

# Peculiarities of magnetic ordering in the system $\text{La}_2(\text{Cu}_{1-x}\text{T}_x)\text{O}_4$ (T = Zn, Ni) according to $^{139}\text{La}$ NQR data

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Systems of the type  $\text{La}_2(\text{Cu}_{1-x}\text{T}_x)\text{O}_4$  (T = Zn, Ni) were investigated by the method of NQR on  $^{139}\text{La}$ . It was observed that, just as in lanthanum-strontium superconductors, doping with Zn leads to the appearance of local magnetic complexes. A transition into a new "intermediate" magnetic phase was observed at concentrations  $\text{Ni} \geq 5\%$ .

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The effective internal magnetic fields and the character of the interaction between the magnetic copper ions ( $\text{Cu}^{2+}$ ) in the  $\text{CuO}_2$  copper-oxygen planes play the determining role in explaining the unique magnetic properties of compounds based on lanthanum cuprate. It has now been established that a strong anisotropic antiferromagnetic (AFM) exchange interaction with exchange interaction constant  $J \sim 1000$  K exists between the moments of the copper ions ( $S = 1/2$ ) in the  $\text{CuO}_2$  planes; the interplanar exchange is equal to  $3.7 \times 10^{-5}$  times the intraplanar exchange.<sup>1</sup> The weak symmetric anisotropic exchange and the antisymmetric Dzyaloshinskiĭ exchange give rise to an easy-plane "checkerboard" noncollinear AFM structure in which the spins are ordered in the basal plane along the axis of the crystal with small cants in the  $bc$  plane.<sup>2-4</sup> One of the effective methods for investigating the antiferromagnetism of the  $\text{CuO}_2$  planes in compounds of the type  $\text{La}_2\text{CuO}_4$  is to replace the copper ions by ions of different elements, since in this case large changes occur directly in the spin sublattice of the magnet. In the present paper we present the results of comparative investigations of the NQR spectra of  $^{139}\text{La}$  in systems based on lanthanum cuprate which are doped with magnetic (Ni) and nonmagnetic (Zn) impurities.

The experimental samples were synthesized according to the standard technology from a mixture of the corresponding oxides. Annealing was performed for  $\sim 40$  h at  $800^\circ\text{C}$  in air followed by quenching of the samples. The characteristic parameters of the  $^{139}\text{La}$  NQR spectra were investigated on a pulsed NQR spectrometer using accumulation of the spin-echo signals. The  $^{139}\text{La}$  NQR echo was recorded by a Hahn double-pulse method during continuous scanning of the carrier frequency of the generator.

The NQR spectrum of  $^{139}\text{La}$  ( $I = 7/2$ ,  $\gamma = 601.44$  Hz/Oe,  $Q = 0.21$  b) in the low-symmetry, orthorhombic phase  $Cmca$  of the unsubstituted compound  $\text{La}_2\text{CuO}_4$  consists of the nine lines  $\nu_1 - \nu_9$  in the frequency range 2–20 MHz. This complicated spectrum is formed as a result of the interaction of the quadrupole moment of the nucleus with the electric-field gradient (EFG), which is not axisymmetric, and the interaction of its mag-

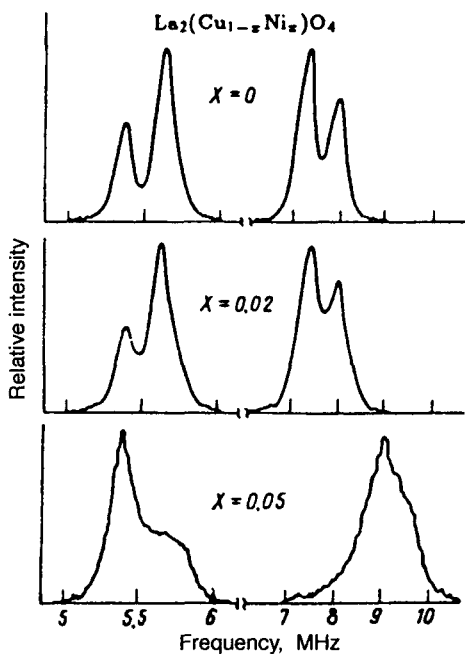


FIG. 1. Zeeman NQR spectrum of  $^{139}\text{La}$  in the system  $\text{La}_2(\text{Cu}_{1-x}\text{Ni}_x)\text{O}_4$ . Transition  $3/2-1/2$ ,  $T=4.2$  K. For Ni concentrations  $> 5\%$  the spectrum is similar to  $x=5\%$  (only a relative decrease of the amplitude of the spectral lines is observed).

netic moment with the local magnetic field  $H_{\text{loc}}$  at the location of the nucleus.<sup>5</sup> In this case the quadrupole Hamiltonian can be represented as follows:

$$H = H_Q + H_M,$$

$$H_Q = \frac{eQq_{zz}}{4I(2I-1)} [3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)], \quad (1)$$

$$H_M = -\gamma H(I_x \sin \theta \cos \phi + I_y \sin \theta \sin \phi + I_z \cos \theta).$$

Here  $eQq_{zz}$  is the quadrupole interaction constant ( $A$ ),  $\eta$  is the EFG asymmetry parameter,  $\gamma$  is the gyromagnetic ratio of the nucleus,  $\theta$  is the angle between the internal magnetic field vector  $H$  and the  $Z$  axis of the EFG tensor, and  $\phi$  is the azimuthal angle.

The  $^{139}\text{La}$  NQR spectra of these compounds were studied for all possible NQR transitions at the temperature  $T=4.2$  K. The investigations of the transitions  $7/2-5/2$  and  $5/2-3/2$  showed only a relative broadening of the resonance lines as the Ni and Zn concentrations increased from 0 to 10%. At the same time, the spectra corresponding to the transitions  $3/2-1/2$  differ appreciably, depending on the type of the impurity (Figs. 1 and 2). The  $^{139}\text{La}$  NQR spectrum (transition  $3/2-1/2$ ) of the system  $\text{La}_2(\text{Cu}_{1-x}\text{Ni}_x)\text{O}_4$  is shown in Fig. 1. One can see that at concentrations Ni  $\geq 5\%$ , in addition to a broadening of the spectral lines, the frequencies of the "upper" doublet of this transition are shifted

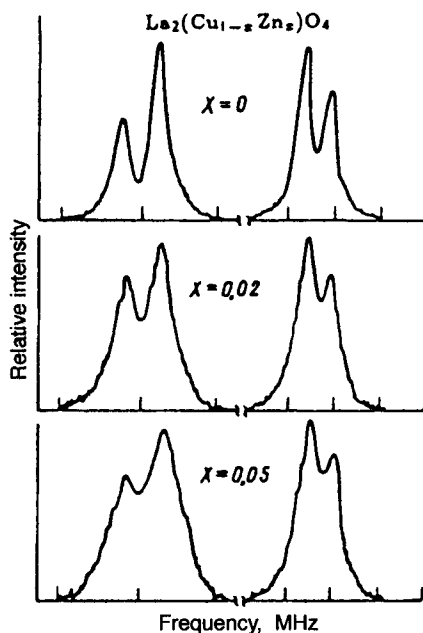


FIG. 2. Zeeman NQR spectrum of  $^{139}\text{La}$  in the system  $\text{La}_2(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ . Transition  $3/2-1/2$ ,  $T=4.2$  K.

in the direction of increasing frequency. To determine these frequencies we decomposed the wide spectral lines corresponding to the transition  $3/2-1/2$  into doublets of the form  $a_i \exp[-(\nu_i - \nu_{0i})^2/\delta_i^2]$ . The frequencies  $\nu_{0i}$  obtained in this manner for the split transition  $3/2-1/2$  in Ni-doped compounds are equal to 5.38, 5.75, 8.75, and 9.07 MHz. Next, the Zeeman splittings of the corresponding quadrupole levels (the case  $\gamma H \ll eQq_{zz}$ ) was analyzed for arbitrary  $\theta$ ,  $\varphi$ ,  $\eta$ , and  $R$  ( $R = \gamma H/eQq_{zz}$ ) in the Hamiltonian (1) by means of computer modeling. Figure 3 shows the computational results for the most suitable values of the frequencies. These results correspond to  $\theta \sim 90^\circ$ ,  $\varphi \sim 0^\circ$ ,  $\eta = 0.01$ , and  $R = 0.168$ , while for "pure"  $\text{La}_2\text{CuO}_4$  (Ref. 5) we have  $\theta = 78^\circ$ ,  $\varphi = 0^\circ$ ,  $\eta = 0.01$ , and  $R = 0.094$ . It can thus be assumed that the peculiarities of the NQR spectra for compounds with concentrations  $\text{Ni} \geq 5\%$  are associated with the rotation of the internal magnetic field  $H$  and the increase in the magnitude of this field. In Ref. 5, where "pure"  $\text{La}_2\text{CuO}_4$  was investigated, it was assumed that the angle  $Q_z$  between the  $b$  axis (the longest axis) and the principal  $Z$  axis of the EFG tensor is equal to approximately  $12^\circ$ , and for angles  $\theta \sim 78^\circ$  the vector of the internal magnetic field lies in the  $ac$  plane and is directed along the  $a$  axis. Correspondingly, the increase in the angle  $\theta$  with doping with Ni causes the internal magnetic field vector to protrude out of the  $ac$  plane by an angle  $\alpha \sim 12^\circ$ . The internal magnetic field component in the  $ac$  plane is directed along the  $a$  axis and its magnitude is  $H_{\parallel} = H \cos \alpha \sim 1.76$  kOe, while the component perpendicular to the  $ac$  plane is  $H_{\perp} = H \sin \alpha \sim 380$  kOe with the total magnitude of the field  $H \sim 1.8$  kOe. It can be assumed that the nickel impurity, whose magnetic moment is different from that of the copper atom, perturbs the nearest-neighbor spin environment (the region  $L_{kor}$ ),

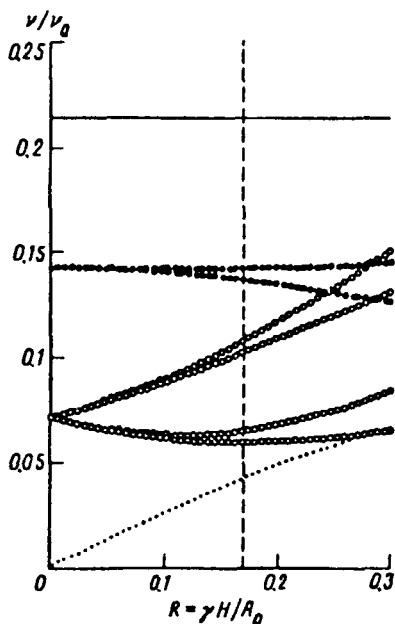


FIG. 3. Computational results for the resonance frequencies in units of  $\nu_Q = 3e^2qQ/2I(2I-1)\hbar$  plotted as a function of the strength of the magnetic field ( $R = \gamma H/A_Q$ ,  $A_Q = 2\pi\nu_Q$ ). For the case presented the parameters have the following values:  $\theta = 90^\circ$ ,  $\varphi = 0^\circ$ ,  $\eta = 0.01$ . The vertical dashed line corresponds to the value  $R = 0.168$  (see text). The solid line corresponds to the transition  $7/2-5/2$ ,  $\bullet$  — transition  $5/2-3/2$ ,  $\circ$  — transition  $3/2-1/2$ , dots — transition  $\pm 1/2$ .

which results in a definite spin orientation reversal in these regions. However, for concentrations  $Ni < 5\%$  these magnetic (spin) perturbations are relatively localized ( $L_{kor} \ll \xi_{2D}$ , where  $\xi_{2D}$  is the correlation length), retaining on the whole the character of the magnetic ordering characteristic of pure  $La_2CuO_4$ . As a result, only a broadening of the spectral lines, which is due to the scatter of the internal magnetic fields, is observed. For concentrations  $Ni \geq 5\%$  the distance between Ni impurities decreases to such an extent that  $L_{kor}$  becomes comparable in magnitude to  $\xi_{2D}$ . As a result, a definite spin orientation reversal occurs throughout the entire magnetic subsystem (sublattice), which can result in a higher internal magnetic field  $H$  and the appearance of an uncompensated magnetic moment perpendicular to the copper-oxygen plane  $ac$ . According to the experiment, the character of the magnetic ordering in the experimental systems with concentrations  $Ni \geq 5\%$  is substantially different from the magnetic order in  $La_2CuO_4$  and  $La_2NiO_4$ , (Refs. 6 and 7), and the spectrum of these compounds cannot be explained by a superposition of these magnetic orders (otherwise, we would have observed a very wide line in the range 2–20 MHz). This suggests the appearance of an intermediate magnetic phase at concentrations  $Ni \geq 5\%$ . It should be noted that such a situation occurred in the investigation of the magnetic phase transition in the antiferromagnetic compounds of the type  $YBa_2(Cu_{1-x}T_x)_3O_6$  ( $T = Fe, Co, \text{ and } Ni$ ),<sup>8</sup> where spin orientation reversal was also observed in the copper-oxygen planes at some critical impurity concentration.

In contrast with Ni, doping with Zn does not produce a shift of the spectral lines (Fig. 2). It can be concluded, therefore, that the magnetic order in these compounds is, on the whole, similar to the magnetic order of the "pure" lanthanum cuprate. At the same time, it should be noted that doping with Zn results in appreciable broadening of the spectral lines of this transition. We investigated NQR of the compound  $\text{La}_{2.03}\text{CuO}_{4+\delta}$ . This stoichiometry corresponds to the appearance of copper vacancies in the magnetic sublattice of lanthanum cuprate (according to the principle of electrical neutrality of a unit cell, in the present case the number of copper vacancies is approximately 2–3%). For this compound, the Néel temperature and the nuclear spin-lattice relaxation rate were identical, within the experimental error, to the corresponding values for the compound doped with 2% Zn. However, no appreciable broadening of the NQR spectral lines were observed in this compound. It can be assumed, therefore, that despite its nonmagnetic character, the Zn impurity perturbs the magnetic sublattice of copper, which produces a definite scatter in the internal magnetic fields. This situation could correspond, in particular, to the appearance of complexes with localized magnetic moments produced as a result of doping with Zn, as was the case<sup>9</sup> in lanthanum-strontium superconductors doped with Zn.

We performed measurements of the nuclear spin-lattice relaxation rate of lanthanum  $T_1^{-1}$  for these lanthanum concentrations. The measurements were performed on the transition  $5/2-3/2$  at 4.2 K. It is well known that nuclear relaxation for multilevel systems (the nuclear spin of  $^{139}\text{La}$  is  $I = 7/2$ ) cannot be described by a single exponential function. However, for the case in which the magnetic mechanism of relaxation predominates we can introduce a single spin-lattice relaxation time and the decay process can be represented by the following expression for the restoration of the equilibrium value of the nuclear magnetization  $M(0)$ :<sup>10</sup>

$$[M(t) - M(0)]/M(0) = A \exp(-3t/T_1) + B \exp(-10t/T_1) + C \exp(-2it/T_1). \quad (2)$$

Here  $T_1$  is the spin-lattice relaxation time and the coefficients  $A$ ,  $B$ , and  $C$  depend on the initial state. In the analysis of the experimental data these coefficients were assumed to be unknown.

The results of the measurements of  $T_1^{-1}$  as a function of the dopant concentration are shown in Fig. 4. As one can see from the figure, the concentration dependences for Zn- and Ni-doped compounds are substantially different. In the case of doping with Zn,  $T_1^{-1}$  decreases as the dopant concentration increases. We assume that in experimental compounds the nuclear spin-lattice relaxation at low temperatures ( $T \sim 4.2$  K) is determined primarily by the scattering by defects present in these compounds. The correlation length determines the effective distance between these defects, and the observed decrease of  $T_1^{-1}$  is related directly to the decrease of  $\epsilon_{2D}$  with increasing Zn content.<sup>11</sup> In the case where the Ni impurities are present, the opposite picture is observed — the nuclear spin-lattice relaxation rate increases appreciably as the nickel concentration increases from 0 to 5% and  $T_1^{-1}$  changes very little with further increases in the Ni concentration. This behavior of  $T_1^{-1}$  apparently confirms the assumption that a orientation-reversal transition of the spins in the copper-oxygen planes occurs as the Ni concentration increases from 0 to 5%.

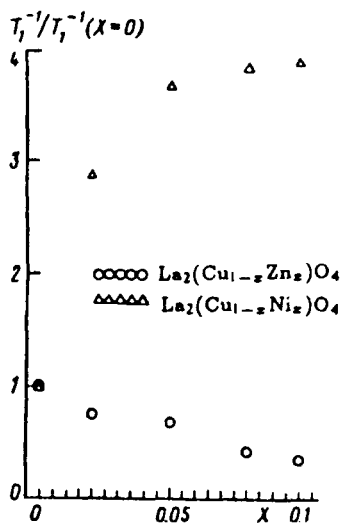


FIG. 4. Concentration dependences of the relative magnitudes of the nuclear spin relaxation rates in the systems  $\text{La}_2(\text{Cu}_{1-x}\text{T}_x)\text{O}_4$  ( $\text{T} = \text{Zn}, \text{Ni}$ ).  $T = 4.2$  K, transition  $5/2-3/2$ ,  $T_1^{-1}(x=0)$  — nuclear spin-lattice relaxation rate of the initial  $\text{La}_2\text{CuO}_4$ .

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