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Spin Bags, Polarons, and Impurity Potentials in $La_{2-x}Sr_xCuO_4$ from First Principles

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A full-potential version of a recently proposed generalization of the local-density method (LDA+U) is used to study the influence of impurities, lattice, and magnetic relaxation in $La_{2-x}Sr_xCuO_4$. The carriers form mean-field analogs of Zhang-Rice singlets, which are only slightly affected by impurity and in-plane lattice relaxation effects. On the other hand, an "anti-Jahn-Teller" polaron, characterized by a 0.26 Å shorter Cu to apical-oxygen bond length and triplet spin, is nearly stable. Although the impurity potentials are similar, the self-localization effects are much stronger in $La_{2-x}Sr_xNiO_4$.

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In the quest to unravel the mysteries of the high-T_c cuprates, both the influence of impurities and the electron-phonon coupling are heavily debated issues. With regard to the effects of the impurities, transport studies suggest that the impurity states are rather extended (~ 10 lattice constants) [1]. However, theoretical estimates seem to point to much more localized states [2]. Another issue is why it is so much harder to obtain a metallic state by doping, e.g., La_2NiO_4 [3]. Opinions on the importance of electron-phonon coupling vary from considering these interactions to be fully irrelevant, to the idea that high-T_c superconductivity is of the bipolaronic sort [4]. Although it seems unlikely that small-polaron formation is related to breathing-mode-like distortions in the Cu-O planes [5], recently Egami *et al.* presented experimental evidence pointing to rather vigorous motions of the apical oxygens in a direction perpendicular to the planes [6]. These findings might point to the existence of an "anti-Jahn-Teller" (anti-JT) polaron [7], where the motion of the apical oxygen is driven by the transfer of a hole to a $(3z^2-1)$-like state. It has been argued [8] that the coexistence of these small polarons with more bandlike carriers can account for the anomalous normal-state properties [9].

The theoretical difficulty lies in the fact that these systems are doped Mott-Hubbard insulators, and the question is how impurity and electron-phonon effects are affected by this unusual electronic environment [10]. The "spin-bag" picture of Schrieffer, Wen, and Zhang [11] offers one way of looking at the problem. In weak-coupling treatments of doped Mott-Hubbard insulators one finds that the carriers tend to self-localize by creating a spin defect, either involving a reduction of the local moments ($U < W$) [11] or the relative orientations of the spins ($U > W$) [12,13]. An amazingly rich picture of self-localization phenomena has emerged from Hartree-Fock studies on Hubbard models, using large supercells to allow for sufficient variational freedom [14]. The procedure is similar to that followed in small-polaron theory, where one first localizes the carrier around a static lattice defect and afterwards restores the kinetic energy, which in principle can be accomplished using instanton techniques [15,16]. For instance, the static spin order suggested by the mean-field calculations will disappear after the kinetic energy (and the spin fluctuations) is restored. So it is expected that by simultaneously relaxing the spins and the lattice (in the presence of the impurity) one gets a feeling for the interplay and relative importance of these effects.

For this purpose one needs a quantitative theory. The local-spin-density approximation (LSDA) has a very good record with respect to structural properties, but it fails to give a proper description of Mott insulators. Neither a gap nor magnetism is found in, e.g., the insulating parents of the high-T_c superconductors, while in the present context the presence of the gap is vital. Recently, we suggested that the problem has its origin in the homogeneous-electron-gas prejudice that magnetism is only driven by Hund's-rule interactions, while in reality the on-site Coulomb interaction is responsible. This motivated us to propose a modified total-energy functional (LDA+U) [17],

$$E_{\rm tot} = E_{\rm LDA} + \sum_{m,m',\sigma} U(n_{m\sigma} - n^0)(n_{m'-\sigma} - n^0) + \sum_{m\neq m',\sigma} (U-J)(n_{m\sigma} - n^0)(n_{m'\sigma} - n^0), \quad (1)$$

leading to a one-electron (orbital-dependent) potential,

$$V_{m\sigma} = V_{\rm LDA} + U\sum_{m'}(n_{m'-\sigma} - n^0) + (U-J)\sum_{m'\neq m}(n_{m'\sigma} - n^0). \quad (2)$$

Here, $n_{m\sigma}$ is the occupancy of the $d_{m\sigma}$ orbital and $n^0 = \sum_{m\sigma} n_{m\sigma}/10$ is the average number of d electrons per or-

bital. The usual LDA single-particle potential (V_{LDA}) is augmented with orbital and spin dependencies as one would find in a mean-field calculation on a Hubbard model containing on-site U and J (Hund's-rule exchange) interactions [18]. The U and J have to be calculated using "constrained LDA" methods [19], ensuring an overall consistency with the nonmagnetic LDA results. We showed [17] that this method is rather successful in the description of the electronic structure of a variety of $3d$ insulators, yielding order-of-magnitude improvements on conventional LDA results.

This LDA+U method can be viewed as a model Hartree-Fock calculation, with a basis of real orbitals and potentials having all the respectable properties of usual LDA calculations insofar as structural properties are concerned. Our previous work [17] was based on the atomic sphere approximation to the linear muffin-tin orbital (LMTO) method, which is not accurate enough to account for lattice distortions. However, it is straightforward to implement Eq. (1) in the full-potential (FP) LMTO method of Methfessel [20], which is very accurate in this respect. The basis set of the FP-LMTO method consists of well-localized atomiclike orbitals which are not orthogonal. However, in order to use Eq. (1) one has only to require that the $3d$ orbitals are orthogonal and it turns out that the nonorthogonality of the FP-LMTO $3d$ orbitals is very small in the $3d$ oxides.

We use this method to investigate Sr-doped (tetragonal) La_2CuO_4. The undoped system is quite well described by LDA+U and we use a 2×2 supercell ($La_{8-n}Sr_nCu_4O_{16}$, so that $x=n/4=0$ or 0.25, and using up to twelve $\mathbf{k}$ points in the irreducible wedge of the Brillioun zone) to investigate the (self-) localization effects. We first consider the problem of the hole in the undistorted lattice to address the magnetic relaxation effects, in both the absence and the presence of the Sr impurity. Subsequently we consider the interaction of the hole with both in-plane and out-of-plane lattice distortions. These calculations are then repeated for $La_{2-x}Sr_xNiO_4$.

Except for the irrelevant La $4f$ states, the LDA+U electronic structure of undoped La_2CuO_4 looks very similar to that of $CaCuO_2$, which we discussed in our previous paper [17]. La_2CuO_4 is according to LDA+U an antiferromagnetic (AFM) insulator of the charge-transfer variety (O-$2p$-Cu-$3d$ gap [21]), with a moment ($\mu_{Cu}=0.74\mu_B$) and a gap (2.3 eV) that compare favorably with experiment ($\mu_{Cu}\sim0.4\mu_B$ [22] and 1.8 eV [23], respectively). To see how well structural properties are handled, we calculated the frequency of the breathing-mode phonon. Using the frozen-phonon technique we find $\omega_{br}=660$ cm^{-1}, quite close to the experimental value of 710 cm^{-1} [24] and slightly better than the result of conventional LDA ($\omega_{br}=609$ cm^{-1} [25]).

We first study a supercell with an additional hole in the absence of the Sr impurity, compensating the charge by adding a negative charge of 0.125 to all La atoms. We searched for inhomogeneous solutions by making Cu_1 (lower left corner of the supercell) slightly inequivalent to Cu_2 (lower right and upper left) and Cu_3 (upper right). No homogeneous solution exists and the inhomogeneous ground state of the supercell is specified in Table I. This spin bag is easily understood in the context of the three-band model [26] and can be looked at as a mean-field analog of the Zhang-Rice singlet [27]: The hole is mostly localized on the four oxygens (O_1) surrounding the central Cu_1, having its spin antiparallel to that of Cu_1. However, in contrast to the assumptions by Zhang and Rice, the hole also induces a ferromagnetic (FM) interaction between the spin of Cu_1 and that of its nearest-neighbor (nn) Cu_2's (see the table). Keeping in mind that spin fluctuations will tend to diminish this effect, this gives some support to the idea of Aharony *et al.* [13] that holes tend to induce FM interactions, at least if the impurity potential centers the hole on an O site.

Consider the Cu_1-O_1-Cu_2 bond, in the spirit of the Hartree-Fock approximation to the three-band model, assuming for simplicity that $U/2\sim\Delta$ (p-d splitting). In the absence of the additional hole, the antiparallel configuration of the Cu spins is favored over the parallel one by an amount $J\sim t^4/\Delta^3$ (t is the p-d hopping) because the occupied Cu $3d$ levels in the AFM case are pushed downwards by the indirect hybridization (via O $2p$) with the unoccupied $3d$ levels of the same spin on the nn Cu (superexchange). In the FM case, on the other hand, the O $2p$ level with the same spin as its Cu neighbors is pushed upwards by the hybridization. In the presence of an additional hole, this level becomes unoccupied and an energy of $\sim2t^2/\Delta\gg J$ is gained. This picture is confirmed by an analysis of the LDA+U electronic structure. As in the model calculations [14], hole-induced states are found in the density of states (DOS) in the former gap region. The Cu_3 and O_2 partial DOS still reflect the Mott-Hubbard gap. Close (0.15 eV) to the top of the (O-$2p$-like) valence band a rather narrow unoccupied gap band is found having mostly (36%) O_1 character (directed towards the Cu x^2-y^2 orbitals), with a substantial admixture of Cu_1 and Cu_2 $3d_{x^2-y^2}$ states (12% and 24%, respectively [28]), corresponding to the oxygenlike state

TABLE I. The dependence of the total energy (δE, in meV) and the magnetic moments (μ, in μ_B) on the displacement (u) of either in-plane ("breathing," BR) or apical oxygens ("Jahn-Teller", JT) towards the central transition-metal ion (TM_1) in the supercell (TM_2 is the nearest and TM_3 the next-nearest TM_1 neighbor) in the case of "doped" La_2CuO_4 (LCO) and La_2NiO_4 (LNO).

	u	δE	μ_{TM_1}	μ_{TM_2}	μ_{TM_3}
LCO	0%	0	−0.55	−0.59	0.72
	2% (BR)	−39	−0.43	−0.63	0.73
	11% (JT)	15	0.96	−0.64	0.73
LNO	0%	0	0.42	−1.58	1.67
	4% (BR)	−210	0.54	−1.58	1.67

pushed upwards by the interaction with the occupied Cu levels with parallel spin. At higher energies, a second gap band is found of mixed Cu_I and Cu_2 $3d_{x^2-y^2}$ character, which has been pushed out of the Cu $3d$-like "upper Hubbard" band, because the hybridization shift of the unoccupied Cu states with parallel spin is not as strong as elsewhere.

Subsequently, we studied the effect of the Sr impurity by removing the additional charge on the La's and replacing the central La with a Sr atom (located with respect to the plane in the middle of the square spanned by the four Cu's in the supercell). It seems to be established that the Sr impurity does not affect the lattice structure in a significant way [29], and we did not attempt to optimize the local atomic geometry surrounding the impurity. We then repeated the above calculation, and found little influence of the impurity, indicating that its potential is small compared to the other scales in the problem. Our supercell contains both nn and next-nearest-neighbor O atoms with respect to Sr. From the difference in the O $2p$ level positions (0.21 eV) we estimate, using $e/\varepsilon^* R$, an effective dielectric constant $\varepsilon^* = 11$, i.e., twice as large as the long-wavelength dielectric constant. Using this impurity potential in the analysis of Rabe and Bhatt [2] (based on the t-J model), an impurity ionization energy of ~ 0.1 eV is expected.

In the study of lattice-polaronic effects the impurity was neglected, and to keep the calculations manageable we focused on two possible types of lattice deformations: We first moved the four neighboring in-plane O atoms along the Cu-O bond axis toward Cu_I, where the hole is localized ("breathing polaron"). Second, we considered the motion of the two apical O's (O_{ap}) along the Cu_I-O_{ap} bond axis ("anti-JT polaron"). As a function of the breathing distortion we find that the energy is at a minimum for a finite distortion, corresponding to a 2% contraction of the Cu_I-O_I bond. The total energy is lowered by 39 meV, and we note that the energy is lower than that of the undistorted lattice up to a distortion of 4%. The main effect of the distortion on the DOS is a shift of the oxygenlike gap band further into the gap by ~ 1 eV, reminiscent of a polaronic shift. The situation is more complicated than in conventional semiconductors. Because of the distortion, the Cu_I-O_I transfer integrals increase (at the expense of the O_I-Cu_2 hopping), concentrating charge on Cu_I. This triggers a Schrieffer-Wen-Zhang-type spin-bag effect. As can be seen from the table, the Cu_I moment gets suppressed, which in turn leads to a further concentration of charge on the central Cu, and the net result is a rather strong dependence of the Cu_I moment on the lattice distortion. Nevertheless, the polaron binding energy in this adiabatic limit is small compared to the estimates for its kinetic energy [30] and small-polaron effects of this sort are not expected.

We found that the contraction of the Cu_I-O_{ap} bond increases the LDA+U total energy if the distortion is small. However, we were able to find a local minimum in the total energy corresponding to a reduction of the Cu_I-O_{ap} bond length of 0.26 Å (11%), in remarkable agreement with the data of Egami *et al.* (~ 0.3 Å) [6]. The total energy of the anti-JT polaron is only 54 meV higher than that of the fully relaxed breathing-mode polaron. It is expected that other lattice relaxation will not change the above result drastically and our results suggest therefore that *the anti-JT polaron lies very close to the ground state.* The electronic structure of this state is similar to that in the insulator except for the additional hole which is localized in a $(3z^2-1)$-like orbital with about equal weights on the Cu_I $3d_{3z^2-1}$ and the $2p_z$ O_{ap} orbitals. Further, the spin of the $3z^2-1$ hole is parallel to that of the x^2-y^2 hole. Hence, the anti-JT polaron *carries a triplet spin.* The physical origin of this triplet character lies in the Hund's-rule coupling [accounted for in Eq. (1)], which is in the end responsible for the stability of the anti-JT polaron [31]).

We repeated the above calculations for Sr-doped La_2NiO_4. We found undoped La_2NiO_4 to be a high-spin ($1.69\mu_B$) antiferromagnetic charge-transfer insulator with a p-d gap of 3.5 eV. The ground state has high spin (x^2-y^2, $3z^2-1$; $S=1$), and the holes are rather strongly localized on Ni (10% O $2p$ admixture). Adding a hole to the supercell leads to an inhomogeneous state, which is qualitatively similar to the one in the cuprate. The additional hole has a large weight on the four in-plane O_I atoms (nn to Ni_I), although the $3d$ admixture has increased compared to the cuprate. This state has x^2-y^2 symmetry with respect to Ni_I and the spin of the additional hole is antiparallel to that of Ni_I; i.e., the hole has low spin. We note that the x^2-y^2 spins do not compensate exactly on Ni_I ($m_x = n_{x^2-y^2\uparrow} - n_{x^2-y^2\downarrow} = -0.30\mu_B$) and together with the larger polarization of the $3z^2-1$ hole ($0.70\mu_B$), we find a net moment of $0.42\mu_B$ (Table I). The additional hole is nearly entirely localized on Ni_I and O_I. Hence, *the magnetic confinement effects are much stronger in the nickelate than in the cuprate.* This is not surprising, considering the larger gap and moment in the former. We then studied the breathing-type lattice relaxation, and we found that *the stabilization energy of the breathing polaron is now 210 meV, 5 times larger than in the cuprate.* The total energy is at minimum if the Ni_I-O_I bond is contracted by 4% (Table I) and the oxygenlike gap band shifts in this case upwards from 0.4 eV (without distortion) to 0.7 eV. To our understanding, this large increase in polaronic energy comes from an interplay with magnetic relaxation effects. As in the cuprate, the x^2-y^2 spin on Ni_I gets smaller due to the enhanced Ni_I-O_I hybridization ($m_z = -0.14\mu_B$; because the $3z^2-1$ local moment is less affected, the net Ni_I moment increases slightly, see Table I). The big difference from the cuprate is that magnetic relaxation already confined the hole to Ni_I and O_I, and the electron-phonon coupling becomes much more effective. We finally studied the strength of the Sr impurity potential and no significant differences from the cuprate were found. So our calcula-

tions suggest that the origin of the much stronger localization effects in the nickelate is not so much caused by a significantly larger impurity potential, but instead by a disproportionate increase of the effective mass of the carriers, originating in the interplay of magnetic and lattice relaxation effects.

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