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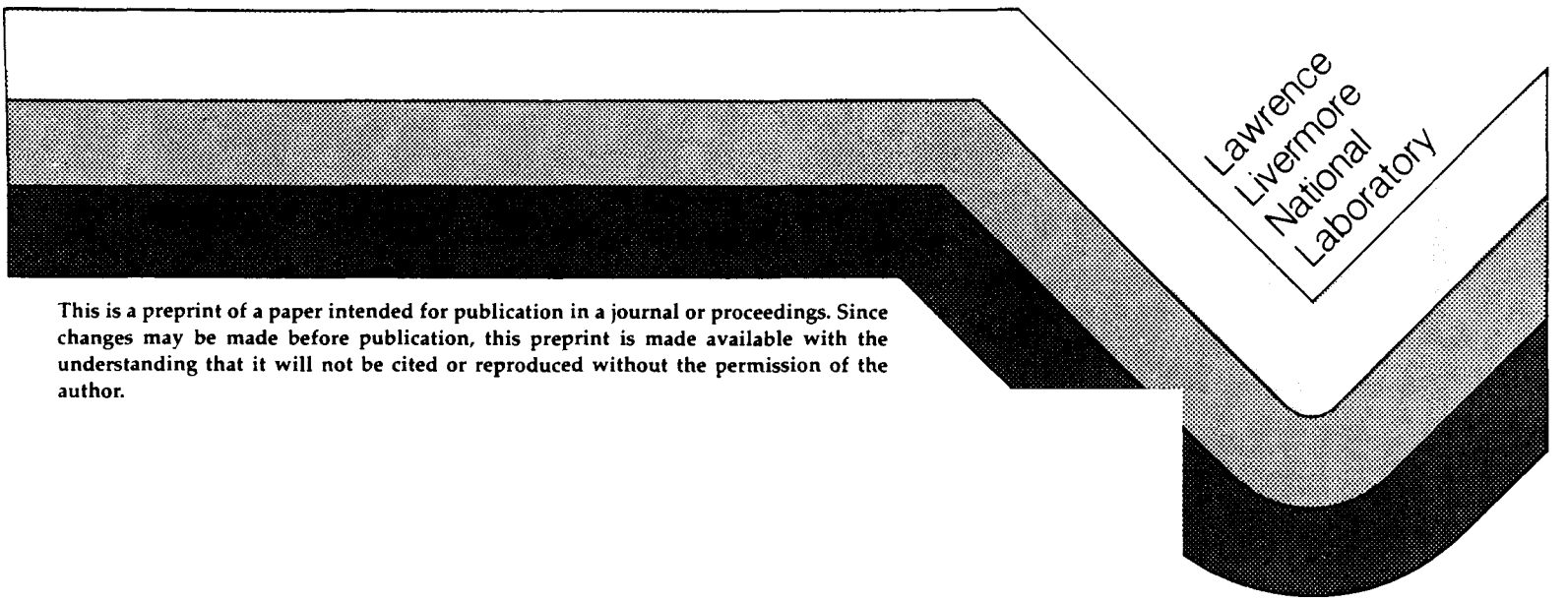

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We report local density calculations of parameters defining extended Hubbard Hamiltonians for La_2CuO_4, La_2NiO_4, and K_2CuF_4, and solve these models for small clusters. These results suggest qualitative differences among the three compounds in regard to spin system, carriers, and carrier – spin interactions.

1. INTRODUCTION

The La_2CuO_4 parent of the original high–T_c superconductors is one of a number of isostructural compounds which exhibit similar electronic and magnetic properties. It would be useful to examine other of these materials in search of features which by comparison to La_2CuO_4 might either preclude or suggest the possibility of high–T_c superconductivity. We report here electronic structure calculations for La_2NiO_4 and K_2CuF_4 carried out in a manner similar to previous work[1] on the cuprate. Specifically, we have used local density theory to obtain parameters defining effective Hamiltonians which are then solved for various sized clusters including electron–electron interactions.

2. PARAMETERS

We have used the linear muffin–tin orbitals[2] (LMTO) method to obtain the band structure for the three materials, and extracted the one–electron parameters in Table I from the X–point LMTO matrices. Here R is the ratio of the apical T–L distance to the in–plane T–L distance [T (transition metal) = Cu, Ni; L (ligand) = O, F], the t's are L(2p)–T(3d) and L(2p)–L(2p) hopping parameters, and the ϵ's are (electron) orbital energies. Subscripts x,y, and z denote both location of the ligand atom and orientation of the p orbital; while $d_x \equiv x^2-y^2$ and $d_z \equiv 3z^2-r^2$ for the transition metal atoms. Orthogonal Wannier functions were used for the T(3d) and L(2p) states, for which simple geometric relations such as $t(p_xd_x) = \sqrt{3}\, t(p_xd_z)$ no longer hold.

The fluoride lattice constant is about 8% larger than those of the two oxides, contributing to more localized L(2p) states, and thus generally smaller t's for K_2CuF_4 in the Table. The apical ligand is closer to Cu in K_2CuF_4, however, leading to larger values of $t(p_zd_z)$ and $t(p_xp_z) > t(p_xp_y)$ in this case.

Total energy calculations yield T(3d) Coulomb interactions $U_d \approx 8$ eV for all three compounds. Addition energies $E(d^{n+1})-E(d^n)$ [n=9 (8) for Cu (Ni)] show a similar ≈ 1 eV rise in moving from La_2CuO_4 to K_2CuF_4 as in Table I. These lie about 2 eV higher than the band–structure derived $\epsilon(d_x)$ values in the Table, and provide an upper bound for these parameters. We have not yet performed comparable calculations for the ligand states; however, take the cuprate values[1] $U_p \approx 6$ eV and $U_{pd} \approx 1$ eV in all cases.

TABLE I
Hopping parameters t and energies ϵ (in eV).

	La_2CuO_4	La_2NiO_4	K_2CuF_4
R	1.28	1.12	0.94
$t(p_xd_x)$	1.43	1.57	0.99
$t(p_xd_z)$	0.71	1.00	0.72
$t(p_zd_z)$	0.67	1.08	1.30
$t(p_xp_y)$	0.70	0.61	0.31
$t(p_xp_z)$	0.58	0.61	0.45
$\epsilon(d_x)-\epsilon(p_x)$	0.7	1.5	2.1
$\epsilon(d_z)-\epsilon(p_x)$	1.1	2.0	2.3
$\epsilon(p_z)-\epsilon(p_x)$	1.2	0.3	0.1

Beyond the scalar U_d, the remaining matrix nature of the T(3d) Coulomb interaction is essential for d^8 Ni. Our calculations of the Slater F^2 and F^4 parameters using T(3d) functions from the solid agree closely with free–atom values. We presume solid–state effects to reduce these values by ≈ 20%, as suggested by Antonides and Sawatzky,[3] leading to a d_x,d_z exchange interaction of ≈ 1 eV in both Cu and Ni compounds.

3. CLUSTER CALCULATIONS

An extended Hubbard Hamiltonian was developed from the above parameters and used to investigate a T–L_6 cluster. The small cluster size is compensated somewhat by a periodic treatment of the ligand states. Still, the results presented in Table II should only be used comparatively.

Each of the materials shows an insulating gap E_{gap}, calculated as the difference between the first electron ionization and affinity levels. The nickelate gap is ≈ 1 eV larger than the others. The calculated intrinsic hole properties are intuitive: R > 1 should give b_1 (x^2–y^2) symmetry; R < 1, a_1 ($3z^2$–r^2) symmetry. Similarly, the d^8 ground state of the nickelate gives the expected a_1b_1 Hund's rule triplet.

We presume the first ionization levels in our calculations for the stoichiometric compounds to be representative of states assumed by added holes in the doped materials. In all cases we find such added holes to have b_1 symmetry,[4] more than 70% L(2p) character, and to have strong (≥ 1/2 eV) interactions with the intrinsic spin lattice. However the cuprate and nickelate have antiferromagnetic interactions between doped and intrinsic holes, whereas the corresponding fluoride interaction appears to be ferromagnetic. Conversely, the cuprate and the fluoride have spin 1/2 lattices whereas the nickelate lattice is spin 1.

TABLE II
Results of T–L_6 Cluster Calculations

	La_2CuO_4	La_2NiO_4	K_2CuF_4
ground state	b_1	a_1b_1	a_1
spin	1/2	1	1/2
E_{gap}(eV)	2.1	3.0	2.2
1st ionization	b_1b_1	$a_1b_1b_1$	a_1b_1
spin	0	1/2	1
L(2p)	84%	77%	72%

4. DISCUSSION

There is as yet no evidence that K_2CuF_4 can be doped to superconductivity, while it has been claimed[5] that one phase of $La_{2-x}Sr_xNiO_4$ is superconducting. The existence or absence of high–T_c superconductivity in these materials is of interest given the qualitative differences found here (many intuitively clear) between these compounds and the isostructural cuprate. In regard to the spin system formed by the intrinsic holes, the nickelate has different spin (1 *vs.* 1/2); the fluoride, different symmetry (a_1 *vs.* b_1). The fluoride spin system is also known[6] to be ferromagnetic. Our results also suggest a ferromagnetic interaction between carriers and these intrinsic spins, as contrasted to antiferromagnetic interactions in the oxides.

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