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Itinerant magnetism in K_2NiF_4 -type compounds

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In honor of Martin Peter's 60th birthday.

Abstract. The discovery of antiferromagnetic order in La_2CuO_{4-y} has led to renewed interest in those models for superconductivity that invoke a magnetic pairing mechanism. To elucidate the mechanism that leads to magnetism here we carried out local-spin-density-functional calculations for a series of compounds having the K_2NiF_4 structure. We found pure La_2CuO_4 to be non-magnetic but our calculations for the compounds K_2NiF_4 and K_2CuF_4 give an itinerant antiferromagnetic ground state for the former with a moment of $1.5 \mu_B$ and an itinerant ferromagnetic one for the latter with a moment of about $0.4 \mu_B$. By means of further calculations for model compounds of the type $A_2Cu(O_{1-x}F_x)_4$ ($A = K, Ca$) we tried to relate the appearance of antiferromagnetism to the transition Cu^{2+} to Cu^{3+} , with the result, that antiferromagnetic solutions are stable if copper is in the Cu^{3+} state and the Fermi surface shows nearly perfect nesting. We briefly discuss the alternative of a resonating valence bond state and possible correlation errors inherent in the spin-density-functional approximation.

Recently, a number of experiments established quite unambiguously that undoped La_2CuO_{4-y} is antiferromagnetic [1–4]. For a value of the parameter y of only $y = 0.03$ the Néel temperature is $T_N = 290$ K rapidly decreasing as y goes to zero. Throughout, the magnetic moment seems to be $\mu = 0.4 \mu_B$ and even for $y \approx 0$ large spin fluctuations are seen at temperatures as high as room temperature [5]. It seems now almost certain that pure La_2CuO_4 is a Mott–Hubbard insulator, and, since Cu^{2+} will have a spin of $S = \frac{1}{2}$, its ground state could be a ‘resonating valence bond’ (RVB) state [6]. Anderson points out [7] that this state is different from the Néel state commonly used to describe antiferromagnetism. Experimentally, however, the antiferromagnetism of La_2CuO_{4-y} is nevertheless described as a Néel state [1–4], the spin-up Cu-ions forming a side-centered orthorhombic lattice with a basis of spin-down Cu-ions at $\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}$, where \mathbf{a} and \mathbf{b} are the short orthorhombic basis vectors.

A number of band-structure calculations have appeared for La_2CuO_4 , all being rather similar to that of Mattheis [8]. It shows a metallic state, but, since it was obtained using tetragonal symmetry, one might argue that the observed orthorhombic distortions could open a gap at the Fermi energy, E_F . This, however, is manifestly not the case. The common opinion then is that this band

structure does not describe the real physical system, and it is, at best, useful as a starting point for many-body treatments. We do not disagree, still, we may ask whether the inclusion of magnetic correlations might not alter the picture somewhat.

The situation is similar to the case of the transition-metal oxides, which are frequently cited as examples where band-structure theory fails completely, even when it is based on density-functional theory. Indeed, the situation is still controversial, but we argued that, when proper care is taken, the results of a local-spin-density-functional (LSDF) treatment do in fact give a correct picture of the physics of e.g. NiO [9]. Here it is essential that magnetic correlations are included and it is never denied that NiO is, in fact, a Mott–Hubbard insulator.

Unfortunately, many groups, including our own, tried unsuccessfully to obtain a stable antiferromagnetic state in La_2CuO_4 – the magnetic moments one attempts to stabilize simply vanish as one tries to reach self-consistency.

It is obviously of great interest to find the exact reason for the failure of LSDF theory to describe La_2CuO_4 . For this reason we first looked at the system K_2NiF_4 which is known to be antiferromagnetic having the same crystal structure with all the two-dimensional aspects as La_2CuO_4 . Birgeneau et al. [10], besides many other things, determined its Néel temperature to be $T_N = 90$ K and discussed it as a spin $S = 1$ system with a magnetic order exactly as that described above for La_2CuO_4 . Figure 1 shows its band structure when it is assumed to be non-magnetic; we here used a body-centered tetragonal lattice with a and c from Ref. [10] and the ASW-method [11] for our calculations.

Five Ni- d bands are seen to straddle the Fermi energy, E_F , at $E = 0$. This complex of bands is nearly in the centre of an 8 eV – wide gap separating F - p states at ~ -4 eV from K - s states of ~ 4 eV. The d -bands (and most of the p -bands) at $Z - \Gamma$ (left-most panel) show no dispersion because the system is two-dimensional. The complex of d -bands along $\Gamma - X - P - \Gamma$ is very similar to that in La_2CuO_4 except that in Fig. 1 the Fermi energy is below the d_{z^2} band (see point X), in contrast to La_2CuO_4 , where it is above nesting being also nearly perfect here. Of course, the location of the p -bands is quite different: no near-degeneracy of the $p - d$ states exists in the case of K_2NiF_4 .

The observed antiferromagnetic order [10] requires a side-centered orthorhombic cell leading to the Brillouin zone and the band structure shown in Fig. 2. Not much has changed to the energetic position of the F - p and K - s bands, but the energy of some of the ten Ni- d bands is now lower and a gap of ~ 0.5 eV is seen to separate occupied from unoccupied d -bands. The appearance of two states above Γ is easily explained by folding the body-centered tetragonal into the side-centered orthorhombic zone. The sublattice spin-up and spin-down density of states of the Ni- d electrons is shown in Fig. 3 and in Table 1 we collect some of our numerical results including those for an assumed ferromagnetic spin-alignment.

The situation is not unlike NiO [9], except for the p - d separation which is much larger in K_2NiF_4 . The same care as in NiO has to be taken when interpreting this band structure and comparing with experiment. The calculated

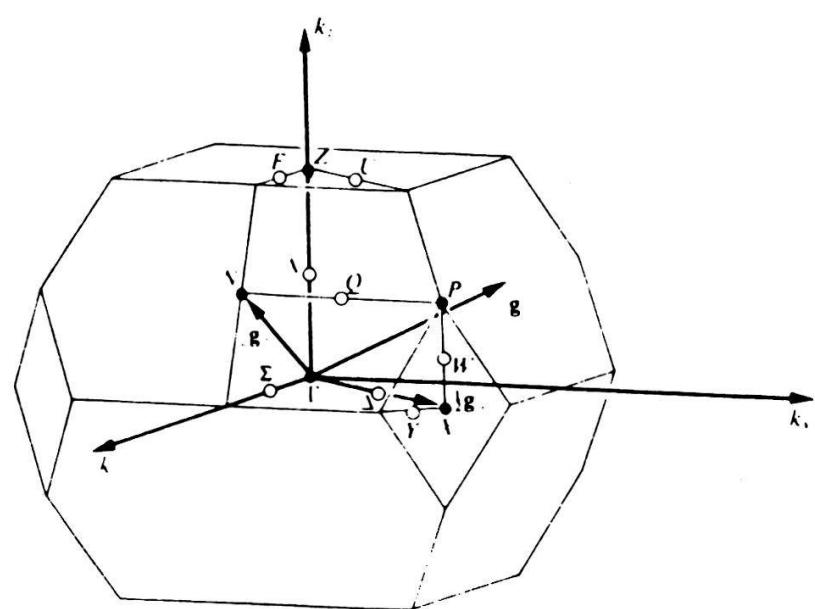
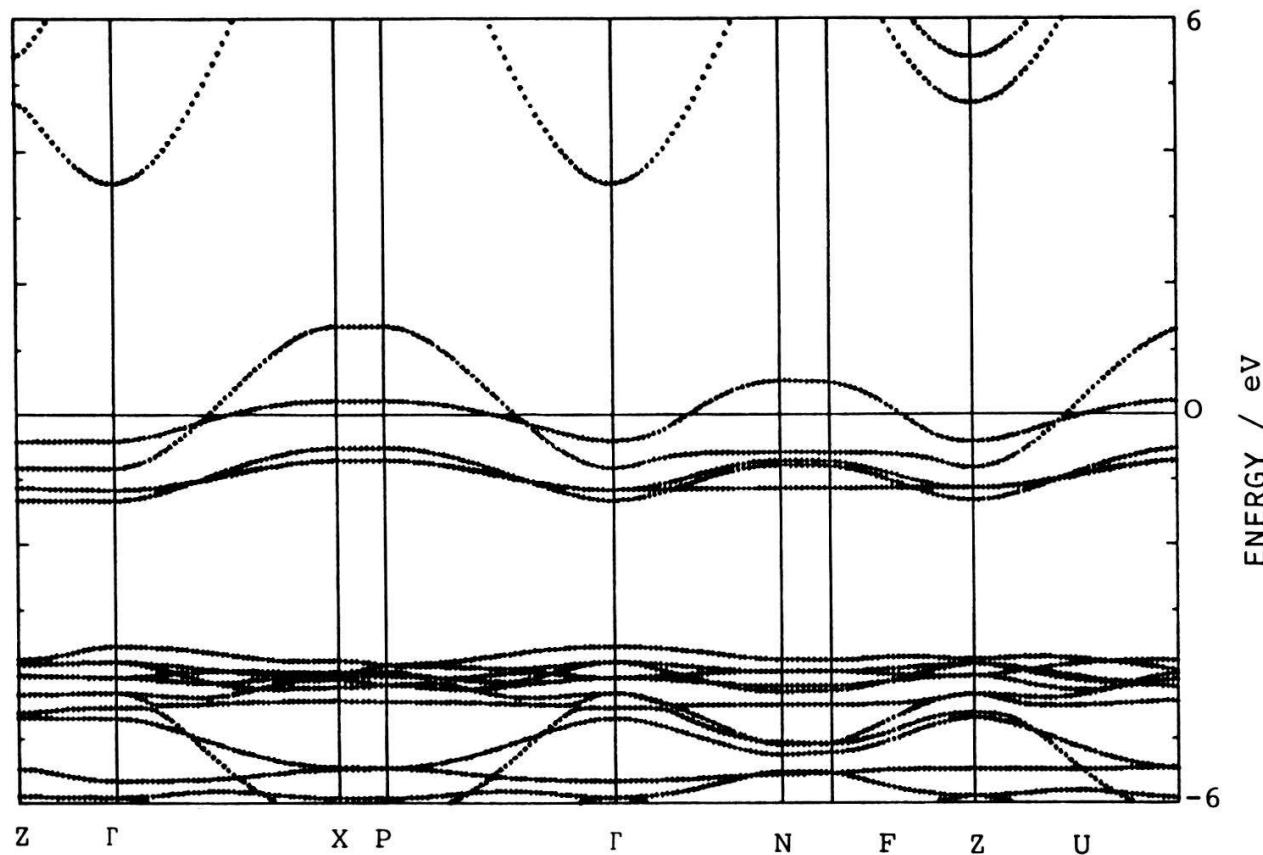


Figure 1
Band structure of assumed non-magnetic K_2NiF_4 and its Brillouin zone.

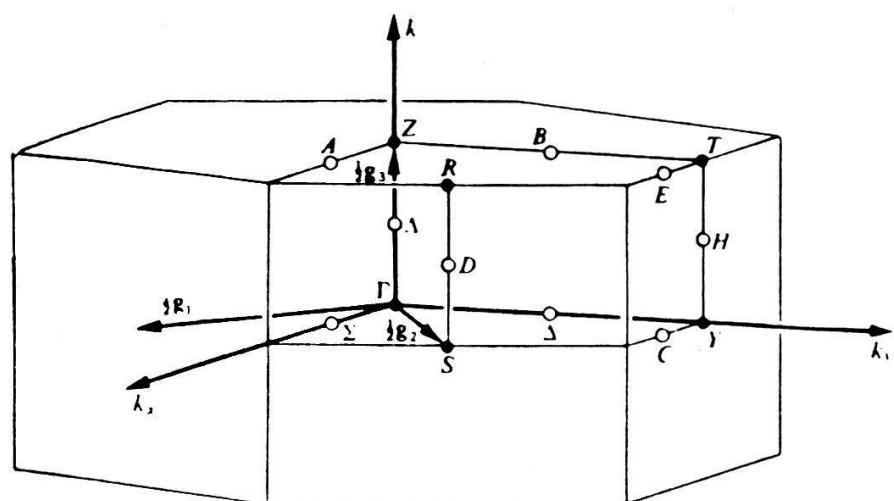
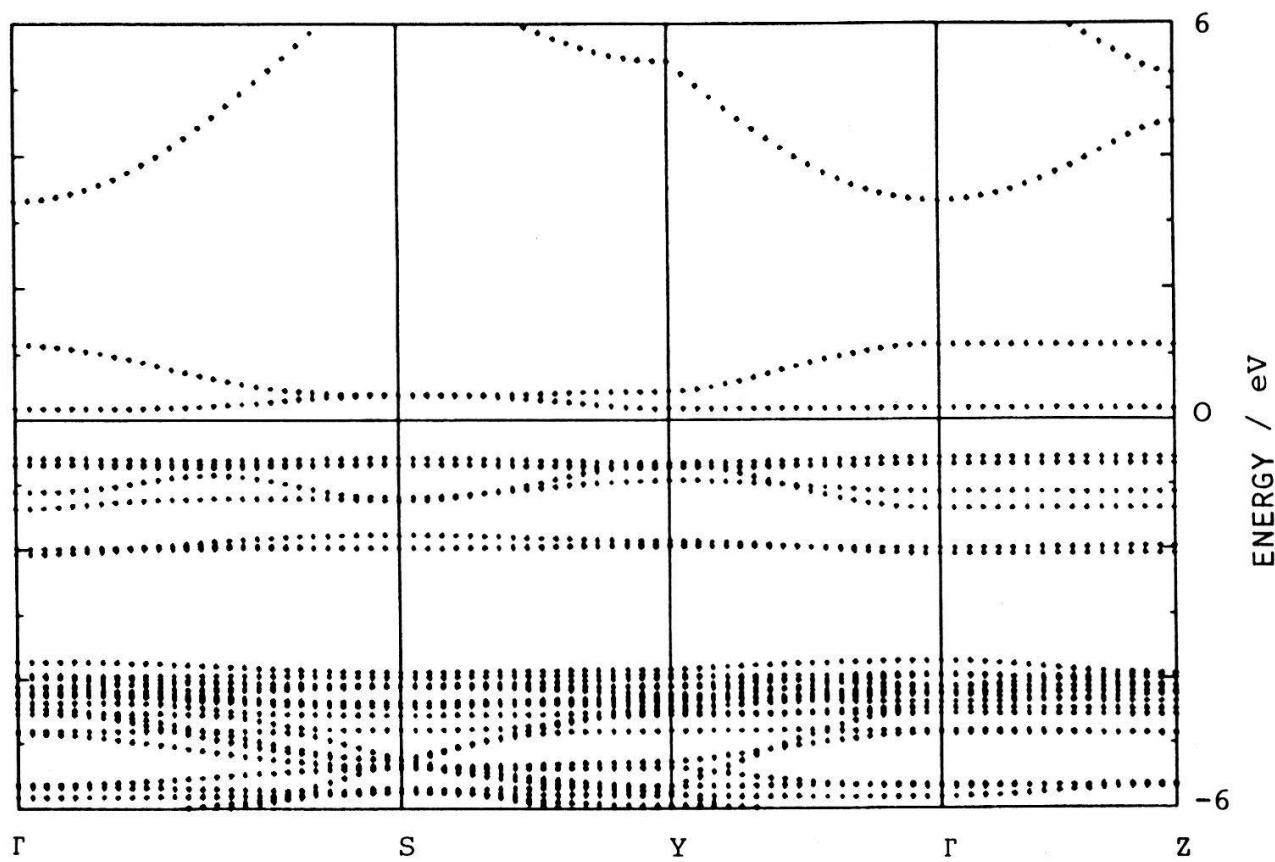


Figure 2
Band structure of antiferromagnetic K_2NiF_4 and its Brillouin zone.

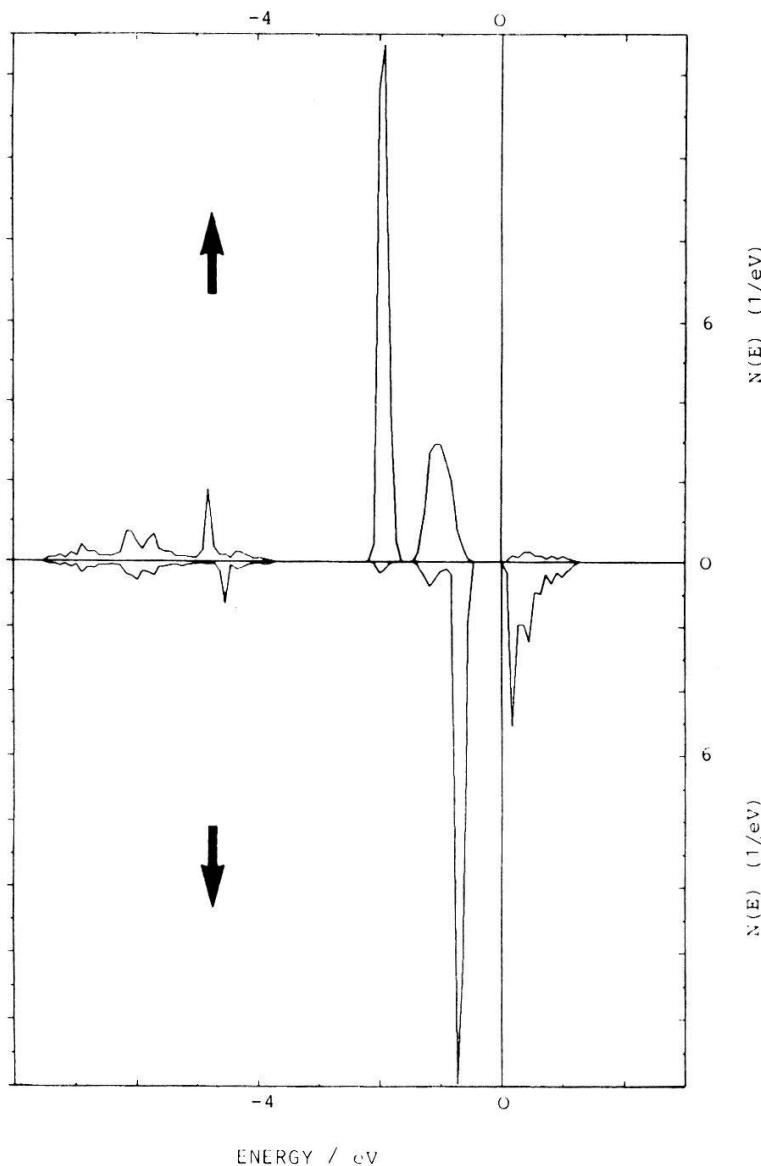


Figure 3
Sublattice up- and down-spin Ni-*d* state density of antiferromagnetic K_2NiF_4 .

ligand-field splitting of 0.9 eV (see Fig. 3) is in good agreement with the experimental value [12] of 0.94 eV, however, BIS or UPS measurements (unfortunately none is known to us) will not 'see' the *d* states where they appear in Fig. 2 or 3; they must be corrected for correlation inherent in non-neutral states. The states appearing in Fig. 2 or 3 are a property of the ground state and therefore not directly detectable by measuring excited-states properties. They

Table 1
Total energy, E_{tot} , per formula unit counted from total energy of the assumed non-magnetic state and calculated magnetic moment, μ , for K_2NiF_4 .

	E_{tot}/eV	μ/μ_B
non-magnetic	0	—
ferromagnetic	~0	1.4
antiferromagnetic	-0.185	1.5

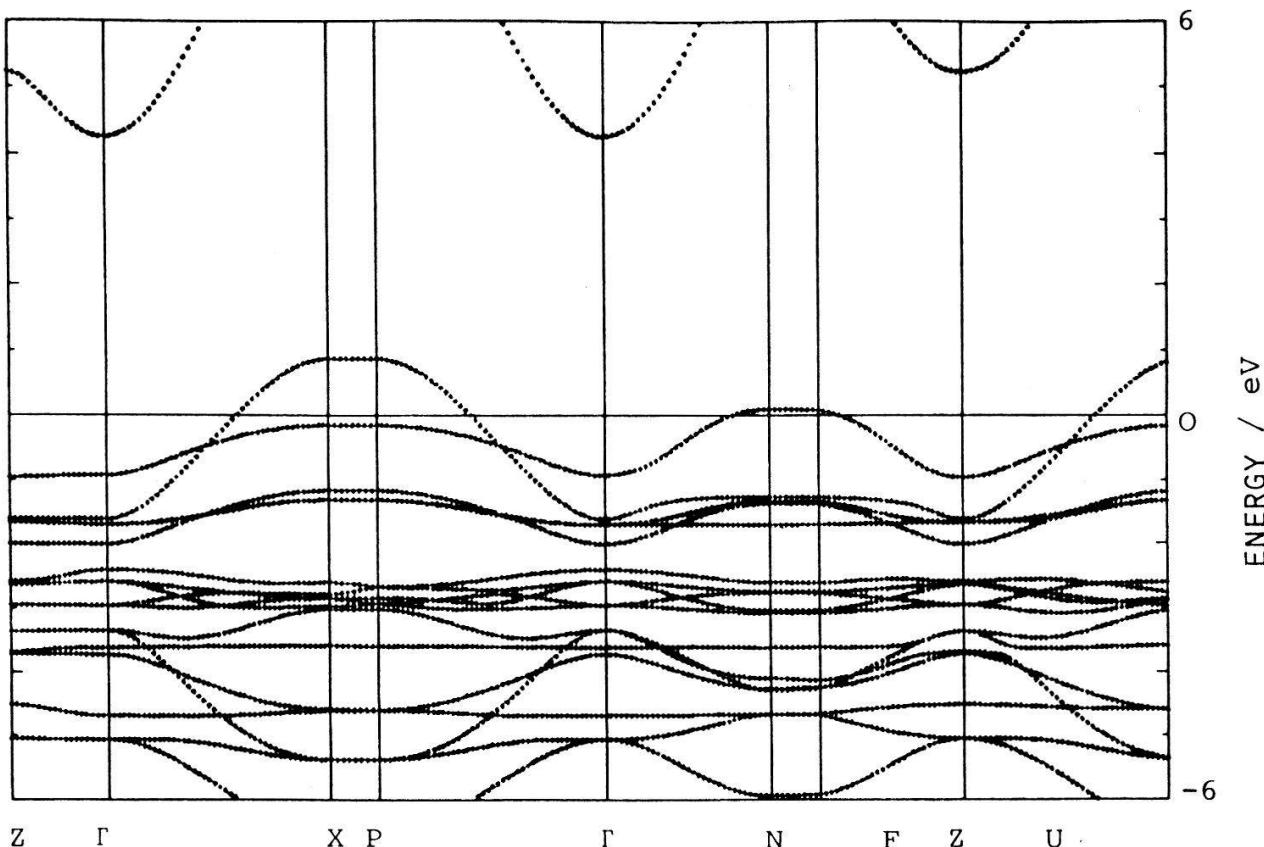


Figure 4
Band structure of assumed non-magnetic K_2CuF_4 .

correspond to completely screened, i.e. completely neutral quasiparticles [9] and it is not *a priori* clear if the system possesses states of this nature in reality. What our results do show is the low total energy of the antiferromagnetic Néel state together with a reasonable value of the calculated magnetic moment.

In a second step we turned to the system K_2CuF_4 which is known to be ferromagnetic with a magnetic moment of $\mu \approx 0.8 \mu_B$ in $B = 4.5$ kOe parallel to c and a Curie temperature of $T_c \approx 10$ K [13]. Its crystal structure is just like that of K_2NiF_4 with nearly identical dimensions [14]. Its band structure in an assumed non-magnetic state is shown in Fig. 4. The d -manifold near E_F is almost identical with that of K_2NiF_4 , but E_F is now above the d_{z^2} state and the $F-p$ states have moved up, still, they do not hybridize with the d -bands unlike La_2CuO_4 . The density of states at E_F is $N(E_F) \sim 2 \text{ eV}^{-1}$ per Cu, thus with the usual estimate for the intraatomic exchange energy, I [15], we estimate the Stoner factor $N(E_F) I \geq 1$. Indeed, when the band structure is allowed to become ferromagnetically spin-polarized we find a magnetic moment of $\mu = 0.4 \mu_B$ per Cu with an average exchange splitting of ~ 0.5 eV but with no noticeable lowering of the total energy. However, a stable antiferromagnetic solution cannot be found.

In an attempt to find Cu-systems that in the K_2NiF_4 structure have a stable antiferromagnetic state we finally studied a number of compounds which do not really exist in nature. We, therefore, call these model systems and deal with cases like $A_2Cu(O_{1-x}F_x)_4$, where $A = K, Ca, La$ and x is adjusted by using for

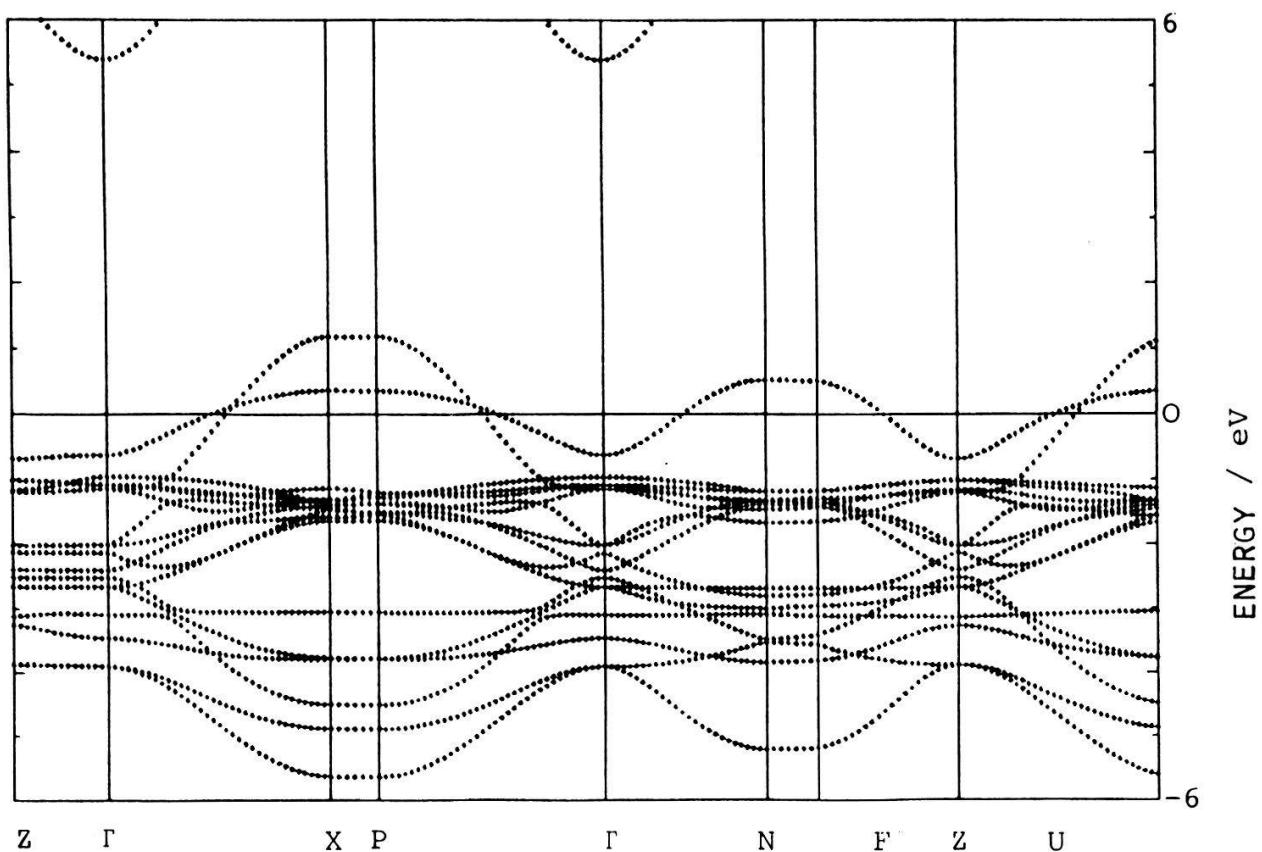
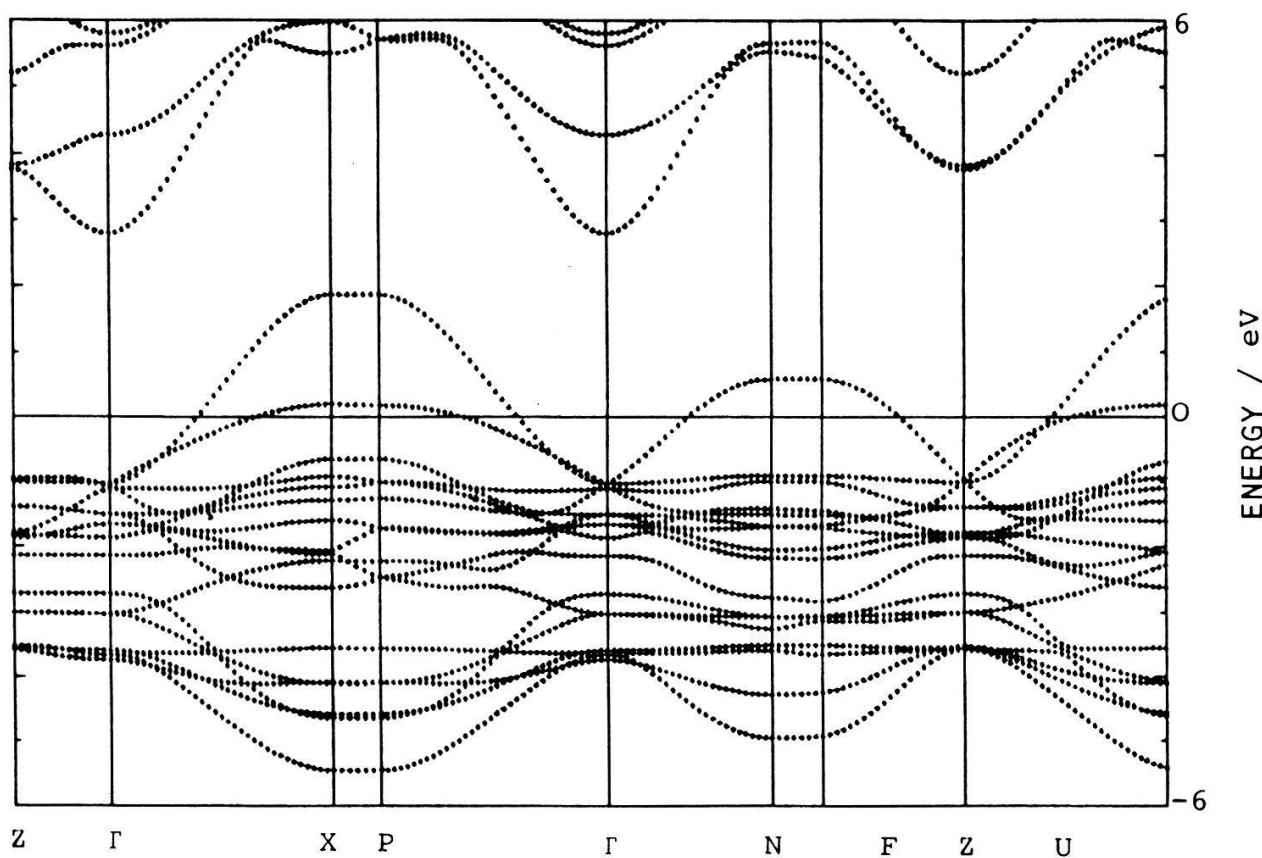


Figure 5

Band structures of assumed non-magnetic $\text{Ca}_2\text{Cu}(\text{O}_{0.75}\text{F}_{0.25})_4$ – upper panel and of $\text{K}_2\text{Cu}(\text{O}_{0.25}\text{F}_{0.75})_4$ – lower panel.

the atomic number $8 \leq Z \leq 9$ for the anion. In all cases studied we can clearly distinguish Cu^{2+} from Cu^{3+} . Thus, trivially, in K_2CuF_4 Cu is Cu^{2+} and, correspondingly, in Fig. 4 the K - s band is unoccupied whereas the F - p band is entirely full. The question we posed was whether we could find one (model) compound having Cu^{2+} and a stable antiferromagnetic Néel state (ANS). We did find none! In contrast to this, we were able to construct model systems having Cu^{3+} and a stable ANS. Thus, for example, Fig. 5 shows the band structure of assumed non-magnetic $Ca_2Cu(O_{0.75}F_{0.25})_4$ and $K_2Cu(O_{0.25}F_{0.75})_4$. In both cases do we have Cu^{3+} and anion p bands that hybridize with the Cu- d bands. It is perhaps not surprising that $Ca_2Cu(O_{0.75}F_{0.25})_4$ does not have a stable ANS, because nesting features are absent at E_F . In contrast to this, $K_2Cu(O_{0.25}F_{0.75})_4$ that does show nearly perfect nesting at E_F has a stable ANS with a calculated magnetic moment of $\mu \approx 0.5 \mu_B$ on Cu.

In closing we briefly summarize our results and attempt to draw a conclusion. Our calculations allow to isolate two broad issues. One concerns the treatment of correlation in the LSDF-approximation, the other one the appropriateness of the antiferromagnetic Néel state.

Anderson [7] points out that for a spin $S = \frac{1}{2}$ -system the resonating-valence-bond state (RVB) may have a lower total energy than the antiferromagnetic Néel state. Since the RVB state consists of pairs of spin singlets it is probably a featureless, liquid-like state. If our inability to obtain an ANS for Cu^{2+} compounds is taken to signal the existence of another, possibly RVB state, then the puzzle remains why the neutron-diffraction data can be analyzed assuming a lattice of alternating up- and down-spins (but see Ref. [4] and [17]).

The treatment of correlation in the LSDF approximation has been repeatedly investigated and was found to be the reason for many, mostly smaller, errors in metals, more controversial being the case of non-metallic systems [16]. Still, our results for K_2NiF_4 seem basically successful. The value of the magnetic moment of $\mu = 1.5 \mu_B$ is smaller than expected, but the magnetic moment of Ni^{2+} in K_2NiF_4 has not yet been directly measured and, hence, one cannot insist that it must correspond to the expected value of $S = 1$. The situation is somewhat different for K_2CuF_4 where our calculated ferromagnetic moment is distinctly lower than a measured value, by a factor of two. So we may assume that correlation is critically underestimated in Cu^{2+} , to such an extent that we fail in bringing about an antiferromagnetic stable moment for K_2NiF_4 type crystals containing Cu^{2+} ions.

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