

# The labile magnetic structure of JT copper and nickel complexes in the layered oxides

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## Abstract

The structure and dynamics of magnetic centers and magnetic structures in oxides of  $A_2BO_4$  type are considered. The local and cooperative Jahn–Teller effect and the lattice perturbations are shown to determine the character of distortions of  $MeO_6$  complexes ( $Me = Cu^{2+}, Ni^{3+}$ ) in  $LaSrAl_{1-x}Me_xO_4$  and in  $La_{2-x}Sr_xCuO_4$ . The opposite character of the JT effect in  $MeO_6$  centers with copper ( $3d^9$ ) and low spin nickel ( $3d^7$ ) is demonstrated. The phenomenon of the chemical phase separation was observed in  $LaSrAl_{1-x}Me_xO_4$ . The single  $CuO_6$  centers in the Al-phase of  $LaSrAl_{1-x}Me_xO_4$  with a hole delocalized at four plane oxygens are suggested. The transformation of such centers into the relatively large magnetic centers (magnetic Jahn–Teller polarons) in the Cu-phase of  $LaSrAl_{1-x}Me_xO_4$  was investigated. The active magnetic centers and labile magnetic structures were discovered in the nonequilibrium state of magnetic system  $La_{2-x}Sr_xCuO_4$  with a very low content of  $Sr^{2+}$  ions. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Copper oxides; Chemical phase separation; Jahn–Teller dynamics; Hole centers; Magnetic JT polarons; Labile magnetic structure

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## 1. Introduction

Layered oxides  $A_2MeO_4$  ( $AA'MeO_4$  or  $A_2MeMe'O_4$ ) are of a great interest for investigation. They may be obtained from various ions A and Me with the appropriate choice of composition and size of ions in different states of oxidation. Compounds with  $Me = Cu^{2+}$  and  $Ni^{3+}$  are particularly specific. The important features of layered oxides containing copper, especially the high temperature superconductivity, result from violating the law of the charge neutrality of initial composition. Both  $Cu^{2+}$  ( $3d^9$ ) and  $Ni^{3+}$  ( $3d^7$ ) are so called Jahn–Teller ions. While the Jahn–Teller properties of copper compounds are relatively well known, the problem of JT behavior of nickel remains open. The layered oxides are also attractive due to the existence of diamagnetic compounds ( $LaSrAlO_4$ ,  $LaSrGaO_4$ ) isostructural with  $La_2CuO_4$ . This allows one to carry out the model investigation of the energy states and states of oxidation of magnetic ions, as well as symmetry, strength and dispersion of the ligand fields at these ions in structures exhibiting the high temperature superconductivity. This also permits one to study the influence of nonstoichiometry of a material on its static and dynamical properties.

We have investigated  $LaSrAl_{1-x}Me_xO_4$  solid solutions (where  $Me = Ni^{3+}$  and  $Cu^{2+}$ ) and  $La_{2-x}Sr_xCuO_4$  with very low content of  $Sr^{2+}$  using EPR as a main experimental method.

## 2. Experimental results and discussion

The  $LaSrAl_{1-x}Me_xO_4$  solid solutions were synthesized from metal oxides and also by the decomposition of nitrates [1,2]. X-ray diffraction has shown that all compositions with  $0 \leq x \leq 1$  have a  $K_2NiO_4$  structure type with the corresponding changes of unit cell parameters (Fig. 1) [3]. It is quite natural that  $Ni^{3+}$  ions substitute  $Al^{3+}$  and do not break the stoichiometry of compounds but it is not expected for two valence copper ions. Experimental data has shown that copper remained in the two-fold charge state. As a consequence, a substitution of  $Al^{3+}$  by  $Cu^{2+}$  should result in the appearance of holes in  $CuO_2$  layers as it takes place in  $La_{2-x}Sr_xCuO_4$  doped by Sr. Iodometric titration gives the average value of the copper oxidation state of  $2.46 +$  [2]. X-ray diffraction data do not support the hypothesis of  $Cu^{3+}$  ions existence [3]. As it is seen from Fig. 1, the  $c$  parameter is strongly influenced by the copper concentration (in  $LaSrAl_{1-x}Me_xO_4$ ) and for  $x = 1$  its value of  $12.97 \text{ \AA}$  virtually coincides with the value  $13.11 \text{ \AA}$  characteristic of  $La_2CuO_4$  [4], which contains elongated JT complexes of copper in the  $2 +$  oxidation state. It may be expected that the existence of  $Cu^{3+}$  in  $LaSrAl_{1-x}Me_xO_4$  (46%) should diminish the  $c$  value in the same way as in the case of  $Al^{3+}$  admixture (their ionic radii are  $0.54$  and  $0.53 \text{ \AA}$  correspondingly). Therefore, the  $2.46 +$  value for the formal oxidation state in the iodometric titration method should be explained by the hole centers appearance.

In  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$  Me ions replace  $\text{Al}^{3+}$  ions being in slightly deformed octahedra ( $\text{Al}-\text{O}$ :  $2 \times 1.97 \text{ \AA}$ ;  $4 \times 1.898 \text{ \AA}$ ). It is well known that the JT effect is responsible for the formation of  $\text{CuX}_6$  octahedra elongated along  $C_4$  axes, but there are no reliable data for the structure of JT  $\text{NiX}_6$  complex. Thus, one of the main aims of our study was to obtain comparative data about the JT effect of  $3d^7$  and  $3d^9$  ions in the layered oxides. The main results of the investigation are discussed below. It will be shown among other that the JT effect tends to compress  $\text{NiO}_6$  octahedra in oxides.

EPR has shown that two static, (1) and (2), and one dynamical (3) varieties of LS  $\text{Ni}^{3+}$  are observed in  $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$ . Dynamical centers (3) become static and distinguishable below 145 K (Fig. 2) [5]. Parameters of Spin Hamiltonian  $H = \beta(HgS)$  of these centers are:  $g_{\perp}^{(1)} = 2.235$ ;  $g_{\parallel}^{(1)} = 2.043$ ;  $g_{\perp}^{(2)} = 2.212$ ;  $g_{\parallel}^{(2)} = 2.043$ ;  $g_1^{(3)} = 2.344$ ;  $g_2^{(3)} = 2.22$ ;  $g_3^{(3)} = 2.043$ . These parameters were obtained in the course of the optimization of model spectra. The values of  $g_i$  observed for (1) and (2) centers allow us to speak about the  $|3dz^2 > \text{Ni}^{3+}$  ground state, i.e. about elongated  $\text{NiO}_6$  configuration.

For  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  the EPR signals typical for the stretched octahedra were also observed (Fig. 3 (I)):  $g_{\perp}^I = 2.069$ ;  $g_{\parallel}^I = 2.320$ ;  $A_{\perp}^I < 10 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $A_{\parallel}^I = 150 \cdot 10^{-4} \text{ cm}^{-1}$ . Besides, a new signal (II) which is a single, essentially symmetric

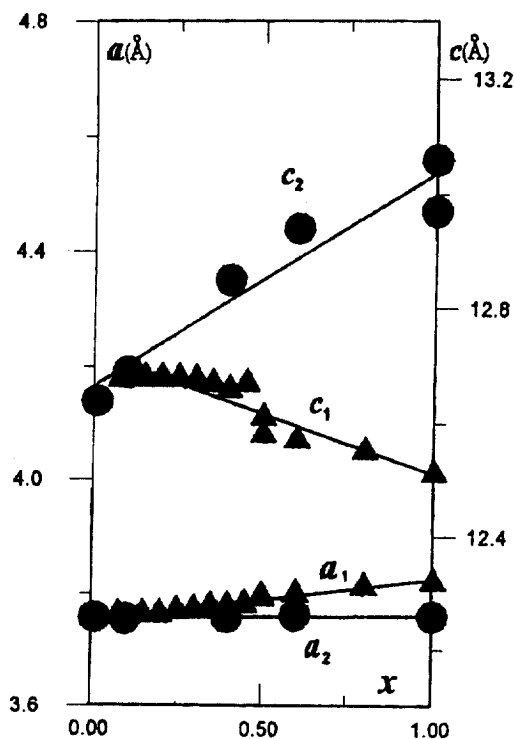


Fig. 1. Concentration dependence of  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$  lattice parameters: (1) Me = Ni; (2) Me = Cu.

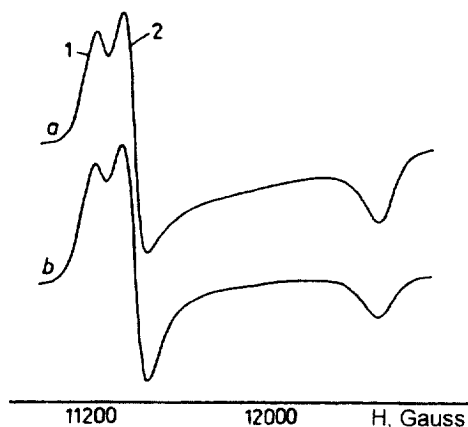


Fig. 2. EPR spectrum of  $\text{LaSrAl}_{0.90}\text{Ni}_{0.10}\text{O}_4$ ,  $T = 293$  K,  $\nu = 35.6$  GHz: (a) experimental spectrum; (b) simulated spectrum.

line with  $g^{\text{II}} = 2.123$  was detected. The temperature dependencies of signal II intensity are different for samples with  $x \leq 0.1$  (IIa) and  $x \geq 0.1$  (IIb). The intensity of signal IIb, analogously to that of signal I, increases with the decrease of temperature. The intensity of signal IIa falls abruptly below 30–40 K.

The EPR spectra yield important information about the peculiarities of the materials studied. It appears that only  $\sim 10\%$  of the introduced copper and nickel ions contribute to the observed spectra. This allows us to suggest the microphase separation of Me and Al ions in  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ , i.e. the existence of Al-phase (a microphase for high  $x$ ) in which Me ions are present and give rise to the EPR signals, and of Me-microphases not contributing to the EPR spectrum, as in the case of  $\text{LaSrNiO}_4$  and  $\text{LaSrCuO}_4$ . The EPR signal in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  is observed up to  $x = 0.8$ – $0.9$  but in  $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$  only up to  $x = 0.4$ .

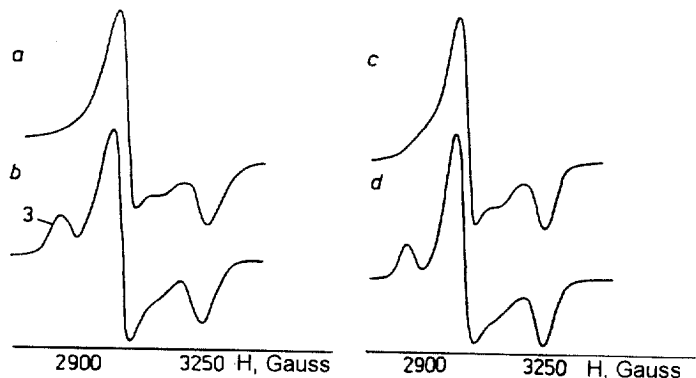


Fig. 3. EPR spectrum of  $\text{LaSrAl}_{0.90}\text{Ni}_{0.02}\text{O}_4$ ,  $\nu = 9.32$  GHz. (a) (b) experimental spectra at  $T = 250$  K and  $T = 70$  K, respectively; (c) (d) the corresponding simulated spectra.

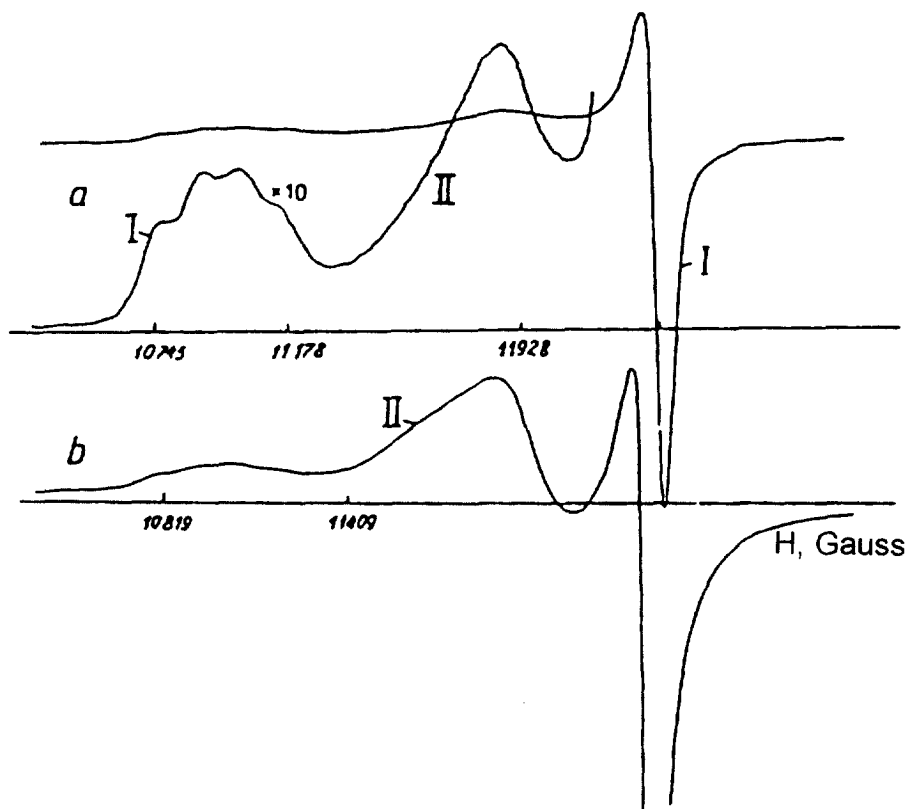


Fig. 4. EPR spectra of  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ ,  $T = 293 \text{ K}$ ;  $\nu = 35.14 \text{ GHz}$ . (a)  $x = 0.02$ ; (b)  $x = 0.10$ .

Experimental data allow us to conclude that configurations of all three center varieties observed for nickel, and two observed for copper differ from the configuration of matrix  $\text{AlO}_6$  octahedron in values of deformations and in dynamics. The observed EPR spectra may be interpreted within the frame of conception of combined influence of JT effect and relatively small lattice deformations [6]. Furthermore, some specific features are inherent in copper and nickel compounds.

The conclusion about the  $|3d_{z^2}\rangle$  ground state of  $\text{Ni}^{3+}$  ions allow us to suppose that the JT effect elongates the  $\text{NiO}_6$  octahedron. This leads to the adiabatic potential with one deep minimum at  $\varphi = 0$  and to observed EPR signals (1) and (2). But the appearance of the rhombic spectrum (3) cannot be understood in this way.

In contrast, the assumption that Ni octahedra are compressed due to the JT effect allow us to explain all experimental results. Such a conclusion allow us to describe (1) and (2) nickel centers by adiabatic potential of the  $\text{NiO}_4\text{O}_2$  complex shown on Fig. 5. Here, the circle section of the adiabatic potential surface ( $\text{Ni}^{3+}$ ,  $d\epsilon^6 d\gamma^1$ ,  $E_g$  ground state) at  $\rho = \text{constant}$  and  $0 \leq \varphi \leq 360$  is shown ( $\rho$  and  $\varphi$  are normal deformations of complex in polar coordinates).  $E_{\text{tet}}/(2\beta) \geq 12$  for varieties (1) and (2) (where  $E_{\text{tet}}$  is the splitting of the ground doublet by tetragonal

distortions and ( $2\beta$ ) is the energy barrier between the equivalent minima in the absence of deformations). The lattice deformation increases the energy of single  $|3dx^2 - y^2\rangle$  electronic configuration compressed along the  $c$  axis. However, fast transitions between two other JT configurations having smaller energy and compressed along  $a$  and  $b$ , but elongated along  $b$ ,  $a$  and  $c$  correspondingly (or the transformation of these configurations to the one with diffuse minimum at  $E/2\beta > 10$ –12; see Fig. 5) result in the observed JT configuration of  $\text{NiO}_6$  complex effectively elongated along  $[001]$  axis. The effective wave function of  $\text{NiO}_6$  complex (centers (1) and (2)) has  $3dz^2$ -symmetry. The axial spectrum is observable within the whole temperature range. For variety (3)  $E_{\text{tet}}/(2\beta) < 12$  ( $\sim 5$ –7). At low temperatures, when  $kT < 2\beta'$  ( $\beta'$  is the energy barrier between minima in deformed complex),  $\text{NiO}_6$  complexes corresponding to the center (3) are stabilized in the lowest adiabatic potential minimum. Their configuration is orthorhombic and the EPR spectra of rhombic symmetry are observed (the situation is similar to that of  $\text{Cu}^{2+}$  in a compressed octahedron). Described here, behavior of  $\text{NiO}_6$  may take place only in the case of octahedron compressed due to the JT effect.

Centers (1) and (2) are formed due to different combinations of  $\text{La}^{3+}$  and  $\text{Sr}^{2+}$  ions along the  $C_4$  axis (e.g. La–La or Sr–Sr). The centers of the third, dynamical variety, having the smallest tetragonal distortions, are attributed to the positions nearest to the interstitial oxygen ions [5] and/or possibly in the following position: interstitial oxygen plus Sr–Sr combination along  $C_4$ .

Let us now consider samples with  $\text{Cu}^{2+}$ . The single centers with EPR spectrum of type I (Fig. 4) are the  $\text{Cu}^{2+}$  ions which replace  $\text{Al}^{3+}$  ions and form  $\text{CuO}_6$  octahedra stretched out along the  $[001]$ -axis. For these centers, changes in lattice parameters and of the ligand field, due to disorder in distribution of La and Sr ions, do not influence the EPR spectra parameters. Moreover, the parameters of spectrum I are the same as those of the  $\text{Cu}^{2+}$  centers in  $\text{La}_{1+x}\text{Sr}_x\text{Ga}_{1-x}\text{Cu}_x\text{O}_4$  solid solutions [7], having another ligand field characteristics.

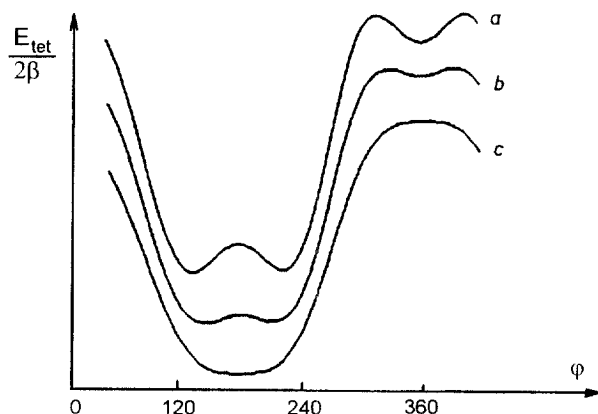


Fig. 5. Adiabatic potential of  $\text{NiO}_6$  complexes in the case of a tetragonally extended octahedron for the following values of  $E_{\text{tet}}/(2\beta)$ : (a) 5.5; (b) 7.5; (c) 12.5.

A situation of this kind is possible for  $\text{CuX}_6$  complexes, with electron–phonon coupling stronger than in  $\text{NiX}_6$  complexes, and the tetragonal component of the ligand field, in description of JT effect, which does not exceed the quadratic constant (or the anharmonic constant of ligand vibrations) by a factor of more than 3 [6,8]. In the course of investigations of copper JT compounds it was shown that such a situation takes place when distortions of the matrix positions do not exceed ‘the limit of JT distortions’ i.e. value of 0.1–0.15 Å [6,9]. As a result, the oxygen octahedron of the ground JT configuration is stretched along the direction of the main lattice deformation. The change of the tetragonal component of the ligand field leads to a change in  $\Delta E$  — separation energy between the ground and excited JT configurations, but has no effect on the extent of the distortions of the complex or on the value of  $g$ -factors in the limit of the experimental errors. The difference between the copper–oxygen distances is  $\sim 0.85 \rho$ . According to Abragam and Bleaney [10], the value of  $\rho$  for  $\text{Cu}^{2+}$  is about 0.03–0.07 Å and tetragonal lattice deformations  $\sim 0.01$  Å cause a change of  $\sim 100 \text{ cm}^{-1}$  in the energy interval between the ground and the two excited configurations. According to these estimations, which are confirmed by the data for Tutton salt type crystals [8] and according to the difference distances between Cu-axial and Cu-planar oxygen ions equal to about 0.08–0.16 Å, the average interval  $\Delta E$  in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  is about 800–1000  $\text{cm}^{-1}$ .

The conclusion that there is a strong electron–phonon coupling in the single  $\text{CuO}_6$  centers in the Al-phase of  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$  supposes that they retain their vibronic nature in the Cu-phase of this system and in all cuprates also. The cooperative JT effect can be used to explain the pronounced stretching of the  $\text{CuO}_6$  octahedron along the [001]-axis in these compounds: in  $\text{La}_2\text{CuO}_4$  the Cu–O distances are  $2 \times 2.46$  and  $4 \times 1.905$  Å; in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  they are  $2 \times 2.41$  and  $4 \times 1.89$  Å [11].

The described properties of copper cuprates correlate with the conclusion that JT effect causes the elongation of complexes with  $3d^9$  ions. The opposite effect takes place in the case of low-spin  $\text{Ni}^{3+}$  complexes, where the JT compression of free octahedra occurs. In  $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$  lattice deformations along the [001]-axis dominates this effect and the single  $\text{NiO}_6$  complexes remain elongated. However, it must be stressed that this elongation along the  $c$  axis has a JT nature differing from ordinary elongation.

Other situations occur in the samples with high Ni concentration. The cooperative interaction between  $\text{Ni}^{3+}$  ions in a Ni-microphase of  $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$  or in  $\text{LaSrNiO}_4$  stabilizes compressed JT configurations of the Ni-phase of the substances and gives rise to the change of  $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$  structural parameters which are observed in experiment and shown in Fig. 1.

Let us now discuss the nature of centers giving II type signals in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ . Radiospectroscopic and structural arguments confirm that signal II does not belong to  $\text{Cu}^{3+}$  centers. It was shown earlier [2], that the II-type EPR signal should be ascribed to the hole on the oxygen connected with the copper ion. We have suggested that the electron vacancy on an oxygen ion is not localized at a single ion but is distributed among four planar oxygens of a  $\text{CuO}_6$  octahedron. The

appearance of a hole delocalized on four planar oxygens of a  $\text{CuO}_6$  octahedron leads to a decrease of the tetragonal component of the ligand field to the point that this component changes its sign. It also leads to the appearance of the interaction between unpaired spins of  $\text{O}^-$  and  $\text{Cu}^{2+}$ . For  $|J| \sim 10^3 \text{ cm}^{-1}$ , the possible value of the exchange in oxides [12], the signal IIa can be observed only if the exchange has a ferromagnetic nature. This statement finds strong support in terms of the molecular orbital scheme of a  $\text{CuO}_4\text{O}_2$  complex. The states close in energy to MOs with  $e_g$ ,  $b_{2u}$ ,  $a_{1g}$  and  $b_{1g}$  symmetry having mainly a 3d metal orbital character are  $a_{2g}(\pi)$  or  $b_{2u}(\pi)$  nonbonding energy states of oxygens. They are built only of in-plane  $-(1/2)[p_y - p_x - p_y + p_x]$  ( $a_{2g}$ ) and of out-of-plane  $-(1/2)[p_z - p_z + p_z - p_z]$  ( $b_{2u}$ ) 2p-states of oxygen;  $a_{2g}$  and  $b_{2u}$  orbitals are written here in a  $\text{CuO}_6$  center coordinates. They are orthogonal to  $a_{1g}$  and  $b_{1g}$  MO including  $z^2$  and  $x^2 - y^2$  states of copper. Nonbonding  $a_{2g}$  and  $b_{2u}$  MOs have lower energy than the orbitals with 3d-character in free complex. However, interactions in the condensed matrix, the Modelung effect first of all, make the bands of these states nondistinguishable in energy and we believe that just the oxygen states of  $a_{2g}$  and  $b_{2u}$  types will occupy the hole in the  $\text{CuO}_6$  complex in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ . Its interaction with the  $\text{Cu}^{2+}$  unpaired electron can only be ferromagnetic. We consider the hole magnetic center  $\text{CuO}_6^-$  with  $S = 1$  in Al-phase as an experimental fact [1,8]. These centers (IIa) conserve the JT dynamical nature and their dynamics average the fine structure of the EPR spectrum at sufficiently high temperatures.

The centers giving EPR signals of type IIb ( $0.1 \leq x \leq 0.8$ ) have the same nature but another composition. Centers of IIa type ( $x < 0.1$ ) are surrounded by the  $\text{AlO}_6$  octahedra and they represent the single octahedron with a hole. At higher Cu concentrations, and due to nonstatistical distribution of Cu ions,  $\text{CuO}_6$  centers are situated in surroundings of another  $\text{CuO}_6$  octahedra. There are at least two distinctions between  $\text{CuO}_6$  with a hole in a doped diamagnetic matrix and in concentrated materials: the change of the character of the energy states of ions and the non single-center character of the hole localization. The energy levels of Cu and O ions are transformed into broad overlapping bands. In particular, this removes the distinctive features of the p-orbitals of oxygens: holes in  $\text{CuO}_2$  layers occupy the orbitals of p- $\sigma$  type and this result in antiferromagnetic character of hole spin-copper spin interaction with  $S = 0$  [13,14]. It is important to emphasize however, that the conclusion about change of spin state character of the  $\text{CuO}_6^-$  center does not affect the conclusion about the ligand field and vibronic nature of the states of the  $\text{CuO}_6$  with the hole though its dynamics become of more complicate character. When its main JT deformations lie in the *ab* plane, antiferrodistortional ferromagnetic cluster including some (at least one or two) coordination spheres of copper ions arises (Fig. 6). It was recognized as magnetic JT polaron (MJTP) and considered in more detail in [15].

The question concerning the existence of MJTP is connected with the effective size of the field of delocalization of the hole in  $\text{CuO}_2$  layers. It was shown in Usachev et al. [3] that a size of this field (let name it 'the field of the hole delocalization', FHDL) essentially depends on several easily controlled factors, such as a position in the structure, concentration and nature of the hole producing

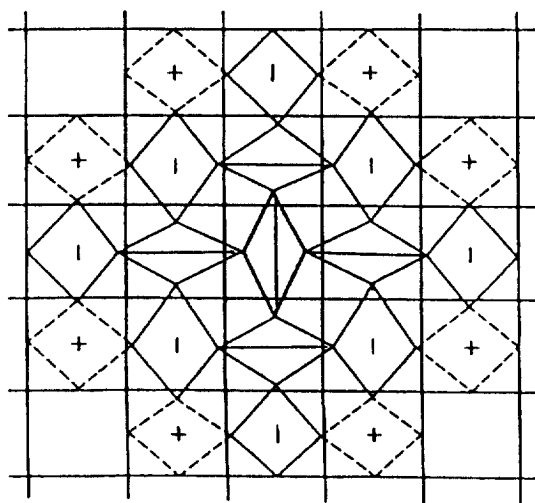


Fig. 6. Deformations of the  $\text{CuO}_2$  plane fragment caused by JT-distortions of the  $\text{CuO}_6$ -center (shown in bold lines in the center of the figure). 'Splash- photo' of magnetic JT-polaron.

element. One may consider, for example,  $\text{Cu}^{2+}$  in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  as such an element, and in the same manner  $\text{Sr}^{2+}$  and  $\text{Cu}^{2+}$  in  $\text{LaSrCuO}_4$  and also interstitial oxygen in all layered oxides. Taking into account the discrete distribution of charges in the real structure and in analytical models, and keeping in mind that an energy of interaction of the hole and hole-producing element is different for holes delocalized on the different coordination spheres, it is not difficult to imagine that FHDL may depend on temperature [3]. In the frame of such simple phenomenological considerations it is easy to understand, for example, the semiconducting character of conductivity in  $\text{LaSrCuO}_4$  — the substance with very high concentration of hole-producing elements and the appearance of metallic conductivity in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  at 6% of Sr only. In the first case FHDL is of the order  $\leq a$  and it is necessary to overcome the energy barrier  $\sim 30\text{--}50\text{ cm}^{-1}$  to combine FHDL in continuous percolating chains and conductivity becomes a metallic one. In the second case FHDL is of order of  $(3.6\text{--}3.8)a$  and the Sr concentration of 6% is enough for the existence of percolative chains.

It was found in Yablokov et al. [15] that the quantity of IIb type centers increases at first with the increase of  $x$ , then decreases quickly, always being small with respect to Cu concentration. It may seem strange that a concentration of holes should be large and should increase proportionally with the Cu content (let us remember that the average copper oxidation state is equal to 2.46 according to iodometric titration). But it is not surprising indeed.

The reasons for the low content of ferromagnetic structures stipulated by the nature of these structures themselves. Due to the equivalency of the copper position a finite probability of a hole jump on another  $\text{CuO}_6$  center exists. Migrating along the layer, the hole wanders together with lattice deformations having both electro-

static and vibronic origin. Colliding with another JT cluster, or coagulating with the copper agglomerates with the holes in 2-p band, magnetic JT polarons are transformed and do not show EPR signal. As for the observable ferromagnetic clusters, they are situated in the fields with the hard conditions of diffusion (for example, the fields where  $\text{Sr}^{2+}$  ions are surrounded by the  $\text{La}^{3+}$  ions) or are combined with the structure defects of another nature. In general, any structure defect suppressing dynamics of its central fragment prevent a movement of the polaron. For example, the perturbations of the microphase boundaries and crystallites are the systematical ones. Creating the axis component of the ligand field directed along the plane Cu–O bonds, the boundary defect distinguishes one of adiabatic potential minimums of JT fragment and localizes the magnetic JT polaron.

The uniform nature of  $\text{CuO}_6$  JT centers in all cuprates with a  $\text{K}_2\text{NiF}_4$  type structure allows us to project the phenomena observed in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  on the processes taking place in the hole doped  $\text{La}_2\text{CuO}_4$ . In this respect one of the main problems deals with a better understanding of the phenomena accompanying the transformation from dielectric antiferromagnet  $\text{La}_2\text{CuO}_4$  into the high-temperature superconductor in the process of the hole doping.

To approach this problem the ceramic cuprates  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with very low content of Sr ( $0 < x < 0.011$ ) were studied by EPR in the temperature range 4.2–300 K [16]. ‘As prepared’ samples and the samples annealed at  $T = 650^\circ\text{C}$  in vacuum of  $10^{-5}$  mmHg were measured. Several new and rather unexpected magnetic centers and labile magnetic structures were observed.

A relatively weak EPR signal consisting of two contributions from two types of centers (Fig. 7): the tetragonal signal with  $g_{\parallel} = 2.31$  and  $g_{\perp} = 2.07$  (AI) and the isotropic signal with  $g = 2.13$ – $2.14$  (AII) was observed. The A-type centers were presented in all samples of the two series prepared from oxides and partly in the third series synthesized by nitrates decomposition. Fig. 7 also shows the temperature variation of the EPR signal intensity for the sample with  $x = 0.002$ . When the temperature increases from 4.2 to 20 K the signal intensity decreases following Boltzman law. Then, between 20–25 K the abrupt fall in intensity takes place and, after that, the intensity practically does not change up to 70 K. During the second cooling, the signal intensity follows Boltzman law and no anomaly was observed, but the intensity at 10 K was about half of the initial value. This means that part of the centers vanish during the first heating (after the first cooling), and do not recover during the second cooling. A similar picture was observed for the ‘as prepared’ samples of other compositions ( $x = 0.0009, 0.002, 0.005, 0.008$  and  $0.011$ ). Keeping in mind that signal A consists of the two signals, we may suggest that a similar and very specific temperature dependence of these EPR signals intensity allows us to draw conclusions about the conditions of these ‘pair’ centers existence, their appearance (‘birth’) and ‘annihilation’.

The AI signals have parameters coinciding with those for  $\text{CuO}_6$  in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ . They may be considered as belonging to the centers located in domains with destroyed antiferromagnetic ordering. We attribute these detectable ‘defects’ to the grains, or domains boundaries. The parameters and the form of signal AII reproduce this characteristic of analogous signals in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  (Fig. 8) and

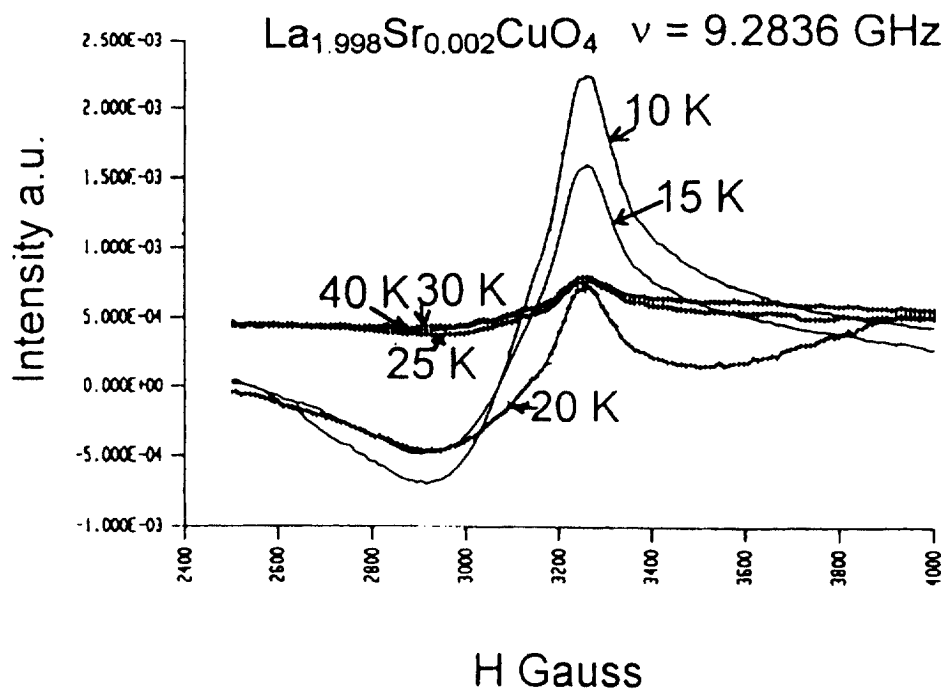


Fig. 7. The temperature behavior of EPR spectrum of a  $\text{La}_{1.998}\text{Sr}_{0.002}\text{CuO}_{4+\delta}$  sample.

we believe that they should be attributed to the clusters with holes of the same nature as magnetic JT polarons in  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ .

It seems that these hole magnetic clusters are localized in the same region as the centers AI. The tendency of combining such clusters in  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$  has been

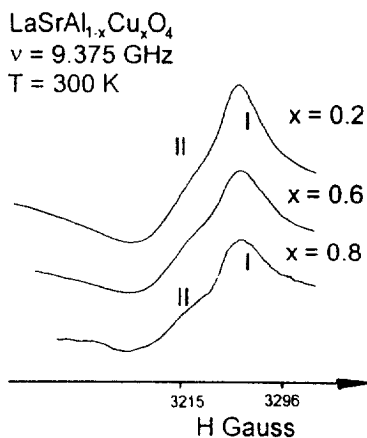


Fig. 8. EPR spectra of  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$  with  $x = 0.2$ ;  $0.6$  and  $0.8$  at  $T = 300 \text{ K}$ .

discussed [15]. This is the way we attribute them to the domain boundaries, having the intermediate character between domains with the long range order and the regions where it is absent. These data show that some of these hole clusters may couple with the localized AI centers (and become not visible by EPR).

Temperature dependence of A type signals (Fig. 7) demonstrates that interaction of AI and AII centers may be temperature dependent. This is based on the considerations of temperature dependence of the hole delocalization field in JT cuprates. The intrinsic reasons for this fact can be explained in terms of the influence of nature, position and local concentration of the host atoms (Sr and/or O) on the shape of the potential surface created by La ions. The process of combining centers seems to be initiated by dynamics of clusters having the nature of MJTP. This approach allows us to understand all peculiarities shown by A type signals and to characterize their transformations.

### 3. Conclusions

The investigations summarized above show that the model compounds  $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$  and cuprates  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  have some very important common features. Firstly, one should emphasize the JT nature of  $\text{MeO}_6$  centers and appearance of the hole centers in compositions with the disturbed charge stoichiometry.

These are JT effects which determine the behavior of the isolated  $\text{MeO}_6$  centers in matrix and the structure parameters of the cooperative systems. For the complexes with  $3d^9$ - and  $3d^7$ -electron configurations JT deformations have a different character. As a result, the cooperative JT interactions essentially increase the weak lattice stretching of the  $\text{MeO}_6$  octahedra in the copper compounds and suppress them in the nickel ones.

The hole  $\text{CuO}_6^-$  centers exist in the Al-phase of  $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ . An analysis of the transformations of these centers into the large ferromagnetic clusters in cuprates and the determination of the conditions of such cluster existence have allowed the direct observation of their annihilation. This shows the possibility of detailed investigation of the initial processes leading to the destruction of the ordered antiferromagnet in the cuprates with a very low hole concentration. On this basis, the investigation of the nonequilibrium spin glass state seems to be possible.

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