Structure of neutral acceptors in insulating La_2CuO_4

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The energy-level diagram for a hole in La_2CuO_4, which is bound to an acceptor which replaces La or Cu, is calculated. The hole is described by the Emery model and the impurity level is assumed to be a deep level. The vibronic effects have been studied. The conditions for the formation of the dipole and magnetic frustrating moments of the impurity state due to the Jahn-Teller distortions have been determined.

The states of the carriers (holes) in slightly doped La_2CuO_4, as we know from the temperature dependence of the conductivity,[1] are localized. Clearly, the holes are bound to acceptors: with Sr^{2+} (or Li^{1+}) ions which replace La^{3+} (or Cu^{2+}) ions. Since the radius of the state is comparable to the lattice constant,[1] the deep-impurity model may prove to be a good approximation ($V_1 - V_2 \gg t$, where $V_{1,2}$ are the potentials of the oxygen sites nearest to the impurity and of those next to them). In this model the hole moves along four nearest oxygen sites, while interacting with the four spins of Cu^{2+} (Fig. 1).

Electronic states. Let us first solve the problem concerning the states of the acceptor in a rigid lattice. The Hamiltonian function of a hole which interacts with the spins of Cu^{2+} for Sr is

$$\mathcal{H}^{\mathrm{Sr}} = t \sum_{\langle ill' \rangle} a_l^+ \hat{P}^i a_{l'} + \tau \sum_{\langle il \rangle} a_l^+ \hat{P}^i a_l \qquad (1)$$

(a Hamiltonian of this sort was studied by Pokrovskiĭ and Uĭmin[2]) and for Li is

$$\mathcal{H}^{\mathrm{Li}} = t' \sum_{l \neq l'} a_l^+ a_{l'} + \tau \sum_{\langle i l \rangle} a_l^+ \hat{P}^i a_l \qquad (2)$$

Here a_l^+ and a_l are the hole operators, and $\hat{P}^i$ is the Dirac operator which forces the spin of the hole and the spin of the ith copper to trade places. Summation over l is restricted to four sites (Fig. 1), $\langle ill' \rangle$ is a triad comprised of copper i and two oxygens ($l \neq l'$) which are next to the copper, and $\langle il \rangle$ are the nearest copper and oxygen sites. The energy is reckoned from V_1. Hamiltonians (1) and (2) are derived from the Emery[3] model in the limit of a strong Coulomb repulsion from copper: t and τ are the integrals describing the hop from oxygen to oxygen via copper ($\tau < t$ because of the Coulomb repulsion from oxygen), and t' is the tunneling through a nonmagnetic Li^{1+} ion.

The hole terms are characterized by the square of the total spin of the system: $S = 1/2$, $3/2$, or $5/2$; by its projection, and by the point symmetry group representation G. Initially, we will disregard the small orthorhombic distortions. In the case of Sr

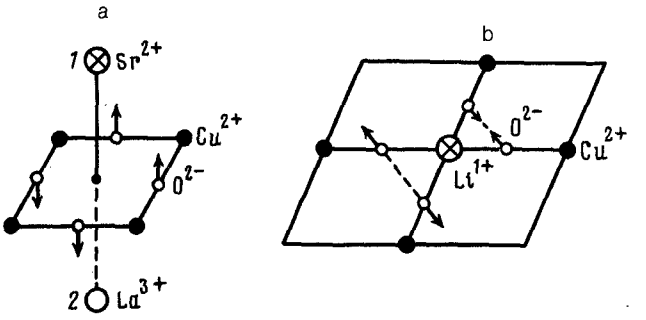

FIG. 1. (a) Geometry of the arrangement of the Sr impurity which replaces La; 1 and 2 — two possible positions of Sr; the arrows indicate the orthorhombic E distortion; (b) the same as in (a), but for the Li impurity which replaces Cu; dipole-active E_u distortion is shown.

impurity we will then have $G = C_{4v}$ with the representations A_1, A_2 (s type), B_1, B_2 (d type), and E (p type). For Li (Fig. 1b) we have $G = D_{4h}$; in the two-dimensional problem the relevant representations are A_{1g},A_{2g},B_{1g},B_{2g}, and E_u.

For the Sr impurity the energy-level diagram in Fig. 2a is similar to that obtained in Ref. 2. At $\tau/t > 0.1$, the ground state is a low-symmetry degenerate $^{1/2}E$ state (the degeneracy is lifted only by spin-orbit coupling), whose energy is $\epsilon_{1/2_E} = -\sqrt{7t}$, where $t = \tau$. The energies $\epsilon_{1/2_{B_2}} = -(\sqrt{33}-1)t/2$ and $\epsilon_{1/2_{B_1}} = -(\sqrt{17}-1)t/2$ correspond to the lowest excited states in the same spin multiplet. The spacing $2\Delta \approx 0.28t$ between the ground level and the first excited level is three times as large as the distance to the next level.

The ground state of the Li impurity is strongly degenerate (the $^{1/2}A_{2g}$ and $^{1/2}E_u$ terms). The degeneracy between the terms corresponding to different representations (Fig. 2b) stems from the fact that the true symmetry group of Hamiltonian (2) is a wider permutation group P_4 than the space group. Allowance for the slight direct tunneling between the oxygen sites lifts the additional symmetry and gives rise to a slight splitting between the terms.

Vibronic effects. Let us consider the lattice distortions. We will first consider the Sr impurity. Since the ground state $^{1/2}E$ is degenerate, the Sr impurity is a Jahn-Teller ion with active modes B_1 and B_2. Furthermore, because Δ is small, the $^{1/2}E$ and $^{1/2}B_2$ levels, which are mixed by the E vibrations, can exhibit a pseudo Jahn-Teller effect. The most important mode apparently is the local soft mode Q_α ($Q_{1,2}$ are the angles of rotation of the oxygen plaquette relative to [110] and [1$\bar{1}$0] axes; Fig. 1a). This mode is directly related to the Σ_4 crystal (orthorhombic) mode. The orthorhombic mode, a soft mode near the point X, is responsible for the structural transition in La_2CuO_4 (Ref. 4). If the vibronic interaction of the $^{1/2}E$ and $^{1/2}B_2$ levels only with Q_α is taken into account, we can find the adiabatic potential in a standard manner[5]: $\epsilon(Q) = (1/2)KQ^2 - \sqrt{\Delta^2 + V^2Q^2}$, where K is the effective stiffness, $Q_1^2 = Q^2 + Q_2^2$, and V is a linear constant of the vibronic interaction. If the condition

$$V^2/K\Delta > 1, \tag{3}$$

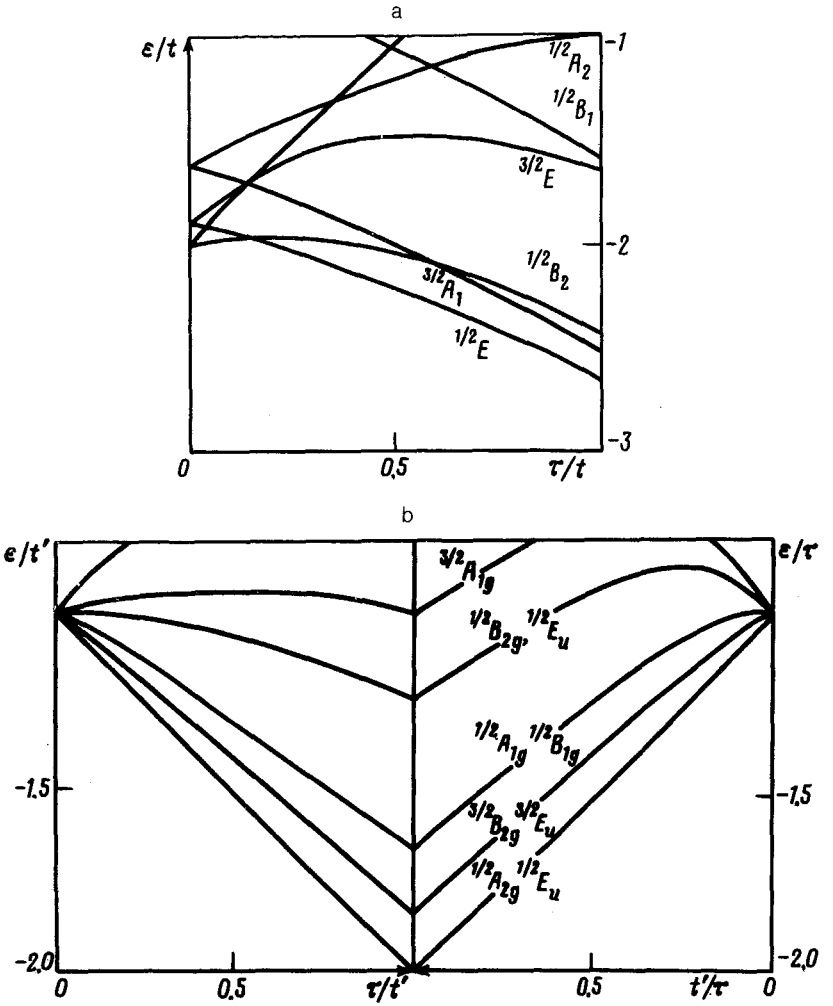

FIG. 2. (a) Energy-level diagram for the Sr impurity; (b) the same as in (a), but for the Li impurity. On the left, $\tau < t'$; on the right $\tau > t'$.

is satisfied, the symmetric configuration $Q = 0$ becomes unstable: We see a trough of minima in the Q_1, Q_2 space with a radius $Q_{JT} = (V^2/K^2 - \Delta^2/V^2)^{1/2}$. Clearly, allowance for the nonlinearity and for the slight interaction with other levels warps the trough: Four minima appear.

Let us determine the values of the parameters in inequality (3). The estimate $t \sim 0.5$–1 eV corresponds to $\Delta \approx 0.14t \sim 0.1$ eV. A crude "ionic" estimate of the vibronic constant is $V \sim 1$ eV. As a result, the value $V^2/K\Delta \sim 10$; i.e., inequality (3) is satisfied by a wide margin (strong pseudo Jahn-Teller effect). This result is not surprising because strong Jahn-Teller distortions have been observed in many related substances.[5]

At $T \leqslant 500$ K La_2CuO_4 has an orthorhombic symmetry. In the case of a strong pseudo Jahn-Teller effect, however, the quantity $Q_{JT} \gg Q_0 \approx 0.05$, much greater than the angle of rotation of the oxygen octahedra in the orthorhombic phase. The orthorhombic state can then be viewed only as a weak perturbation which stabilizes the Jahn-Teller distortions. The pseudo Jahn-Teller effect can be interpreted as a local enhancement of orthorhombic symmetry near the neutral Sr impurity.

Because of the distortion of the lattice, Q_α, the impurity acquires a dipole moment $\mathbf{d}$ and magnetic frustrating moment $\vec{\mu}$ (Ref. 7):

$$\vec{\mu} = f(VQ/\Delta) \sum_{\alpha=1}^{2} \vec{\mu}_\alpha^{(0)} Q_\alpha / Q;$$
$$f(x) = x(1+x^2)^{-1/2}, \quad \vec{\mu}_\alpha^{(0)} = \langle {}^{1/2}B_2 | \sum_i \kappa_i (\mathbf{S}\mathbf{S}_i)\mathbf{r}_i | {}^{1/2}E\alpha \rangle, \tag{4}$$

where $\mathbf{S}$ is the total spin of the state, and $\kappa_i = \pm 1$ at various copper sublattices ($\vec{\mu} \to -\vec{\mu}$ upon substitution of sublattices or upon a transition of Sr from position 1 to position 2; Fig. 1a). In the tetragonal phase $\mathbf{d} = 0$ and $\vec{\mu} = 0$ (Ref. 2). In the orthorhombic phase, μ is now a noticeable part of $\mu_{\max} \equiv |\mu_\alpha^{(0)}| \sim 1$Å, even without the Jahn-Teller distortions (i.e., at $Q = Q_0$), since $f \sim 0.5$ when $V/\Delta \sim 10$. In the case of a strong pseudo Jahn-Teller effect, we have $\mu = \mu_{\max}$.

In the case of an Li impurity, in addition to the modes which are active inside the ${}^{1/2}E$ level, the E_u mode (Fig. 1b), which mixes the ${}^{1/2}A_{2g}$ and ${}^{1/2}E_u$ states, is also a Jahn-Teller mode. This mode is weakly linked with the orthorhombic Σ_4 mode. The resultant Jahn-Teller distortion is not stabilized in the orthorhombic phase and is smaller than it is in the case of Sr since it consists of stiffer modes. Allowance for the splitting of 2Δ between ${}^{1/2}A_{2g}$ and ${}^{1/2}E_u$ levels shows that the threshold of the pseudo Jahn-Teller effect lies much lower, in terms of Δ, then it does in the case of Sr because of the greater stiffness of K. Since the soft Q_α mode of the symmetry E_g discussed above is generally inactive, the orthorhombic distortion Q_0 does not lead to the appearance of $\mathbf{d}$ and $\vec{\mu}$ — they are linked exclusively with the Jahn-Teller distortions. If these distortions are found to be suppressed because of the splitting, then $\mathbf{d}$ and $\vec{\mu}$ will also be suppressed.

Interestingly, because of the large gap $2\Delta = 2t$ which separates the ground state and the first excited state, the vibronic effects should be weak in the problem which considers the state of the neutral donor Ce in Nd_2CuO_4, in which the electron moves along the plaquette consisting of four coppers. In this case $\mathbf{d} = \vec{\mu} = 0$.

The high-lying levels were disregarded in the discussion above. This omission is justifiable if the Jahn-Teller energy is $V^2/K\Delta \lesssim t$, consistent with the estimates presented above. If, on the other hand, $V^2/K\Delta \gg 6t$—much greater than the width of the multiplet with $S = 1/2$ (i.e., with an anomalously small t), then we have a polaron model with a hole which is self-trapped at a single oxygen site, as in the model proposed by Aharony *et al.*[8]

We note in conclusion that the large value of μ, which we obtained for the Sr impurity in La_2CuO_4, allows us to link the strong concentration dependence of the Néel temperature T_N with the mechanism for the long-range dipole frustration.[7] A

weaker effect of Li impurities in La_2CuO_4 and of Ce impurities in Nd_2CuO_4 on T_N would suggest that there is no strong pseudo Jahn-Teller effect in these cases.

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