Hole centers in $LaSrAl_{1-x}Cu_xO_{4-\delta}$ in connection with magnetic Jahn–Teller polarons in $La_2CuO_{4+\delta}$

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A study of CuO_6 centers with a hole at planar oxygens in $LaSrAl_{1-x}Cu_xO_4$ suggests that the occurrence of a hole at a CuO_6 fragment in La_2CuO_4 gives rise to Coulomb and vibron deformations of the CuO_6 center and the neighboring octahedra. A ferromagnetic cluster undergoing a random walk as a result of migration of a hole is a magnetic Jahn–Teller polaron. Conclusions are drawn regarding the electronic structure and dynamic characteristics of this cluster.

According to a concept which has developed over the past few years,[1,2] the disruption of the stoichiometry of layered La_2CuO_4 cuprates (A) by the introduction of Sr or Ba in a La site or by the provision of excess oxygen causes the structure of the cuprate to become nonuniform at a microscopic scale. The nonconducting antiferromagnetic phase of La_2CuO_4 is joined by a percolation phase, which is responsible for the conductivity and also (below 40 K) the superconductivity of the material. It has been suggested that magnetic quasiparticles are the seeds of the conducting phase and the structural fragments of the percolation networks. These quasiparticles arise from a disruption of the antiferromagnetic order by holes in oxygen p states, which appear upon doping, and they include about 15 spins undergoing a ferromagnetic interaction. The formation of a conducting phase becomes possible as the result of a diffusion of magnetic quasiparticles.[3] The existence of magnetic particles under the experimental conditions of Ref. 3 was confirmed in Ref. 4 by ESR observations. Two model clusters containing a hole and either five or four Cu^{2+} ions were discussed theoretically in Ref. 5. In the present letter we propose a microscopic model for a magnetic quasiparticle which is based on new facts and on an analysis of the ESR signals from CuO_6 centers in $LaSrAl_{1-x}Cu_xO_{4-\delta}$ (B) (Ref. 6).

An x-ray analysis of the B solid solutions to identify the phases present revealed that the K_2NiF_4 structural type persists at all copper concentrations ($0 \leqslant x \leqslant 1$). The existence of series B was somewhat unexpected, since in this case the Al^{3+} ions are replaced by doubly charged Cu^{2+} ions in progressively greater numbers. Indeed, it follows from the ESR work that Cu^{2+} ions in the B samples are present and that the CuO_6 centers are characterized by the following parameters: $g_{\parallel}=2.320\pm0.002$, $g_{\perp}=2.069\pm0.002$, $A_{\parallel}=(150\pm1)\times10^{14}$ cm^{-1}, and $A_{\perp}<10\times10^{-4}$ cm^{-1} (the centers of type I in Fig. 1). Analysis of these data and also the results of studies of $La_{1+x}Sr_{1-x}Ga_{1-x}Cu_xO_4$ (Ref. 7) and $LaSrAl_{1-x}Ni_xO_4$ (Ref. 8) led to the conclusion that the magnitude and nature of the

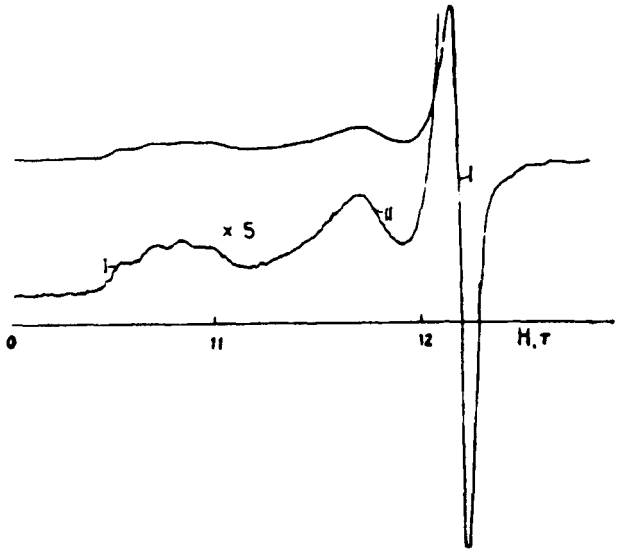

FIG. 1. ESR spectrum of $LaSrAl_{0.98}Cu_{0.02}O_4$. $T=300$ K, $\nu=35.14$ GHz.

distortion of the CuO_6 octahedra in B, the nature of the energy states, and the binding of the copper ions with the lattice are governed by internal electronic–vibrational factors, i.e., that they are of Jahn–Teller nature. Combined with data on the parameters of the A and B structures,[9,7] this circumstance indicates that the CuO_6 centers in the A cuprates are also of a Jahn–Teller nature.

Clearly, the $Cu^{2+}O_6$ centers disrupt the B stoichiometry and set the stage for the formation of holes in $Al_{1-x}Cu_xO_2$ layers. It has been found by iodometric titration that the effective charge state of the copper is $+2.47$, and that the state is essentially independent of x; the values $\delta=0.05$, 0.11, 0.16 and 0.22 were found for $x=0.2$, 0.4, 0.6, and 0.8, respectively. The restoration of the charge balance leads to new magnetic centers, which are observed by the ESR method in series B at $x>0.02$ (signal II in Fig. 1). The ESR signal of these centers consists of a single symmetric line with $g^{II}=2.123\pm0.003$ and $\Delta H^{II}=100$ Oe (for $x=0.1$; the X band); the value of g^{II} is independent of x and T. In samples with $x<0.1$, the intensity of signal II falls off sharply below 30–40 K, and essentially no ESR is seen at 4.2 K. In the samples with $x>0.1$, this anomaly in the temperature dependence of signal II is not found. The intensity of this signal increases with decreasing temperature in the same way as the intensity of signal I.

The centers of type II can be interpreted as CuO_6 centers with a hole which is delocalized among four planar oxygens. To explain the nature of the states and the magnetism of the CuO_6 centers, we use the scheme of molecular orbitals of a tetragonally deformed CuO_6 octahedron. Those states which form predominantly from copper d orbitals and which are most nearly molecular orbitals with symmetries e_g, b_{2g}, a_{1g}, and b_{1g} are orbitals constructed exclusively from planar $\{a_{2g}(\pi)=1/2[py_1-px_2-py_3+px_4]\}$ and extraplanar $\{b_{2u}(\pi)=1/2[pz_1-pz_2+pz_3-pz_4]\}$ $2p$ states of oxygens. The $a_{2g}(\pi)$ and $b_{2u}(\pi)$ orbitals are written here in the coordinate system of the CuO_6 center. These orbitals are orthogonal with respect to the orbitals a_{1g} and b_{1g},

which include the $|z^2\rangle$ and $|x^2-y^2\rangle$ states of copper. We believe that oxygen states of the $a_{2g}(\pi)$ and $b_{2u}(\pi)$ types are the states which are occupied by the hole in the CuO_6 complexes in series B.

The appearance of a hole, delocalized among four planar oxygens, in the nearest neighborhood of a Cu^{2+} ion causes a decrease in the tetragonal component of the crystal field at the copper ion, to the point that the sign of this field may change. The hole gives rise to a spin–spin coupling between unpaired O^- and Cu^{2+} electrons. Since the corresponding orbitals are orthogonal, this interaction is ferromagnetic. As a result, we have a Jahn–Teller CuO_6 center with $S=1$ and with three approximately equiprobable configurations of the complex, with tetragonal axes along the a, b, and c axes of the structure. Isolated CuO_6^- centers are dynamic. The averaging of the various Jahn–Teller configurations at high temperatures, at which the frequency of transitions between them is higher than the ESR frequency, gives rise to a single symmetric signal. The freezing of one of the tetragonal configurations makes it difficult to detect the fine-structure lines, broadened by the dispersion of the crystal fields. Two stable positions arise for both planar and apical oxygens, with a very anharmonic potential.

The CuO_6 centers in series B are of the same physical nature as in $LaSrCuO_4$ and in A: Jahn–Teller centers which are tetragonally deformed by the Jahn–Teller effect and by a cooperative effect. The hole centers in these compounds should also be related, since the primary cause of the Jahn–Teller dynamics is the same in all cases: a decrease in the tetragonal component of the crystal field. This is true regardless of the method by which the hole enters the nearest neighborhood of the Cu^{2+}. Let us compare the CuO_6^- centers which we observed with what one might expect in materials with CuO_2 layers.

It has been established experimentally that holes are in a band which includes oxygen $2p$ states[10] and which overlaps a partially filled band of copper $3d$ states.[7] At high temperatures $T>300$ K, the A samples have a metallic conductivity. In the B samples with $x=1$ the conductivity is semiconducting, with a small activation energy—on the order of kT at room temperature. That result confirms our measurements of the conductivity in the B samples. As the temperature is lowered, there is a progressively increasing probability that the holes will localize at oxygens near a copper ion. Jahn–Teller deformations of the CuO_6^- center cause the distortions of the neighboring octahedra in the ac plane to have an antiferromagnetic distortion nature,[11] and they give rise to a ferromagnetic cluster of 5 to 13 copper ions (Fig. 2). The symmetry of the structure and the comparatively weak Coulomb bond of a hole with an Sr^{2+} ion do not prevent hops of a hole to another CuO_6 center (not necessarily a neighboring center), which cause a simultaneous shift of lattice deformations. As it migrates along a layer, a hole can undergo a random walk along with lattice deformations caused by both a static Coulomb deformation and a deformation of vibron origin. A ferromagnetic cluster which arises is essentially a magnetic Jahn–Teller polaron.

Magnetic polarons were postulated in Ref. 1 in connection with a discussion of the phase nonuniformity of cuprates. Ferromagnetic polarons (ferons) generated by electrons in CuO_2 layers with an antiferromagnetic order were also discussed in Refs. 12 and 13. We believe that the model of a Jahn–Teller polaron proposed in the present letter reflects the actual situation in cuprates. It correlates with an ESR signal observed[4] in

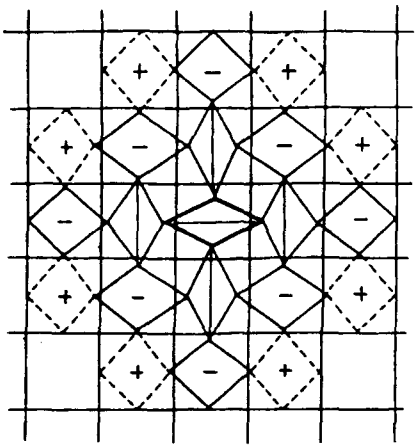

FIG. 2. Model of a Jahn–Teller polaron.

$La_2CuO_{4+\delta}$: a signal with $g=2.12\mp0.02$, $\Delta H=350$ Oe, arises after a sample is heated to 500–800 K and then rapidly cooled.

The Jahn–Teller polarons in the A samples have the same origin as the CuO_6^- hole centers in dilute B samples, but they do have several substantial distinctions. The first stems from the nature of the oxygen p states containing the hole. In the B samples, p_σ states are added to the planar and extraplanar p_π oxygen states in the p band of the A compounds. According to x-ray spectroscopy,[10] the holes can occupy planar p_π or p_σ orbitals of oxygens. The spin–spin coupling in CuO_6^- is correspondingly either ferromagnetic ($S=1$) or antiferromagnetic ($S=0$). In each case the CuO_6^- center remains of a Jahn–Teller nature. The second distinction arises from the size of the magnetic cluster that appears. This cluster combines two or three spheres of the nearest neighborhood of the Cu_6^- center. The distortions of the CuO_6 complexes are of an antiferromagnetic distortion nature (Ref. 11, for example) and give rise to a ferromagnetic cluster, regardless of the spin of the central fragment (Fig. 2). A third distinction stems from the lifetime of the magnetic Jahn–Teller polaron that arises. Clearly, a snapshot of this polaron should have anisotropic properties; only the dynamics and the fast random walk of the polaron cause an averaging of these properties. The lifetime of a polaron in a certain position in the structure, τ, can be estimated from the ESR data. The time τ is determined by the rate at which the anisotropy of the Zeeman interactions of the Jahn–Teller polaron or the exchange anisotropy in it is averaged: $\tau<h/\Delta g\beta H$ or $\tau<D$ ($\tau<10^{-8}$ s).

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