

DYNAMICS OF JAHN–TELLER IONS IN LAYERED OXIDES

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Abstract. The EPR investigation of $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ ($\text{Me}=\text{Ni}^{3+}$ and Cu^{2+}) solid solutions was carried out. The subjects of investigation were the energy states of magnetic ions, the symmetry, strength and dispersion of crystal fields on Me ions and the effect of nonstoichiometry of materials. A JT nature of NiO_6 and CuO_6 centres was proved. Dynamic JT NiO_6 centres were determined in the samples containing interstitial oxygen. New-type dynamic centres ($\text{CuO}_6 = \text{CuO}_6 + \text{electron hole localized on four planar oxygens}$) were discovered. The local and cooperative properties of $\text{La}_{1-y}\text{Sr}_y\text{Al}_{1-x}\text{Cu}_x\text{O}_4$ ceramics were discussed.

Key words: Jahn–Teller effect, MeO_6 dynamics, hole + CuO_6 centre, magnetic polaron.

INTRODUCTION

Layered oxides of K_2NiF_4 type (A_2BX_4 or $\text{AA}'\text{BX}_4$) have some interesting peculiarities. They can be obtained by choosing suitable compositions and sizes of ions in different valence states [1]. In such oxides it is possible to investigate, for example, different Jahn–Teller (JT) ions in a related situation. Another attractive peculiarity of layered oxides lies in the existence of diamagnetic compounds (LaSrAlO_4 , LaSrGaO_4) among them, which are isostructural with some high- T_c superconductors. This circumstance allows the model investigations of energy states and states of oxidation of magnetic ions, the symmetry, strength and dispersion of the crystal fields on these ions in potentially superconducting structures [2–4]. This permits also to study the influence of nonstoichiometry of a material on its properties [5].

We have investigated the solid solutions of $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$, where $\text{Me}=\text{Ni}^{3+}$ and Cu^{2+} . EPR was used as a main experimental method. The following aspects are accented:

1. The reaction of $3d^7$ and $3d^9$ JT ions on the "quantized" or the distributed deformations of the crystal fields at a B position.

2. JT properties of Ni^{3+} and Cu^{2+} ions in layered oxides; the conditions of their dynamical behaviour.

3. A discussion of the new centres discovered in $\text{LaSr}_{1-x}\text{Cu}_x\text{O}_4$ [5]; an analysis of the fitness of the suggested centre model (CuO_4O_2 + a hole localized on four planar oxygens).

4. Local and cooperative properties of a $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ ceramic; their transformation on the changes of the composition to the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ one.

EXPERIMENTAL RESULTS

The $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ solid solutions were synthesized by the decomposition of nitrates. The procedure and conditions of the synthesis have been described in [3].

Nickel ions enter the matrix in threefold-charged states and they do not distort the stoichiometry of compounds. We have not observed any peculiarities connected with the possible presence of Ni^{2+} ions. The structure of solid solutions is of a K_2NiF_4 type at various values of x , as it has been shown by X-ray diffractions. The unit cell parameters a and c change from 3.763 Å and 12.74 Å for $x=0.08$ to 3.82 Å and 12.51 Å for $x=1$.

It has been determined that the same type of structure is realized also when Al^{3+} ions are replaced by copper ions. The X-ray diffraction data are shown in Fig. 1. With the increase of the concentration of copper ions the lattice constant c increases, while a practically does not change. Two varieties of the structure are observed at $x=1$ only, but they both belong to the K_2NiF_4 type.

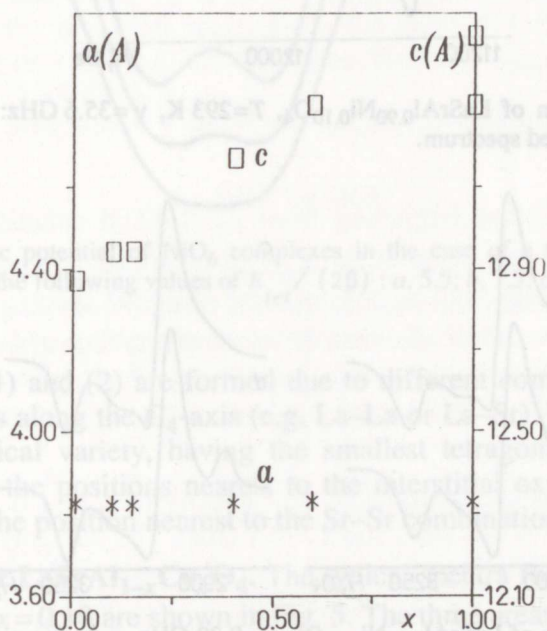


Fig. 1. Concentration dependence of $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ lattice constants.

EPR spectra were recorded on an ERS-230 rf spectrometer over the temperature range of 4–300 K at the frequencies $\nu_1 = 9.3$ GHz (the X band) and $\nu_2 = 35.9$ GHz (the Q band).

The data for $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$. Ni^{3+} centres in a low-spin (LS, $3d\epsilon^6 d\gamma^1$) state and in a high-spin (HS, $3d\epsilon^5 d\gamma^2$) state have been observed [2]. Two static varieties, (1) and (2), of Ni^{3+} were found (Fig. 2). A third variety (3) was also discovered at the temperatures $T < 145$ K (Fig. 3), which was attributed to a dynamic NiO_6 centre. The parameters of the spin Hamiltonian,

$$\mathcal{H} = \beta (H \cdot g \cdot S),$$

are: $g_{\perp}^{(1)} = 2.235$; $g_{\parallel}^{(1)} = 2.043$; $K^{(1)} = 0.28$; $g_{\perp}^{(2)} = 2.212$; $g_{\parallel}^{(2)} = 2.043$; $K^{(2)} = 0.23$; $g_1^{(3)} = 2.344$; $g_2^{(3)} = 2.22$; $g_3^{(3)} = 2.043$; $K^{(3)} = 0.49$. Here $K^{(i)}$ are the weight factors in the sum of spectra (1), (2), and (3) ($K^{(1)} + K^{(2)} + K^{(3)} = 1$). These parameter values were found through a procedure of the optimization of model spectra.

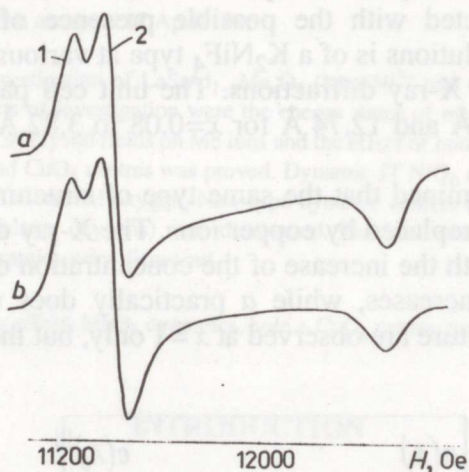


Fig. 2. EPR spectrum of $\text{LaSrAl}_{0.90}\text{Ni}_{0.10}\text{O}_4$, $T = 293$ K, $\nu = 35.6$ GHz: *a*, experimental spectrum; *b*, simulated spectrum.

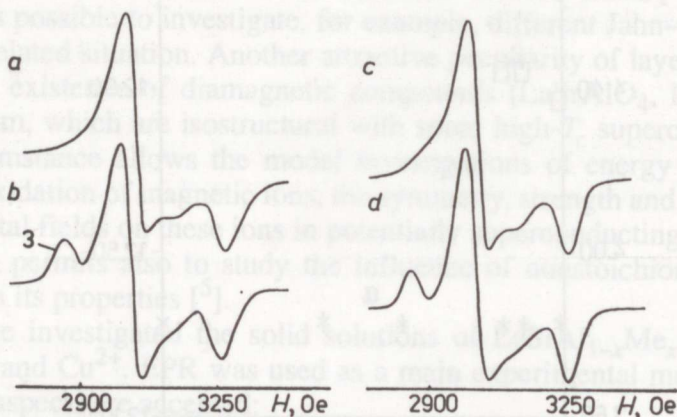


Fig. 3. EPR spectrum of $\text{LaSrAl}_{0.98}\text{Ni}_{0.02}\text{O}_4$, $\nu = 9.32$ GHz. *a*, *b*, experimental spectra at $T = 250$ K and $T = 70$ K, respectively; *c*, *d*, the corresponding simulated spectra.

These data allow a conclusion that all the three varieties observed are the JT ones. By using this term we mean that the deformation values of NiO_6 , or more exactly, NiO_4O_2 centres, are determined by an inner, JT mechanism. The characteristic deformations themselves depend on the value of perturbing lattice deformations.

Within the frame of such concepts, the observed EPR spectra show unambiguously that such combination of crystal fields and JT deformations is realized in the samples investigated, which leads to the adiabatic potential of the NiO_4O_2 complex shown in Fig. 4. Here the circle section of the adiabatic potential surface (Ni^{3+} , $d\epsilon_6 d\gamma_1$, E_g ground state) at $\rho = \text{const}$ and $0 \leq \varphi \leq 360^\circ$ is shown. $E_{tet}/(2\beta) > 12$ for varieties (1) and (2). Here E_{tet} is the splitting of the ground doublet by tetragonal distortions (stretching of the octahedron along the C_4 -axis) and (2β) is the energy barrier height between the equivalent minima in the absence of deformations. The adiabatic potential is a single valley and the axial spectrum is observable within the whole temperature interval. For variety (3) $E_{tet}/(2\beta) < 12$. NiO_6 complexes are stabilized in adiabatic potential minima; their configuration is a rhombic one and the EPR spectra of rhombic symmetry are observable (the situation is analogous to that of a Cu^{2+} in a compressed octahedron [6]).

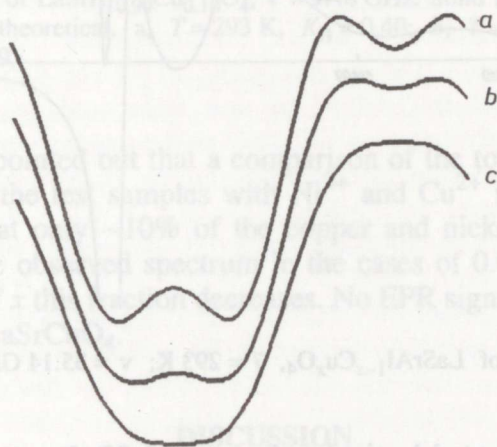


Fig. 4. Adiabatic potential of NiO_6 complexes in the case of a tetragonally extended octahedron for the following values of $E_{tet}/(2\beta)$: a, 5.5; b, 7.5; c, 12.5.

Centres (1) and (2) are formed due to different combinations of La^{2+} and Sr^{2+} ions along the C_4 -axis (e.g. La-La or La-Sr). The centres of the third dynamical variety, having the smallest tetragonal distortions, are attributed to the positions nearest to the interstitial oxygen ions [4] and, possibly, to the position nearest to the Sr-Sr combination along C_4 .

The data for $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$. The typical spectra for the samples with $x=0.02$ and $x=0.10$ are shown in Fig. 5. The three areas of concentrations may be distinguished by the types of the spectra observable. At small

concentrations ($x \leq 0.01$) only one signal is observable (signal I). Signal I is observable for all values of x up to $x \sim 0.6$. This signal is typical of isolated Cu^{2+} centres and can be described by a spin Hamiltonian of axial symmetry with the parameter values $g_{\parallel}^{\text{I}} = 2.320 \pm 0.002$; $g_{\perp}^{\text{I}} = 2.069 \pm 0.003$; $A_{\parallel}^{\text{I}} = (150 \pm 1) \times 10^{-4} \text{cm}^{-1}$ (the hyperfine structure is resolved at $x \leq 0.10$) and $A_{\perp}^{\text{I}} < 10 \times 10^{-4} \text{cm}^{-1}$. The intensity of signal I is a nonmonotonic function of x , going through a maximum at $x = 0.04$. In the case of an equiprobable distribution of isolated centres, the highest number of these centres would correspond to $x \cong 0.08$.

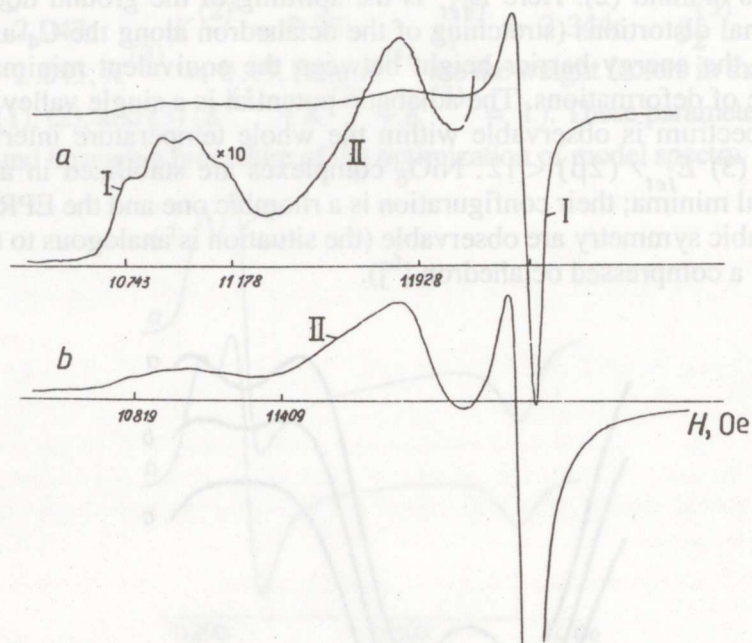


Fig. 5. EPR spectra of $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$, $T = 293 \text{ K}$; $\nu = 35.14 \text{ GHz}$. *a*, $x = 0.02$; *b*, $x = 0.10$.

Signal II is detected beginning from $x \geq 0.02$. It consists of a single, essentially symmetric line with $g^{\text{II}} = 2.123 \pm 0.003$. These parameter values were found through an optimization of model spectra. In the course of the modelling we also calculated the relative contents of I and II centres, i.e. K_{I} and K_{II} ($K_{\text{I}} + K_{\text{II}} = 1$). The parameters g_i , A_i , g^{II} are essentially independent of x and T . The relative content of II centres increases with the increasing of x .

The temperature dependence of the intensity of signal II is different in the samples with $x \leq 0.1$ (IIa) and $x > 0.1$ (IIb). The intensity of signal IIb, like that of signal I, increases with the decreasing of temperature. At $x = 0.4$, for example, we have $K_{\text{II}}(293 \text{ K}) = 0.61$ and $K_{\text{II}}(4.2 \text{ K}) = 0.68$. In other words, these results are the same within the errors of estimates.

The intensity of signal IIa falls sharply below 30–40 K: at $x = 0.10$ we have $K_{II}(> 30 \text{ K}) \cong 0.41$ and $K_{II}(4.2 \text{ K}) = 0.09$ (Fig. 6). Centres IIa are predominant at $x > 0.1$.

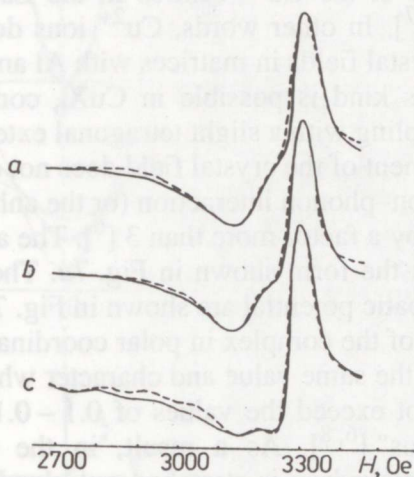


Fig. 6. EPR spectra of $\text{LaSrAl}_{0.90}\text{Cu}_{0.10}\text{O}_4$, $\nu = 9.48 \text{ GHz}$. Solid lines — experimental; dashed lines — theoretical. a, $T = 293 \text{ K}$, $K_{II} = 0.40$; b, $T = 30 \text{ K}$, $K_{II} = 0.39$; c, $T = 4.2 \text{ K}$, $K_{II} = 0.09$.

It should be pointed out that a comparison of the total intensity of the EPR spectra of the test samples with Ni^{3+} and Cu^{2+} ions with standard ones showed that only $\sim 10\%$ of the copper and nickel ions introduced contribute to the observed spectrum in the cases of $0.01 \leq x \leq 0.1$. With the increasing of x this fraction decreases. No EPR signals are observed in LaSrNiO_4 and LaSrCuO_4 .

DISCUSSION

The origin of signals (1), (2), and (3) of low-spin Ni^{3+} ions has been described in detail in [2–4] and partly in the previous chapter. Thus here we will concentrate our attention to ceramics with $\text{Cu}(\text{II})$.

The results described suggest the following models for centres I and II. The single centres of type I are Cu^{2+} ions which replace Al^{3+} ions and which form CuO_6 octahedra stretched out along the [001]-axis. It is interesting that for these centres the change in lattice constants, within certain limits, does not result in the changes in the parameters of EPR spectra:

- There is no essential concentration dependence of g factors, when x increases and the lattice constants a and c are varied.

- There are no types of centres which are clearly observable in the system with Ni^{3+} and which could be associated with the change in the tetragonal component of the crystal field for various combinations of the La and Sr ions along the [001]-axis [²⁻⁴].
- The parameters of spectra I are the same, within the experimental errors, as those of the Cu^{2+} centres in the $\text{La}_{1+x}\text{Sr}_{1-x}\text{Ga}_{1-x}\text{Cu}_x\text{O}_4$ solid solution [⁷]. In other words, Cu^{2+} ions do not feel difference between the crystal fields in matrices with Al and Ga.

A situation of this kind 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 ligand vibrations) by a factor more than 3 [⁶]. The adiabatic potential of the complex has then the form shown in Fig. 7a. The distortions at each minimum of the adiabatic potential are shown in Fig. 7c (here ρ and φ are normal deformations of the complex in polar coordinates) and they can be considered as having the same value and character when distortions of the matrix position do not exceed the values of 0.1 – 0.15 Å – "the limit of Jahn-Teller distortions" [^{6, 8}]. As a result, in the main configuration ($\varphi = 0$) the oxygen octahedron is stretched out along the z-axis, and the change in the tetragonal component of the crystal field leads to a change in ΔE alone, having no essential effect on the extent of the distortions of the complex or the value of g factors. The difference between the copper-oxygen distances is $\sim 0.85 \rho$. According to [⁹], the values of ρ for Cu^{2+} lie in the interval 0.03 – 0.07 Å, and tetragonal lattice deformations ~ 0.01 Å cause a change of $\sim 100 \text{ cm}^{-1}$ in the energy interval ΔE between the ground and the two excited configurations. According to our estimates, the average interval in $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ is $\Delta E \sim 800 \text{ cm}^{-1}$, and the difference between the distances of axial and planar oxygen ions in the matrix is 0.08 – 0.16 Å.

CuO_6 complexes are thus Jahn-Teller complexes. In other words, the nature of their distortions is determined by internal vibronic forces, and the lattice perturbations are manifested primarily in the particulars of the dynamics of these complexes. The conclusion that there is a strong electron-phonon coupling in $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ presupposes that they remain of a vibronic nature in the cuprates $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. 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 2×2.46 Å and 4×1.905 Å; in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ they are 2×2.41 Å and 4×1.89 Å [¹⁰].

Let us consider the nature of type II signals. Trying to understand it, we had to keep in mind that it is a single signal with a symmetric form. The corresponding centres arise because of electron defects in the $\text{Al}_{1-x}\text{Cu}_x\text{O}_2$ layer. The requirement of charge neutrality of the compound $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ presupposes that, along with copper ions in the stable oxidation state of Cu^{2+} , there exist some Cu^{3+} ions, some oxygen O^- ions and possibly some oxygen vacancies.

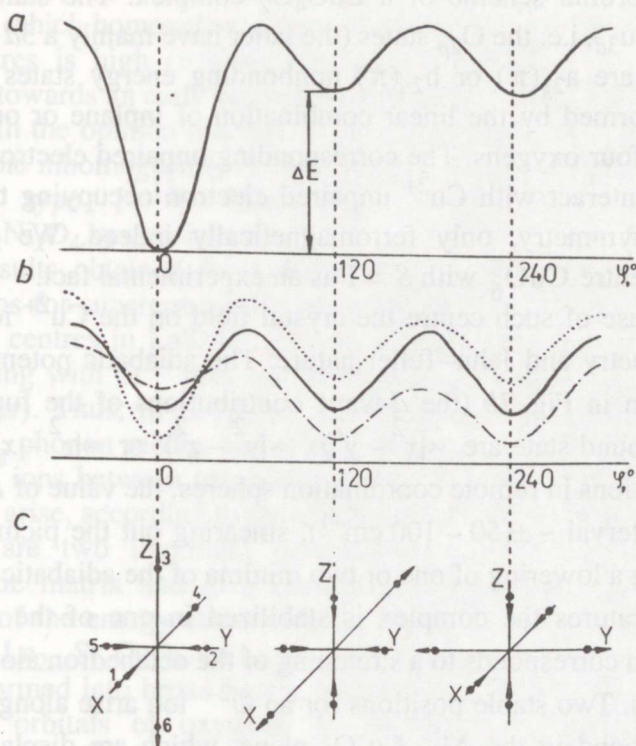


Fig. 7. Adiabatic potential of CuO_6 complexes in the cases of (a) a tetragonally extended octahedron, (b) an octahedron deformed by the hole delocalized on four-plane oxygen ions, and (c) distortions of the complex at the corresponding minima of the adiabatic potential.

Signal II does not belong to Cu^{3+} ions. They have $S = 1$ in the high-spin state, but the position of cubic symmetry is absent in LaSrAlO_4 . This signal cannot be connected with oxygen vacancies. In this case there would be some CuO_5 configuration and a strongly anisotropic EPR spectrum. What remains is the O^- centres. At the same time, one has to conclude that such vacancy of an electron should be connected by some way with a Cu^{2+} ion, as only in such a case the value of $g = 2.123$ would be understandable. There are no other ions with a sufficiently large value of a spin-orbit coupling parameter in the matrix under consideration.

We suggest that the electron vacancy on an oxygen ion is not localized on a single ion but is distributed among four planar oxygens of a CuO_6 octahedron. The appearance of a "hole" localized on four planar oxygens of a CuO_6 octahedron leads to a decrease of the tetragonal component of the crystal field to the point that this component changes its sign. It also leads to the appearance of spin-spin interaction between unpaired O^- and Cu^{2+} electrons. In the case of $|J| \sim 10^3 \text{ cm}^{-1}$, the possible value of the exchange in oxides [11], signal IIa can be observed only if the exchange is of a ferromagnetic nature. This statement finds strong support in the

molecular orbital scheme of a CuO_4O_2 complex. The states nearest in energy to Cu_{3d} , i.e. the O_{2p} states (the latter have mainly a $3d$ metal orbital character), are $a_{2g}(\pi)$ or $b_{2u}(\pi)$ nonbonding energy states of oxygens. They are formed by the linear combination of inplane or out-of-plane p orbitals of four oxygens. The corresponding unpaired electron situated on them will interact with Cu^{2+} unpaired electron occupying the orbital of $|x^2 - y^2\rangle$ symmetry, only ferromagnetically indeed. We consider the magnetic centre CuO_6^- with $S = 1$ as an experimental fact.

In the case of such centre the crystal field on the Cu^{2+} ion retains its axial symmetry and Jahn–Teller nature. The adiabatic potential takes the form shown in Fig. 7b (the d -wave contributions of the function of the electron 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 the interval $\sim \pm(50 - 100 \text{ cm}^{-1})$, smearing out the picture in Fig. 7b and causing a lowering of 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 $\langle 100 \rangle$ -axes. Two stable positions for an O^{2-} ion arise along each axis of the Cu–O bond in the $\text{Al}_{1-x}\text{Cu}_x\text{O}_2$ plane, which are displaced by $0.2 - 0.4 \text{ \AA}$ with respect to the centre. In this case the EPR spectrum has large anisotropy and cannot be detected in powder samples. As the temperature rises, the complex migrates between the minima of the adiabatic potential. At a jump frequency $\nu > D/\hbar$, $\Delta g\beta A/\hbar$, 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 of frequencies $\sim 10^7 \text{ Hz}$, above a certain temperature the system is delocalized between these positions.

Signals of type IIb ($0.1 \leq x \leq 0.8$), whose intensity increases all the way to the temperature of 4.2 K , are of exchange origin. They arise from an exchange narrowing of the spectra: 1) of the single centre of type IIa, in which the Jahn–Teller dynamics is suppressed by interaction through the field of phonons [12]; 2) of ferromagnetic antiferrodistortion dimers of the IIa–IIa or IIa–I type [12], with g and D tensors having axes in different directions; and 3) of multicentre ferromagnetic clusters including Cu^{2+} , Cu^{3+} , and O^- . It is important to note that the participation of IIa vibronic centres is necessary in all cases.

Centres producing no EPR signal in ceramic $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ may 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; $\text{Cu}^{2+}\text{-Cu}^{2+}$ or $\text{Cu}^{3+}\text{-Cu}^{3+}$ dimers or conglomerates of centres in which homovalent copper ions are predominant. The number of such centres is high ($>90\%$) even at small values of x , indicating a tendency towards an early clustering of copper octahedra. This conclusion agrees with the opinion reached at by several investigators that there is a microscopic inhomogeneity of this type in materials belonging to a single structural type [2, 13]. Everything mentioned here holds for $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$ system as well.

The results obtained for $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ allow one to make some conclusions for superconducting materials. The distortions and dynamics of the IIa centres in $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ and 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). Thus, in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ centres with a strong coupling through e_g phonon modes and with significantly nonharmonic vibrations of oxygen ions between two stable positions along the line of Cu-O-Cu bond may arise, according to the mechanism proposed here.

There are two important distinctions between CuO_6 in a doped diamagnetic matrix and in a concentrated material: the change of the character of the energy states of ions and the nonlocal character of hole centres in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. In La_2CuO_4 the energy levels of Cu and O ions are transformed into broad bands. In particular, it removes the specificity of the p orbitals of oxygens. In the frame of high-energy X-ray spectroscopy it has been shown [14] that the holes in CuO_2 layers are situated in the states of the oxygens' $2p$ band and they occupy the corresponding orbitals of $p\text{-}\sigma$ or inplane $p\text{-}\pi$ types. This conclusion confirms the succession of the properties of the CuO_6 centre in high- T_c superconductors, but does not exclude the change of magnetic states of these centres (the interaction of a Cu^{2+} unpaired electron in $|x^2 - y^2\rangle$ state with a hole in the orbital consisting of the $p\text{-}\sigma$ orbitals of oxygens is of an antiferromagnetic character with $S=0$ for the ground state). In both cases the Jahn-Teller nature of the centres and their dynamics is preserved. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ the dynamics of CuO_6 becomes undoubtedly of a more complicated character. The dynamics of oxygens in the layer arises now due to both JT properties of CuO_6 and the jumps of holes from one copper ion to another. It leads to at least two important effects: the appearance of a so-called "breathing mode" of oxygen vibrations in CuO_2 and the shortening of Cu-O distances along the c -axis (shortening of the c parameter of the unit cell).

The appearance of CuO_6 centres will also lead to the appearance of ferromagnetic clusters including one or two nearest coordination spheres of copper ions [12]. The total magnetic moment of such cluster depends on the spin state of CuO_6 ($S=1$ or $S=0$), but the latter one does not change the ferromagnetic nature of the cluster (Fig. 8). The formation of these clusters may explain the exceedingly low value, $x \approx 0.02$, at which the antiferromagnetic order of the system disappears [11]. The clusters themselves represent a certain variety of the magnetic polaron suggested in [15].

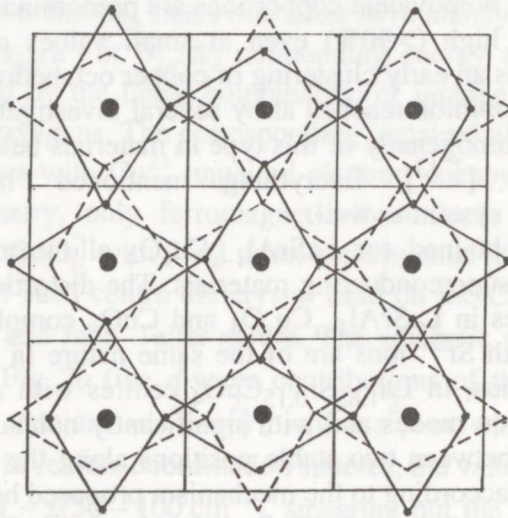


Fig. 8. Structure of a ferromagnetic cluster in a CuO_2 layer.

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JAHNI–TELLERI IOONIDE DÜNAAMIKA KIHILISTES OKSIIDIDES

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On tehtud tahkete lahuste $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ ($\text{Me} = \text{Ni}^{3+}, \text{Cu}^{2+}$) EPR-uuringud. Uurimisobjektiks olid magnetiliste ioonide energiaseisundid, kristallivälja sümmeetria, tugevus ja dispersioon Me ioonil ning materjalide mittetõhhiomeetrilise mõju. On tõestatud, et NiO_6 ja CuO_6 tsentrid on Jahni–Telleri tüüpi, ning leitud NiO_6 dünaamilised Jahni–Telleri tsentrid interstitsiaalse hapnikuga katsekehades. $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ -s on leitud uut tüüpi dünaamilised tsentrid: $\text{CuO}_6^- = \text{CuO}_6 + \text{elektronauk}$ tasandi neljal hapnikul. Arutletud on $\text{La}_{1-y}\text{Sr}_y\text{Al}_{1-x}\text{Cu}_x\text{O}_4$ lokaalsete ja kooperatiivsete omaduste üle.

ДИНАМИКА ЯН–ТЕЛЛЕРОВСКИХ ИОНОВ В СЛОИСТЫХ ОКСИДАХ

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Выполнено исследование ЭПР твердых растворов $\text{LaSrAl}_{1-x}\text{Me}_x\text{O}_4$ ($\text{Me} = \text{Ni}^{3+}, \text{Cu}^{2+}$). Предметом исследования служили энергетические состояния магнитных ионов, симметрия, сила и разброс кристаллических полей на ионе Me и влияние нестехиометрии материалов. Доказана ян–теллеровская природа статических центров NiO_6 и CuO_6 . Обнаружены динамические ян–теллеровские центры NiO_6 в образцах, содержащих интерстиционный кислород. Установлен новый тип динамических центров в $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_4$ ($\text{CuO}_6^- = \text{CuO}_6 + \text{электронная дырка}$ на четырех плоскостных кислородах). Обсуждены локальные и кооперативные свойства $\text{La}_{1-y}\text{Sr}_y\text{Al}_{1-x}\text{Cu}_x\text{O}_4$.