axis such that the O atoms form trigonal prismatic coordinated sites between them. Refinements of the O height have not been reported, but our local density approximation (LDA) calculations give $z_0 = 0.084c = 0.91$ Å above the Co plane, corresponding to a significant rhombohedral distortion of the octahedra. The Co-O-Co bond angle, which would be 90° for perfect octahedra, is increased to 98.5°. The Na ions are in the plane between the CoO_2 sheets and presumed disordered. Although in the reported crystal structure all the Co atoms are equivalent, Ray and co-workers[19] have reported the observation by NMR electric field gradient measurements of two distinct Co ions with population ratio 2:1 in $NaCo_2O_4$ powder. This could be due

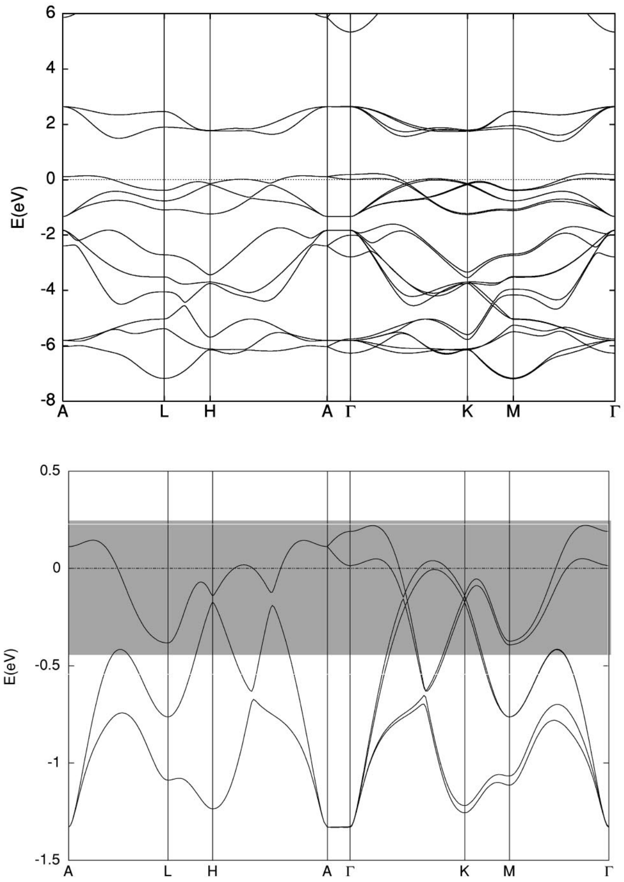

FIG. 1. LDA paramagnetic band structure of $NaCo_2O_4$. The horizontal reference denotes E_F. The bottom panel is an enlargement around E_F showing the Co t_{2g} manifold. The interlayer bonding-antibonding splitting in the $k_z=0$ plane is related to the amount of a_{1g} character (see text). The shading indicates part of the manifold where significant a_{1g} character is present.

to the presence of a second phase in the samples, or a separation of the Co into two types in the $NaCo_2O_4$ phase itself (e.g., Co^{3+} and Co^{4+}). However, in the latter case, it would be necessary to explain the insulating temperature dependence of the Knight shift for the minority site. This could possibly be done by invoking a striped phase. In any case, there is no evidence of any temperature dependent phase transition between 4 K and 300 K in existing electrical transport, specific heat, susceptibility, or Knight shift data.

The reported susceptibility $\chi(T)$ in powders shows Curie-Weiss behavior, with a strong negative temperature, $\Theta = -118.5$ K, and Curie constant below the spin 1/2 value.[19] The thermopower is positive and unusually large for a metal, reaching 100 μV/K at 300 K.[14,20] The resistivity is strongly anisotropic. Single crystal data[14] show incoherent transport perpendicular to the layers (c axis), at least above 200 K, and good conduction in plane: 200 $\mu\Omega$ cm at 300 K and ~ 10 $\mu\Omega$ cm at low temperature. Based on these results, and the low thermal conductivity, it has been suggested that $NaCo_2O_4$ may form the basis of a useful thermoelectric compound. The main challenge to realizing thermoelectric figures of merit near or above unity will be further increasing the thermopower.[21]

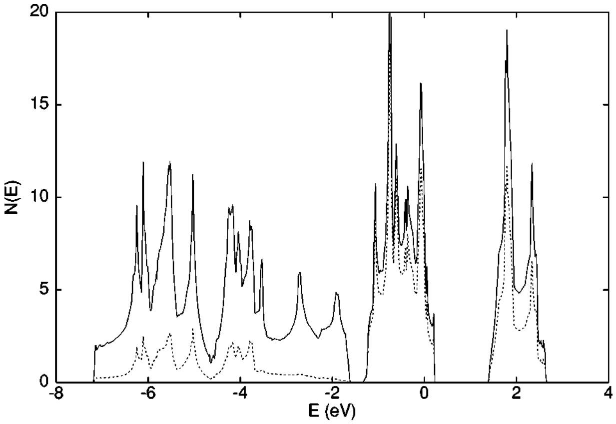

FIG. 2. LDA paramagnetic DOS, $N(E)$, of $NaCo_2O_4$. The DOS is on a per formula unit (two Co) basis with E_F at 0. The solid curve is the total DOS while the dotted curve is the projection of Co d character in the LAPW spheres, radius 1.95 bohr.

II. APPROACH

The purpose of this paper is to elucidate the electronic structure of $NaCo_2O_4$ using density functional calculations within the local density approximation. These were done using the general potential linearized augmented plane wave (LAPW) method[22] with local orbital extensions[23] to relax linearization errors and treat semicore states. This method is well suited to materials that have low site symmetries and open crystal structures, like $NaCo_2O_4$. The Hedin-Lundqvist exchange-correlation function was used, with the addition of von Barth–Hedin spin scaling for the spin-polarized calculations. Well converged basis sets and Brillouin zone samplings were employed. The crystal structure is based on that reported by Jansen and Hoppe, who obtained the hexagonal structure mentioned above, with space group $P6_322$, $a = 2.84$ Å, and $c = 10.81$ Å.[18] However, the O height was not refined, and the Na ions were reported as being distributed on sites $2b$ and $2d$. A fully random Na distribution is highly unlikely, as in this case Na atoms on adjacent $2b$ and $2d$ sites would be too close. For the calculations reported here, the O height was relaxed using LDA energy calculations, and found to be at $z_0 = 0.084$ in the notation of Jansen and Hoppe. This value was used for the electronic structure calculations reported here. The minimization yields the a_g Raman phonon frequency corresponding to this coordinate as 617 cm^{-1}. As mentioned, z_0 determines the rhombohedral distortion of the O octahedra. As discussed below, this is an important ingredient in the electronic structure, so measurements would be valuable. The Na ions were treated using the virtual crystal approximation on the trigonal prismatic site (0.5 occupation), $2b$. This approximation is reasonable to the extent that the only role of the Na ions is to donate charge to the Co_2O_4 framework. The low basal plane residual resistivity in single crystal samples implies that electronic scattering due to Na disorder must indeed be weak. However, the c-axis dispersions are very small, and it may well be that scattering associated with the Na disorder needs to be considered to understand transport in that direction.

III. BAND STRUCTURE AND FERMIOLOGY

The paramagnetic band structure is shown in Fig. 1. The corresponding electronic density of states (DOS) is shown in Fig. 2. The O $2p$ bands extend from approximately -7 eV to -2 eV, relative to the Fermi energy, E_F. They are cleanly separated from the transition metal d bands, which lie above. The Co d–O p hybridization is weak, as in LiV_2O_4. The Co d bands are crystal field split as usual in the octahedral O environment into a lower lying t_{2g} and an upper lying e_g manifold, separated by approximately 2.5 eV. Again, there is a clean gap between the manifolds due to the narrow bandwidths. The t_{2g} width is 1.6 eV and the e_g width is 1.2 eV. E_F is in the top of the t_{2g} manifold, 0.22 eV below the band edge, corresponding to 0.5 holes per Co ion (1 hole per unit cell).

In the following, I focus exclusively on the t_{2g} manifold as these are the only states that are likely to play a role in the low energy properties. There have not to date been detailed photoemission studies of $NaCo_2O_4$ but trends for other octahedrally coordinated $3d$ transition metal compounds (i.e., U estimated from photoemission satellite positions as the atomic number and ionicity are varied) would suggest an effective on-site Hubbard U of 5–8 eV. As noted, this manifold of t_{2g} states is quite narrow, and in particular it is in the regime $W \ll U$ with any plausible U. Nonetheless, since $NaCo_2O_4$ is known to be metallic, and apparently is not magnetically ordered, we discuss the electronic structure beginning with the LDA bands. This is in analogy with discussions of properties of metallic high-T_c superconducting phases, starting with LDA band structures.[24]

The six bands comprising the t_{2g} manifold in $NaCo_2O_4$ are further split in the rhombohedral crystal field into two a_{1g} and four e_g bands (denoted e_g' in the following to distinguish them from the higher lying e_g manifold). The amount of splitting is sensitive to the rhombohedral distortion of the O octahedra. Although the a_{1g} and e_g' overlap, and mix to some extent, these states are roughly separated in energy by the rhombohedral crystal field. In this respect, $NaCo_2O_4$ differs from LiV_2O_4, where the a_{1g} and e_g' bands overlap, providing ‘‘light’’ and ‘‘heavy’’ carriers at E_F. In $NaCo_2O_4$ the states at the top of the t_{2g} manifold where E_F sits have dominant a_{1g} character. In particular, the large cylindrical hole Fermi surfaces (see Fig. 3) around the Γ-A line have dominant a_{1g} character, while the small holelike sections centered about 2/3 of the way out on the Γ-K and A-H directions have mixed a_{1g} and e_g' character. The large Fermi surface sections are flattened along the Γ-K directions. This reflects the fact that the hopping that gives rise to the dispersion of the a_{1g} derived bands is via the O p_z orbitals, while direct a_{1g}-a_{1g} hopping is small, as might be expected from the Co-Co distance. This means that the bandwidth and band structure near E_F will be sensitive to the O height, which provides a possibility for rationalizing the differences between $NaCo_2O_4$ and KCo_2O_4. The nesting vector connecting the flattened parts of the large section is $(\frac{4}{5})$ K. It would be interesting to look experimentally for spin and/or charge fluctuations around this point, especially for spin fluctuations using neutron scattering.

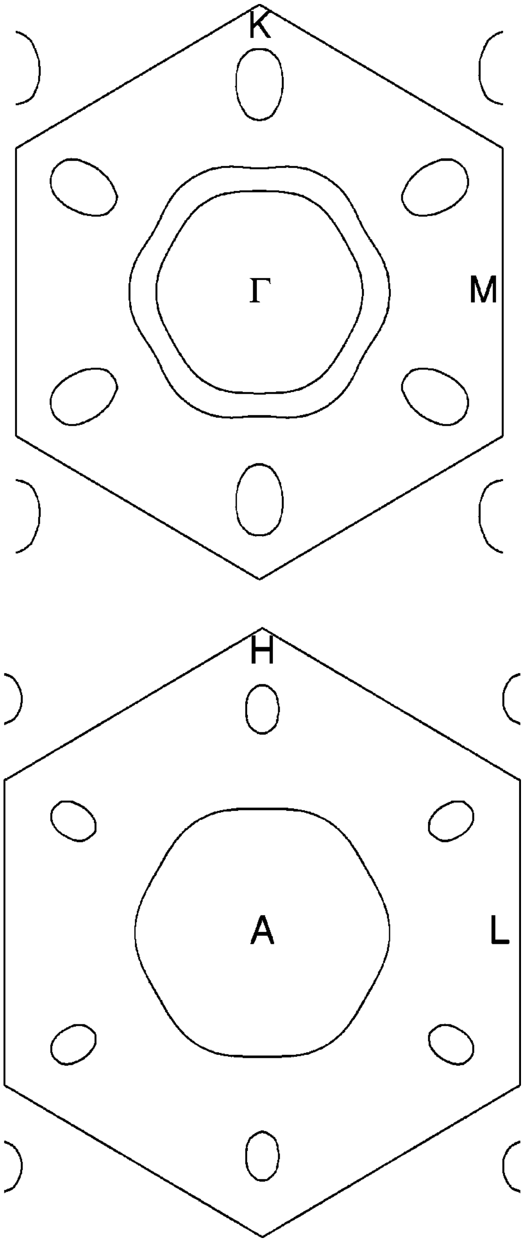

FIG. 3. LDA Fermi surfaces of $NaCo_2O_4$ in the $k_z = 0$ (top) and $k_z = 0.5$ (bottom) planes.

As in the high-T_c layered cuprates, the band structure shows very little c-axis dispersion. This is evident by noting the band dispersions along the Γ-A line as well as the sizes of the bonding-antibonding splittings induced in the bands due to the interaction of the two CoO_2 sheets in the unit cell. These are zero in the A-L-H plane and maximal in the Γ-M-K basal plane. Also, the c-axis dispersion of a_{1g} derived states is higher than that of e_g' derived states, as the a_{1g} states are directed along the c axis and mix with combinations of O $2p$ states that are also directed along c. However, it should be emphasized that near E_F these are weak effects. The c-axis Fermi velocity is calculated as 2.3×10^6 cm/s to be compared with the in-plane value of 6.6×10^6 cm/s. If the effective scattering times τ for a-axis and c-axis transport were the same, this would yield a resistivity anisotropy of 8. Experimentally, the single crystal anisotropy is far higher, ~ 100 with substantial T dependence. This could be a result of effects of scattering due to Na disorder, which would tend to make the c-axis transport less coherent or even localized.

Another related possibility is that a_{1g} derived states could be more strongly scattered than e_g' states, so that the effective τ for the more a_{1g} derived parts of the Fermi surface (which are the ones that give the c-axis velocity) would be shorter. However, one would not ordinarily expect such a strong effect from variation of τ on the Fermi surface, so the former possibility seems more plausible.

The average Fermi velocity in the basal plane is also quite low for a metal. This reflects the narrow bandwidth. Another consequence of the narrow bandwidth is a very high value of the DOS at E_F, $N(E_F)=8.8\ \mathrm{eV}^{-1}$ on a per formula unit (2 Co atom) basis. This corresponds to a LDA band structure $\gamma=21\ \mathrm{mJ/mol\,K^2}$. Extrapolating the specific heat data of Ando and co-workers[17] to 0 K using only the data above 10 K and thereby missing the low T upturn, one would obtain $\gamma_{HT}\sim 55\ \mathrm{mJ/mol\,K^2}$. Thus, neglecting the upturn below 10 K, only a moderate many body renormalization would be needed to account for the specific heat data, depending on the assumed amount of electron-phonon enhancement (there is also some uncertainty because the measurements were on off-stoichiometric polycrystalline samples). As noted, the thermopower is very high for a metal; values approaching 100 μV/K in high carrier density metals are usually associated with Kondo effects, as in valence fluctuation Ce intermetallics. However, another way to get high thermopower is through high effective mass. If the notion that little renormalization of the LDA bands is needed above 10 K is correct, one should be able to estimate the thermopower quantitatively. For transport in the basal plane, this may be done using standard kinetic transport theory, and the assumption that, on the scale of KT, the effective scattering time τ has no energy dependence (though it may have arbitrary T dependence). For the degenerate case ($KT \ll E_F$), one has $S/T=(\pi^2K^2/3e)[d\ln(\sigma)/dE]|_{E=E_F}$. We may replace σ by $N(E)\langle v_F(E)^2\rangle$ due to the above assumption regarding τ; the average is over the Fermi surface and v_F is the band velocity.

Applying this formula to the LDA band structure yields $S/T=3.6\times10^{-7}\ \mathrm{V/K^2}$. Remarkably, this is only 20% lower than the single crystal in-plane data of Terasaki and co-workers,[14] indicating weak renormalization of the LDA band structure above 10 K. The 300 K value predicted by the calculation is $S=110\ \mu\mathrm{V/K}$ as compared to a measured value of 100 μV/K, but by this temperature the experimental $S(T)$ is already sublinear. In regard to thermoelectric applications, the behavior of the transport function is normal in the sense that lower carrier density would lead to higher thermopower, though, in this strongly correlated d-band system, it is unclear that the rigid band picture as a function of doping will hold.

IV. SPIN AND CHARGE INSTABILITIES

So far, it would seem that the electronic properties above 10 K are reasonably accounted for by the LDA band structure. However, there are some problems. Leaving aside for now the fact that $NaCo_2O_4$ is in the regime $W \ll U$, it may be noted that $N(E_F)$ is exceedingly large, so instabilities should be anticipated. Some common possibilities are lattice instabilities, charge ordering, and magnetism. None of these are seen experimentally, but the upturn in $\chi(T)$ below 10 K could suggest incipient spin ordering of some kind. The single crystal resistivity data provide some information about electron-phonon couplings and possible lattice instabilities. In particular, combining the calculated plasma frequency with the measured slope of the in-plane $\rho(T)$ one may roughly estimate the transport electron-phonon coupling λ_{tr}, using the theory of Allen and co-workers,[25] as $\lambda_{tr}\approx0.3$. While the average is not high, this does not exclude strong coupling or even instabilities for some modes, e.g., due to nesting. However, the low value of the single crystal residual resistivity and the lack of structure in $\rho(T)$ provide some evidence against lattice instabilities.

Spin-polarized local spin density approximation (LSDA) calculations were done in order to address the possibility of magnetic ordering. In these calculations, the ordering was constrained to be ferromagnetic. A stable low spin solution was obtained, with a spin moment of exactly $1\mu_B$ per formula unit ($0.5\mu_B$ per Co). This solution was lower in energy relative to the non-spin-polarized solution discussed above by only 18 meV/Co ion. This small energy is consistent with the low moment of $0.5\mu_B$ and the fact that, although $N(E_F)$ is high in the paramagnetic DOS, E_F is on the side of a peak and near a band edge, weakening the Stoner instability. In any case, as in LiV_2O_4, LSDA calculations predict a magnetic instability, while no magnetic ordering is seen experimentally. As emphasized by Mazin, if the magnetic interactions are highly anisotropic, as seems likely here, the magnetic ordering may take on nearly two dimensional character (i.e., Kosterlitz-Thouless).[26]

Fixed spin moment calculations were also done, looking for a high spin solution, but no stable configuration was found and the energetics of forced high spin configurations were highly unfavorable. This is because the exchange energies are too small to make up for the crystal field gap between the t_{2g} and e_g manifolds.

Interestingly, the ferromagnetic band structure is fully half metallic; E_F in the majority spin channel lies in the crystal field gap, while in the minority channel it is deeper in the top of the t_{2g} band structure, yielding a total $N(E_F)=8.1\ \mathrm{eV}^{-1}$, only slightly lower than the non-spin-polarized case. The spin density, which is defined as the majority spin density minus the minority spin density, is shown in Fig. 4. It is of mainly a_{1g} character, reflecting the character of the exchange split bands around the top of the t_{2g} manifold, as expected. It should be emphasized that, in the half-metallic state, spin excitations are reduced at low energy. This is because the Stoner continuum is removed, and in addition in $NaCo_2O_4$ the rhombohedral site symmetry combined with spin-orbit coupling may lead to a gap in the magnon dispersion at Γ, especially if the easy axis is along c.

As mentioned, the Stoner instability (band ferromagnetism) is weakened because E_F lies on the edge of a narrow DOS peak, so the Stoner energy is gained only up to a small value of the exchange splitting. It is also noteworthy that exchange splitting the bands leads to a decrease in the majority spin $N(E_F)$ to zero but an almost compensating increase in the minority spin value. This is seen in the ferromagnetic DOS, shown in Fig. 5. In particular, the Fermi level lies at the top of a high peak in the DOS in the minority spin channel and is pinned there by the half metallicity. This suggests some further instability of the ferromagnetic state,

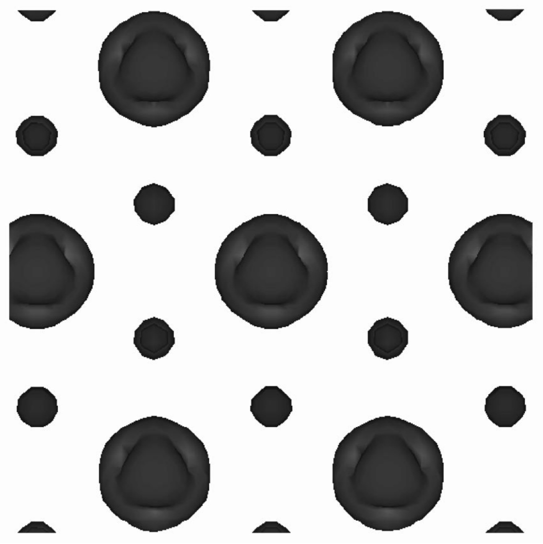

FIG. 4. Spin density isosurface in ferromagnetically ordered $NaCo_2O_2$. The surface is at 0.01 e/bohr^3. This shows the nature of the electronic states that contribute to the magnetism. Note the dominant, but not complete, a_{1g} character around the Co sites, and the weak but noticeable polarization of O $2p$ combinations directed on the c axis.

perhaps a different spin ordering or some other symmetry lowering.

Antiferromagnetic interactions are geometrically frustrated on the 2D triangular lattice possibly leading to interesting low temperature spin physics if such interactions are present. Calculations were done using a unit cell doubled along the a axis to check this. One Co moment was flipped in this cell. The result was an ordering with equal numbers of up and down spin Co atoms, and where each Co ion has two nearest neighbors of like spin and four of opposite spin, forming chains of aligned Co spins along the b axis and alternating spins along the other two equivalent hexagonal directions. The LSDA calculations yielded a self-consistent Co moment for this configuration (based on the moment contained within the Co LAPW sphere) of almost exactly half that in the ferromagnetically ordered case ($0.21\mu_B$ vs $0.42\mu_B$), with an energy gain relative to the non-spin-polarized calculation of 8 meV per Co. Thus, at least in the LSDA, and neglecting any other ordering tendencies, $NaCo_2O_4$ is not described as a strong local moment system, and has predominantly ferromagnetic spin ordering tendencies. This itinerant magnetic character is not inconsistent with strong correlations, as, for example, Ni metal is generally thought more itinerant and also more correlated than Fe or Co.

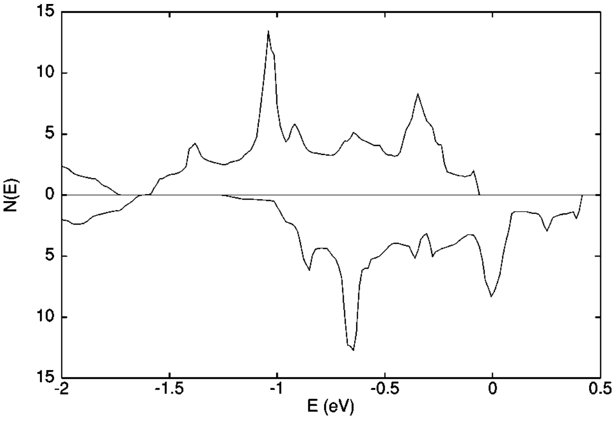

FIG. 5. LDA ferromagnetic DOS, $N(E)$, of $NaCo_2O_4$. The DOS is on a per formula unit (two Co) basis with E_F at 0. The spin up DOS is shown above the horizontal line and spin down below. Note the half-metallic character, and the minority spin peak at E_F.

One may note that the LSDA energy scale for the Co moment formation is unusually low. This comes from the low carrier density, i.e., 0.5 holes per Co, and the fact that the exchange energy varies roughly as m^2. One possibility for increasing this energy would be a combination of charge and spin ordering. While charge ordering, like collinear antiferromagnetism, is geometrically frustrated on the 2D triangular lattice, a separation into Co^{3+} and Co^{4+} would allow an increase in the magnetic stabilization via local moment formation on the Co^{4+} sites, and the cost in kinetic energy could be modest as the bands are quite narrow to begin with.

Supercell calculations were done, doubling and tripling one of the in-plane lattice vectors to search for a charge ordering instability of the ferromagnetic state, but none was found. On the other hand, the antiferromagnetic solution was found to be very soft in these calculations. In the doubled unit cell, two additional self-consistent LSDA solutions besides the (symmetry imposed) antiferromagnetic solution were found. Both of these were obtained within 2 meV of the antiferromagnetic solution, which is below the precision of the calculations. Both were ferrimagnetic with oppositely aligned but different moments within the two inequivalent Co LAPW spheres; in the first the moments were $0.26\mu_B$ and $0.18\mu_B$ (compared to $0.21\mu_B$ for the antiferromagnetic solution). The second solution, which was calculated slightly lower in energy (but note, within the estimated precision indistinguishable) than the antiferromagnetic solution, had moments of $0.28\mu_B$ and $0.09\mu_B$. Disproportionated solutions like this were also found in the tripled unit cell, but it was very hard to converge them well due to the softness of the system. No solution was found that is energetically competitive with the ferromagnetic solution. The strong correlations that are no doubt present in this material may have the effect of reducing the importance of the band kinetic energy relative to the LSDA so that the charge ordering tendency suggested by the existence of such solutions will be stronger. However, the lack of structure in the single crystal $\rho(T)$ argues against actual static charge ordering, at least over the temperature range of the transport measurements.

V. SUMMARY AND DISCUSSION

Non-spin-polarized LDA calculations yield a strongly energy dependent transport function and very high $N(E_F)$ that at first sight would account for the known specific heat and thermopower of $NaCo_2O_4$ above 10 K, with only a modest many body renormalization. However, such values do not in general occur in band metals as they should rather lead to instabilities. In $NaCo_2O_4$, LSDA calculations predict a ferromagnetic instability of itinerant half-metallic character.

However, this instability is relatively weak because of the proximity to a band edge and the details of the band structure. Because of the half metallicity of the ferromagnetic solution it is expected to be stiff in the sense of a suppression of low energy spin degrees of freedom. In contrast, the paramagnetic solution is found to be unusually soft against what appears to be a large space of spin and charge orderings that are nearly degenerate with each other and the paramagnetic solution. These fluctuations potentially provide a mechanism for stabilizing the paramagnetic solution at finite temperature (via entropy) and even at 0 K via quantum fluctuations. A detailed analysis is, however, beyond the capabilities of the present LDA based approach. Within the framework of the above speculation, low temperature specific heat and susceptibility measurements will be very interesting, as they will show whether $NaCo_2O_4$ eventually settles into a magnetically ordered (possibly ferromagnetic) state at low temperature, or forms a renormalized paramagnetic Fermi liquid stabilized by quantum fluctuations.

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