THEORETICAL STUDIES OF Sr$_2$VO$_4$, A CHARGE CONJUGATE ANALOG OF La$_2$CuO$_4$.

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We have used local (spin) density theory to study the atomic geometry and electronic structure of K$_2$NiF$_4$-structure Sr$_2$VO$_4$. The calculations correctly predict the Cu-O distance, reflecting a negative Jahn-Teller distortion (relative to La$_2$CuO$_4$). 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 Na$_2$CuO$_2$-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$_2$VO$_4$, for which formal valence counting leads to (Sr$^{2+}$)$_2$(V$^{4+}$O$^{2-}$)$_4$, containing only one d electron per V outside closed shells. This compound exists in the K$_2$NiF$_4$ structure, and is tentatively identified as a narrow gap (<0.1 eV) antiferromagnetic (AFM) insulator ($T_C$<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 to compute the electronic band structure and total energy of Sr$_2$VO$_4$, using the Hedin-Lundqvist (von Barth-Hedin) exchange-correlation functionals for the paramagnetic (spin-polarized) cases. The experimental values $a=3.827$ Å, $c=12.574$ Å, and $\Delta E_c=0.355$ were used. Total energy studies determined the minimum at a Vu Q 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$_2$CuO$_4$, 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 FM 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

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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 as is found in La$_2$CuO$_4$. 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 $\Gamma$.

The 5 eV bandwidth of the O p complex is not surprising, since McMahan et al. showed that direct O-O overlap leads to a similar bandwidth in La$_2$CuO$_4$. 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 CuQ octahedron is not far from cubic, such contributions may be secondary.

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