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THEORETICAL STUDIES OF Sr_2VO_4, A CHARGE CONJUGATE ANALOG OF La_2CuO_4.

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We have used local (spin) density theory to study the atomic geometry and electronic structure of K_2NiF_4-structure Sr_2VO_4. The calculations correctly predict the Cu-O_z distance, reflecting a negative Jahn-Teller distortion (relative to La_2CuO_4). The oxygen p bands are filled, leaving one d electron per V, but in the paramagnetic phase three bands cross E_F rather than having a single half-filled band. We find a ferromagnetic instability within local spin density theory, rather than the antiferromagnetic insulator seen experimentally.

Since the only known compounds having superconducting transition temperature T_c above 35 K contain CuO_2 layers as a basic structural unit, there is strong interest in determining whether there are new systems without CuO_2 layers which contain high T_c materials. Since these systems are hole conductors, at least in the sense that the broad complex of Cu-O valence bands are nearly filled, an alternative is to look for charge conjugate counterparts which are electron conductors. The Nd_2CuO_4-based materials have Hall coefficients of opposite sign to the other Cu-O systems, but the overall electronic structure is very similar.

An unusually interesting material is Sr_2VO_4, for which formal valence counting leads to $(Sr^{2+})_2V^{4+}(O^{2-})_4$, containing only one d electon per V outside closed shells. This compound exists in the K_2NiO_4 structure, and is tentatively identified[1] as a narrow gap (<0.1 eV) antiferromagnetic (AFM) insulator (T_N<100 K. The AFM state is not unexpected, since the single d electron per V can be expected to lead to a half-filled d band and the accompanying AFM instability.

We have applied the full-potential Linearized Augmented Plane Wave method[2] to compute the electronic band structure and total energy of Sr_2VO_4, using the Hedin-Lundqvist (von Barth-Hedin) exchange-correlation functionals for the paramagnetic (spin-polarized) cases. The experimental values[1] a=3.827 Å, c=12.574 Å, and z_{Sr}=0.355 were used. Total energy studies determined the minimum at a Vu O_z distance of 2.01 Å, subsequently verified by neutron diffraction studies. Although this distance is 5% larger than the Vu-O_{xy} distance of 1.91 Å, it is much smaller than the 2.4 Å distance in La_2CuO_4, consistent with a JT effect of opposite sign.

Self-consistent solutions indicated the ferromagnetic (FM) state is more stable than the paramagnetic state by 6.1 mRy/cell. In the PM case we find 12 filled O p bands 5 eV wide, separated by 1 eV from the valence V d bands containing one electron per V atom (Fig. 1). However, there are three bands crossing

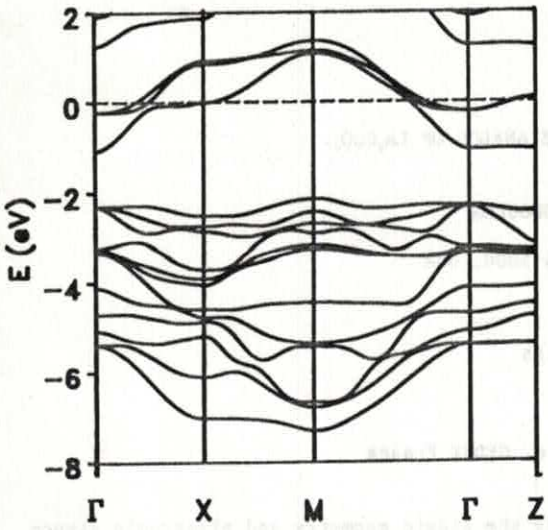

Figure 1. Paramagnetic bands of Sr_2VO_4. Here X=(1,0,0)π/a, M=(1,1,0)π/a.

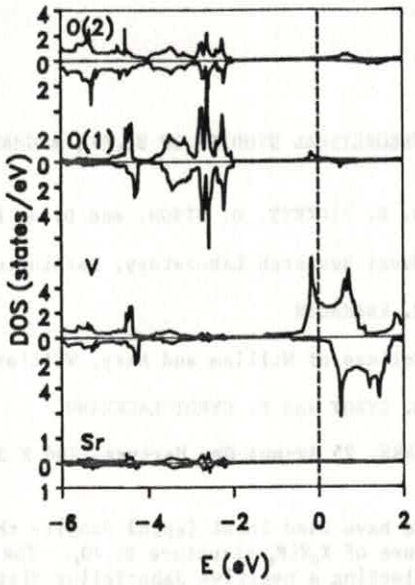

Figure 2. Local DOS for the FM case: upper lines, majority; lower lines, minority.

the Fermi level E_F, two light mass bands and a heavy mass band leading to a highly anisotropic FS and a large peak at E_F. This peak promotes the FM instability, the resulting d band exchange splitting being 0.7 eV. The FM spin-resolved partial densities of states are shown in Fig. 2; note there is no appreciable polarization of the O p states.

We have made careful attempts (including extensive tests of k-point sampling) without success, to obtain an AFM solution of the same symmetry[3] as is found in La_2CuO_4. The FS is neither simple nor two dimensional, due to the considerable dispersion of bands at E_F along the c direction, which leads to a pair of closed, three dimensional spheroids as well as a more complex shaped FS, each centered at Γ.

The 5 eV bandwidth of the O p complex is not surprising, since McMahan et al.[4] showed that direct O-O overlap leads to a similar bandwidth in La_2CuO_4. The dispersion of the V d bands (greater than 4 eV) is somewhat more surprising, since the d states are well separated from one another and interaction must proceed through the intermediate O p states, which are lower in energy and filled. Nevertheless, substantial p-d hybridization exists. Crystal field splittings can also contribute to the total d band width; however, since the CuO_6 octahedron is not far from cubic, such contributions may be secondary.

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