Dynamics of oxygen in the CuO_2 plane in $LaSrAl_{1-x}Cu_xO_4$

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(Submitted 23 October 1992; resubmitted 4 December 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **57**, No. 1, 60–64 (10 January 1993)

It is shown that Cu^{2+} centers in $LaSrAl_{1-x}Cu_xO_4$ are Jahn–Teller centers. Experiments reveal some Cu centers at which the ligand oxygens in the CuO_2 plane migrate between positions corresponding to two minima of the adiabatic potential. A model is constructed for these centers.

Various aspects of the phonon mechanism for carrier pairing in high-T_c superconductors have been the subject of several studies.[1–5] It has been established that the anharmonicity of the vibrations of the oxygen atoms plays an important role in strengthening the electron–phonon pairing mechanism.[2,5] The pairing energy has been calculated from estimates which incorporate several vibrations which are active in the Jahn–Teller effect.[3] Although ESR is a direct method for observing Jahn–Teller dynamics, the individual CuO_6 centers in a high-T_c superconductor do not exhibit a paramagnetic resonance. Our purposes in the present study were to model the crystal chemistry (the crystal fields acting on the copper ion, the charge states, and the spin states in the CuO_2 layers) of high-T_c superconductors of the $La_{1.85}Sr_{0.15}CuO_4$ type (system A) and to experimentally detect and study, by the ESR method, vibron interactions in copper-oxygen complexes of these cuprates.

A convenient system for these purposes is $LaSrAl_{1-x}M_xO_4$ (system B). We have verified that this system allows diamagnetic dilution to any extent not only with $M=Cr^{3+}$, Ni^{3+} (Refs. 6 and 7) but also with M=Cu ($0 \leqslant x \leqslant 1$). Systems A and B are isostructural and have approximately equal lattice constants.[6,8] The crystal fields acting on the M ion are determined primarily by the nearest neighborhood of six oxygen ions and the second sphere of ten La and Sr ions. In system B with Ni^{3+}, one observes a strong coupling of the electron and phonon subsystems.[9] This coupling leads us to expect a manifestation of Jahn–Teller dynamics at Cu^{2+} centers also, since copper has spin–phonon coupling constants larger than those of nickel.

The ESR spectra of ceramic $LaSrAl_{1-x}Cu_xO_4$ were studied in the X band ($\nu=9.3$ GHz) and the Q band ($\nu=37$ GHz) in the temperature range 4.2–300 K. A DRON-2 diffractometer was used to verify that the samples consisted of only a single phase and to measure the concentration dependence of the lattice constants a and c. As x is varied, the lattice constants change in a monotonic manner, within the experimental errors, from $a=375.8$ and $c=1264$ pm at $x=0$ to $a=375.9$ and $c=1297$ pm at $x=1$.

Two types of ESR signals are observed (Fig. 1). Signal I is observed for all values of x up to $x \leqslant 0.6$. This signal is typical of isolated Cu^{2+} centers and can be described

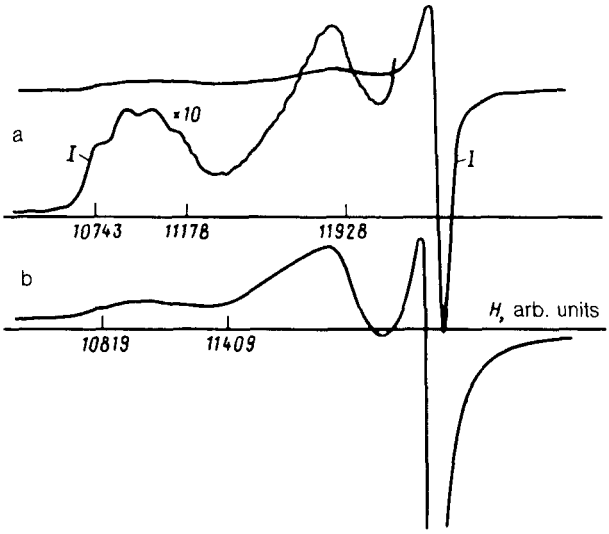

FIG. 1. ESR spectra of $LaSrAl_{1-x}Cu_xO_4$ at $T=293$ K and $\nu=35.14$ HGz. *a*—$x=0.02$; *b*—$x=0.10$.

by a spin Hamiltonian of axial symmetry with the parameter values $g_{\parallel}^{I}=2.320\pm0.002$, $g_{\perp}^{I}=2.069\pm0.003$, $A_{\parallel}^{I}=(150\pm1)\times10^{-4}$ cm^{-1} (the hyperfine structure is resolved at $x\leqslant0.10$), and $A_{\perp}^{I}<10\times10^{-4}$ cm^{-1}. For $x=0.01$ in the X band we have $\Delta H_{\perp}^{I}=3.8$ mT and $\Delta H_{\parallel}^{I}=6$ mT. The intensity of signal I is a nonmonotonic function of x, going through a maximum at $x=0.04$. The decrease in this intensity at $x>0.04$ stems from the formation of exchange-coupled pairs and larger clusters of copper, which cannot be seen directly in the ESR spectra. In the case of a statistically equiprobable distribution of isolated centers, the highest number of these centers would correspond to $x\sim0.08$. Signal II is detected beginning at $x\geqslant0.02$. It consists of a single, essentially symmetric line with $g^{II}=2.123\pm0.003$ and $\Delta H^{II}=10$ mT ($x=0.02$; the X band). These parameter values were found through an optimization of model spectra. In the course of the modeling we also calculated the relative contents of I and II centers, i.e., K_I and K_{II}, which are the weight factors in the summation of spectra I and II ($K_I+K_{II}=1$). The parameters g_i^I, A_i^I, g^{II} are essentially independent of x and T (we will not discuss here the slight changes observed in g^{II} as T was varied). The quantity ΔH_i^I increases with increasing x, and we have $\Delta H_{\parallel}^{I}>\Delta H_{\perp}^{I}$ and $\Delta H_{\parallel}^{I}(Q)>H_{\parallel}^{I}(X)$. These results indicate that there are contributions from dipole–dipole broadening and that the spread in local crystal fields at the Cu^{2+} ions is having an effect. The quantity ΔH^{II} also increases with increasing x and with increasing frequency of the microwave source. There is no change in lineshape here, with the implication that signal II is of an exchange nature. The relative content of the II centers increases with increasing x.

The temperature dependence of the intensity of signal II is different in the samples with $x\leqslant0.1$(IIa) and $x>0.1$(IIb). The intensity of signal IIb, like that of signal I,

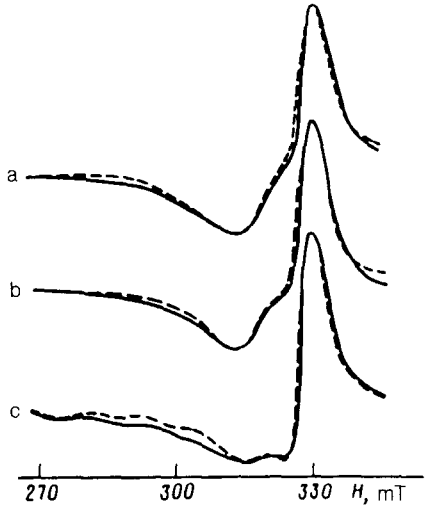

FIG. 2. ESR spectra of $LaSrAl_{0.90}Cu_{0.10}O_4$ with $\nu=9.48$ GHz. Solid lines—Experimental; dashed lines—theoretical. a) $T=293$ K, $K_{II}=0.4$; b) $T=30$ K, $K_{II}=0.39$; c) $T=4.2$, $K_{II}=0.09$.

increases with decreasing temperature. At $x=0.4$, for example, we have $K_{II}(293\ \text{K})=0.61$ and $K_{II}(4.2\ \text{K})=0.68$. In other words, these results are the same, within the errors of the estimates. The intensity of signal IIa falls off sharply below 30–40 K: at $x=0.10$ we have $K_{II}(>30\ \text{K})\simeq 0.41$ and $K_{II}(4.2\ \text{K})=0.09$ (Fig. 2). This result indicates that centers of a different nature are contributing to signal II. The centers of type IIa are predominant in the samples with $x<0.1$. With increasing x, their contribution to signal II decreases, and centers of type IIb are predominant at $x>0.1$.

A comparison of the total intensity of the ESR spectra of these test samples with a standard showed that only $\sim 10\%$ of the copper ions introduced are contributing to the observed spectrum in the case $x=0.01$. With increasing x, this fraction decreases. An ESR signal is not observed in $LaSrCuO_4$.

These results suggest the following models for the centers. The single centers of type I are Cu^{2+} ions which replace Al^{3+} ions and which form CuO_6 octahedra stretched out along the [001] axis. For these centers, a change in the lattice constants, within certain limits, does not result in changes in the parameters of the ESR spectra:

- There is essentially no concentration dependence of the g-factors as x is increased and as the lattice constants a and c are varied.
- There are no types of centers which are observed clearly in the system with Ni^{3+} and which are associated with a change in the tetragonal component of the crystal field for various combinations of the La and Sr ions along the [001] axis.[6]
- The parameters of spectra I are the same, within the experimental errors, as those of the Cu^{2+} centers in $La_{1+x}Sr_{1-x}Ga_{1-x}Cu_xO_4$ solid solutions.[7] In other words, the Cu^{2+} ions do not sense a difference between the crystal fields in matrices with Al and Ga.

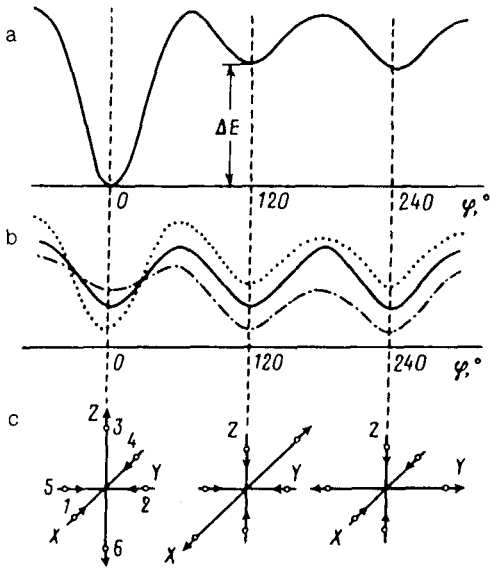

FIG. 3. a, b: Adiabatic potential of CuO_6 complex. *a*—In the case of a tetragonally extended CuO_6 octahedron (centers I); *b*—in the case of a CuO_5O^- octahedron deformed by the remote coordination spheres (centers IIa). c: nature of the distortions of the complex at the corresponding minima of the adiabatic potential.

A situation of this sort is possible in CuX_6 complexes with strong electron–phonon coupling with a slight tetragonal extension, provided that the tetragonal component of the crystal field does not exceed the quadratic constant of the electron–phonon interaction (or the anharmonicity constant of the ligand vibrations) by a factor of more than 3 (Ref. 8). The adiabatic potential of the complex then has the form shown in Fig. 3a. The distortions at each minimum of the adiabatic potential are shown in Fig. 3c; here ρ and φ are the normal deformations of the CuX_6 complex in polar coordinates. In the main configuration ($\varphi=0$) the oxygen octahedron is stretched out along the Z axis, and a change in the tetragonal component of the crystal field leads to a change in ΔE alone, having essentially no effect on the extent of the distortions of the complex or the values of the g-factors. The difference between the copper–oxygen distances is $\sim 0.85\rho$. According to Ref. 10, the values of ρ for Cu^{2+} lie in the interval 30–70 pm, and tetragonal lattice deformations ~ 1 pm cause a change of ~ 100 cm^{-1} in the energy interval ΔE between the ground and two excited levels. According to our estimates, the average interval in $LaSrAl_{1-x}Cu_xO_4$ is $\Delta E \sim 800$ cm^{-1}, and the difference between the distances between the axial and planar oxygen ions is 8–16 pm.

The CuO_6 complexes are thus Jahn–Teller complexes. In other words, the nature of their distortions is determined by internal vibron forces, and the lattice perturbations are manifested primarily in the particular features of the dynamics of these complexes. The conclusion that there is a strong electron–phonon coupling in the Cu^{2+} complexes in B presupposes that they remain of a vibron nature in the cuprates $La_{2-x}Sr_xCuO_4$. This circumstance explains the pronounced stretching of the CuO_6 octahedron along the [001] axis in these compounds: In La_2CuO_4 the Cu–O distances are 2×246 pm and 4×190.5 pm (Ref. 7), while in $La_{1.85}Sr_{0.15}CuO_4$ they are 2×241 and 4×189 pm (Ref. 11).

The type-II centers arise because of electron defects in the $Al_{1-x}Cu_xO_2$ layer. The requirement of charge neutrality of the compound $LaSrAl_{1-x}Cu_xO_4$ presupposes that there exist, along with the copper ions in the stable oxidation state Cu^{2+}, some Cu^{3+} ions, some oxygen O^- ions, and possibly some oxygen vacancies. The appearance, in the nearest neighborhood of a Cu^{2+} ion, of a "hole" (an O^- ion) delocalized among four planar oxygens of a CuO_6 octahedron, leads to a decrease in the tetragonal component of the crystal field, to the point that this component changes sign. It also leads to the appearance of a spin–spin interaction between unpaired O^- and Cu^{2+} electrons. At $|J| \sim 10^3$ cm^{-1}, signal IIa can be observed only if the exchange is of a ferromagnetic nature. In this case the crystal field at the Cu^{2+} ion retains its axial symmetry, while the adiabatic potential takes the form shown in Fig. 3b (the *d*-wave contributions of the function of the electronic ground state are $\propto |x^2-y^2\rangle$, $\propto |y^2-z^2\rangle$ or $\propto |z^2-x^2\rangle$. Because of deformations in remote coordination spheres, the value of ΔE may vary over an interval $\sim (\pm 50$ cm$^{-1})$, smearing out the picture in Fig. 3b and causing a decrease in one or two minima of the adiabatic potential. At low temperatures the complex is stabilized in one of the minima; this stabilization corresponds to a stretching of the octahedron along one of the ⟨100⟩ axes. Two stable positions for an O^{2-} ion arise along each axis of the Cu–O bond in the $Al_{1-x}Cu_xO_2$ plane, displaced $\sim$(20–40 pm) with respect to the center. In this case the ESR spectrum has a large anisotropy and cannot be detected. As the temperature is raised, the complex migrates between minima of the adiabatic potential. At a jump frequency $\nu > D/\hbar$, $\Delta g\beta H/\hbar$, a dynamic signal of type IIa appears in the spectrum. The appearance of this signal implies a change in the wave function of the CuO_6 ground state and a change in the nature of the motion of the oxygen. While this motion at low temperatures consists of abrupt transitions between stable positions at frequencies $\sim 10^7$ Hz, above a certain temperature the system is delocalized between these positions.

Signals of type IIb ($0.1 < x < 0.8$), whose intensity increases all the way to a temperature of 4.2 K, are of exchange origin. They arise from an exchange narrowing of the spectra: the single centers of type IIa, in which the Jahn–Teller dynamics is suppressed by an interaction through the field of phonons;[9] ferromagnetic antiferrodistortion dimers of the IIa–IIa or IIa–I type, with *g* and *D* tensors having axes in different directions; and multicenter ferromagnetic clusters including Cu^{2+}, Cu^{3+}, and O^-. It is important to note that the participation of IIa vibron centers is necessary in all cases.

The centers from which an ESR is not observed in ceramic $LaSrAl_{1-x}Cu_xO_4$ might be as follows: microscopic inclusions of the $LaSrCuO_4$ phase which do not disrupt the phase homogeneity of the sample according to x-ray measurements; Cu^{3+} centers; Cu^{2+}–Cu^{2+} or Cu^{3+}–Cu^{3+} dimers, or conglomerates of centers in which homovalent copper ions are predominant. The number of such centers is high ($>90\%$) even at small values of *x*, indicating a tendency toward an early clustering of copper octahedra. This conclusion agrees with the conclusion, which has been reached by several investigators, that there is a microscopic inhomogeneity of this type in materials belonging to a single structural type.[12,13]

The distortion of the IIa centers in $LaSrAl_{1-x}Cu_xO_4$ and of the CuO_6 complexes in La_2CuO_4 upon doping with Sr^{2+} ions are of the same nature (a hole appears in a

CuO_2 layer). In $La_{1.85}Sr_{0.15}CuO_4$, centers with a strong coupling through e_g phonon modes and with significantly anharmonic vibrations of oxygen ions between two stable positions along the line of the Cu–O–Cu bond may thus arise according to the mechanism proposed here. The appearance of such centers would also lead to the appearance of ferromagnetic clusters including one or two nearest coordination spheres of copper ions.[8] The formation of these clusters might explain the exceedingly low value, $x \simeq 0.02$, at which the antiferromagnetic order disappears from the system.[14]

We wish to thank M. V. Eremin for interest in this study and for useful discussions.

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Translated by D. Parsons