

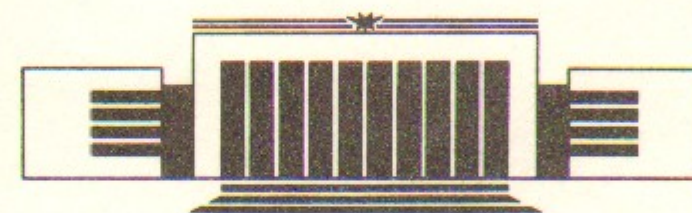


34
ИНСТИТУТ ЯДЕРНОЙ ФИЗИКИ СО АН СССР

V.V. Flambaum and O.P. Sushkov

**FREQUENCIES OF NUCLEAR
RESONANCES FOR COPPER AND
ELECTRONIC WAVE FUNCTION
OF ANTIFERROMAGNETIC La_2CuO_4**

PREPRINT 89-138



НОВОСИБИРСК

Frequencies of Nuclear
Resonances for Copper and
Electronic Wave Function
of Antiferromagnetic La_2CuO_4

V.V. Flambaum and O.P. Sushkov

Institute of Nuclear Physics
630090, Novosibirsk, USSR

ABSTRACT

Calculated values of the frequencies of nuclear magnetic and quadrupole resonances (for ^{65}Cu $\nu(\text{NMR}) = 107$ MHz, $\nu(\text{NQR}) = 32$ MHz) are close to the experimental values (100 and 29.5 MHz). This coincidence is reliable test of obtained electronic wave function.

© Институт ядерной физики СО АН СССР

INTRODUCTION

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are the good probes of electronic wave function of solid. In particular, they are the probes of magnetic structure. At present there are some speculations about connection of high temperature superconductivity with magnetic structure but there is no clear understanding of magnetic structure of these compounds. We shall discuss as simplest example $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The qualitative phase diagram of this compound is presented in Ref. [1]. At $x \leq 0.05$ it is antiferromagnetic insulator with magnetic moments localized at copper ions. At $x \geq 0.06$ it is superconducting metal. However there are localized antiferromagnetic moments in metallic phase too according to neutron scattering data [2]. At first sight the natural explanation is that the system is quasi-two-dimensional and long-range order is destroyed after doping but short-range antiferromagnetic correlations in CuO_2 -plane survive. For example, there is something like spin liquid or spin glass. However this scenario seems in contradiction with data on NMR and NQR on copper nuclei [3]. According to this work NMR frequency in doped compound is two orders of magnitude smaller than in undoped compound. Meanwhile NQR frequency varies very slowly and resonance line remains narrow (in undoped compound NMR frequency is three times larger than NQR frequency). These data can be considered as a hint that system at $x \geq 0.06$ transfers into state with paired spins

of Cu^{2+} ions (e. g. into RVB-state or some other quantum state of the system with zero average value of electron spin at every copper ion).

In the present work we consider only undoped antiferromagnetic La_2CuO_4 . Calculation of NMR and NQR frequencies is necessary for verification of electronic wave function of CuO_2 -plane obtained in our work [4] and for the further development for the case of doped compound.

ELECTRONIC ORBITALS AND ENERGY LEVELS

Ground state of CuO_2 -plane in undoped La_2CuO_4 corresponds to d^9p^6 -configuration where d^9 is $3d^9\text{Cu}^{2+}$ configuration and p^6 is $2p^6\text{O}^{2-}$ configuration. The system is Mott insulator. Wave function of O^{2-} ion is calculated in the stabilizing field of crystal lattice. In the work [4] the excitation energy of electron hopping from oxygen to copper was calculated:

$$\Delta = E(d^{10}p^5) - E(d^9p^6) \approx 5 \text{ eV}. \quad (1)$$

This value is in reasonable agreement with value obtained from spectra analysis [5]. In the work [4] the splitting of oxygen $2p$ orbitals was also calculated: $\Delta\varepsilon = \varepsilon_{z,y} - \varepsilon_x = 4.5 \text{ eV}$ (x is CuO axis). Now we understand that this value is strongly overestimated. The reasons of overestimation of this splitting in Ref. [4] were the following. Firstly, contribution of oxygen $2p$ -state mixing with copper $4s$ -state was estimated in tight-binding approximation which was not correct for this case. Secondly, approximation of point-like ions strongly overestimated crystal field contribution into splitting. More accurate calculation carried out in connection with the present work shows that splitting of O^{2-} $2p$ -orbitals $\Delta\varepsilon = \varepsilon_{z,y} - \varepsilon_x \sim 1 \text{ eV}$. This estimation agrees with results of other authors (see review [6]).

In this work we need spectrum of excitations on the Cu^{2+} ion, corresponding to the transitions of $3d$ -hole $|x^2-y^2\rangle$ to the hole states $|xy\rangle$, $|z^2\rangle$, $|xz\rangle$, $|yz\rangle$ (z -axis is orthogonal to the CuO_2 -plane). Splitting of this states is due firstly to the Coulomb crystal field of second and fourth multipolarity and secondly to the virtual hopping of the hole to the neighbouring oxygen ions. We calculated this spectrum in the work [4]. In the present work more careful analysis have been carried out which leads to small changes of

calculated spectrum. Firstly, calculation of realistic electron density shows that approximation of point-like ions is not correct and contributions of crystal field of the second and fourth multipolarity practically vanish. As far as virtual hopping is concerned it is necessary to take into account the absence of large splitting of oxygen $2p$ -orbitals. We have chosen the following values of matrix elements of the hopping between nearest Cu and O:

$$\begin{aligned} t_{x^2-y^2,x} &= \frac{\sqrt{3}}{2} (pd\sigma), & t_{z^2,x} &= -\frac{1}{2} (pd\sigma), \\ t_{xy,y} &= t_{xz,z} = (pd\pi), \\ (pd\sigma) &\approx -1.6 \text{ eV}, & (pd\pi) &\approx -0.8 \text{ eV}. \end{aligned} \quad (2)$$

These values agree with generally accepted values [6] and give correct value of superexchange responsible for antiferromagnetic spin-spin interaction in CuO_2 -plane. Parameter t/Δ is not very small and perturbation theory used in Ref. [4] should be refined. It is easy to do by solving the problem for cluster consisting of copper ion and four oxygen ions. Thus we find the energies of $3d$ -hole states:

$$\begin{aligned} \varepsilon_{x^2-y^2} &= \frac{\Delta}{2} - \sqrt{\frac{\Delta^2}{4} + 3(pd\sigma)^2} \approx -1.23 \text{ eV}, \\ \varepsilon_{xy} &= \frac{\Delta}{2} - \sqrt{\frac{\Delta^2}{4} + 4(pd\pi)^2} \approx -0.47 \text{ eV}, \\ \varepsilon_{z^2} &= \frac{\Delta}{2} - \sqrt{\frac{\Delta^2}{4} + (pd\sigma)^2} \approx -0.47 \text{ eV}, \\ \varepsilon_{xz} = \varepsilon_{yz} &= \frac{\Delta}{2} - \sqrt{\frac{\Delta^2}{4} + 2(pd\pi)^2} \approx -0.24 \text{ eV}. \end{aligned} \quad (3)$$

We should note that spectrum of $3d$ -excitations was calculated earlier in Ref. [7]. It differs a little from our result (3). The main reason of the difference is the use of perturbation theory in parameter t/Δ in Ref. [7]. Besides that we take $\Delta = 5 \text{ eV}$ instead of $\Delta = 3 \text{ eV}$ in Ref. [7].

NMR Frequency

Hamiltonian of magnetic electron-nucleus interaction is of the form (see e. g. [8]):

$$W_M = a_l \bar{l} \bar{I} - a_l (\bar{s} - 3(\bar{s} \bar{n}) \bar{n}) \bar{I}, \quad \text{at } l \neq 0, \quad (4)$$

$$W_M = a_s \bar{s} \bar{I}, \quad \text{at } l = 0.$$

Here \bar{l} is an orbital angular momentum and \bar{s} is spin of electron, \bar{I} is nuclear spin, \bar{n} is unit vector in the electron direction. At first, let us find the constants a_l for isolated copper atom. They can be both calculated theoretically and determined from the experimental data on atomic hyperfine structure [9]. Experimental data on configurations $3d^9 4s^2$, $3d^{10} 4s$, $3d^{10} 4p$ give:

$$a_{3d} = 1205 \text{ MHz},$$

$$a_{4p} = 297 \text{ MHz},$$

$$a_{4s} = 6284 \text{ MHz}. \quad (5)$$

All the values are presented for ^{65}Cu nucleus. Calculation using Hartree—Fock wave functions give the values of a_l which are 10—40% smaller than the experimental these. The disagreement is due to many-body effects. Mainly it is polarization of electron shells by magnetic field of the nucleus and Brueckner-type correlations which renormalize wave function of external unpaired electron [10, 11]. After calculations of these effects disagreement practically vanishes.

According to (3) $3d$ -hole is in $|x^2 - y^2\rangle$ state of Cu^{2+} ion. Orbital contribution vanishes in this state. Electron spin contribution (4) is transformed to

$$\langle x^2 - y^2 | W_M | x^2 - y^2 \rangle = -a_{3d} s_\alpha I_\beta \langle x^2 - y^2 | \delta_{\alpha\beta} - 3n_\alpha n_\beta | x^2 - y^2 \rangle. \quad (6)$$

From symmetry relations it is obvious that

$$T_{\alpha\beta} = \langle x^2 - y^2 | \delta_{\alpha\beta} - 3n_\alpha n_\beta | x^2 - y^2 \rangle = 0 \quad \text{at } \alpha \neq \beta.$$

Diagonal components are equal to

$$T_{xx} = T_{yy} = -\frac{1}{2} T_{zz} = -\frac{2}{7}.$$

Taking into account that hole spin lies in xy -plane (see e. g. Ref. [1]) we obtain

$$\langle x^2 - y^2 | W_M | x^2 - y^2 \rangle = \frac{2}{7} a_{3d} (\bar{s} \cdot \bar{I}). \quad (7)$$

Constant of magnetic spin-nucleus interaction is very sensitive to spin-orbit correction since it allows to «switch on» large orbital magnetic moment of d -electron. Spin-orbit interaction of $3d$ -hole is

$$H_{ls} = A \bar{l} \cdot \bar{s}, \quad A = -0.103 \text{ eV}. \quad (8)$$

The value of A follows from Cu^{2+} spectrum [12]. Interaction (8) leads to mixing of orbital states (3). In the second order of perturbation theory it gives correction to hyperfine interaction

$$2 \sum_{d \neq x^2 - y^2} \frac{\langle x^2 - y^2 | H_{ls} | d \rangle \langle d | W_M | x^2 - y^2 \rangle}{\epsilon_{x^2 - y^2} - \epsilon_d}. \quad (9)$$

Here in W_M (see (4)) it is enough to keep orbital term only which is much larger than the spin term. Spin of the hole lies in xy -plane. Therefore only xz - and yz -states contribute to the sum in formula (9). Contribution to hyperfine interaction induced by spin-orbit interaction is of the form:

$$2 \frac{A}{\epsilon_{x^2 - y^2} - \epsilon_{xz}} a_{3d} (\bar{l} \bar{s}) \approx 0.21 a_{3d} (\bar{l} \bar{s}). \quad (10)$$

Sum of expressions (7) and (10) gives the single-particle contribution of $3d$ -hole into magnetic field at the nucleus. However, the holes localized at the four nearest copper ions give essential contribution also. The reason of enhancement of this contribution is the following. Consider element of CuO_2 -plane shown at Figure. The holes localized at the ions 2, 3, 4, 5 hop to oxygen ions nearest to copper 1 with noticeable probability. Oxygen wave function $2p_\sigma$ expanded in orbitals of copper 1 give considerable s -wave component near copper nucleus. Hyperfine interaction in s -wave is an order of magnitude larger than that in d -wave (see formula (5)). This enhancement compensates the suppression due to large distance between copper ions.

Let us carry out calculation according to this mechanism. Amplitude of $|x^2 - y^2\rangle$ hole hopping to oxygen $2p_\sigma$ -state is determined by matrix element $t_{x^2 - y^2, x}$ (2). We have mentioned that parameter t/Δ is not very small. Therefore oxygen amplitude we should find by solving the problem for cluster consisting from copper ion and four oxygen ions. Thus amplitude of probability of hole presence at the oxygen is equal to

$$\alpha = -\frac{1}{2\sqrt{2}} \left[1 - \frac{\Delta}{\sqrt{\Delta^2 + 12(pd\sigma)^2}} \right]^{1/2} = -0.203. \quad (11)$$

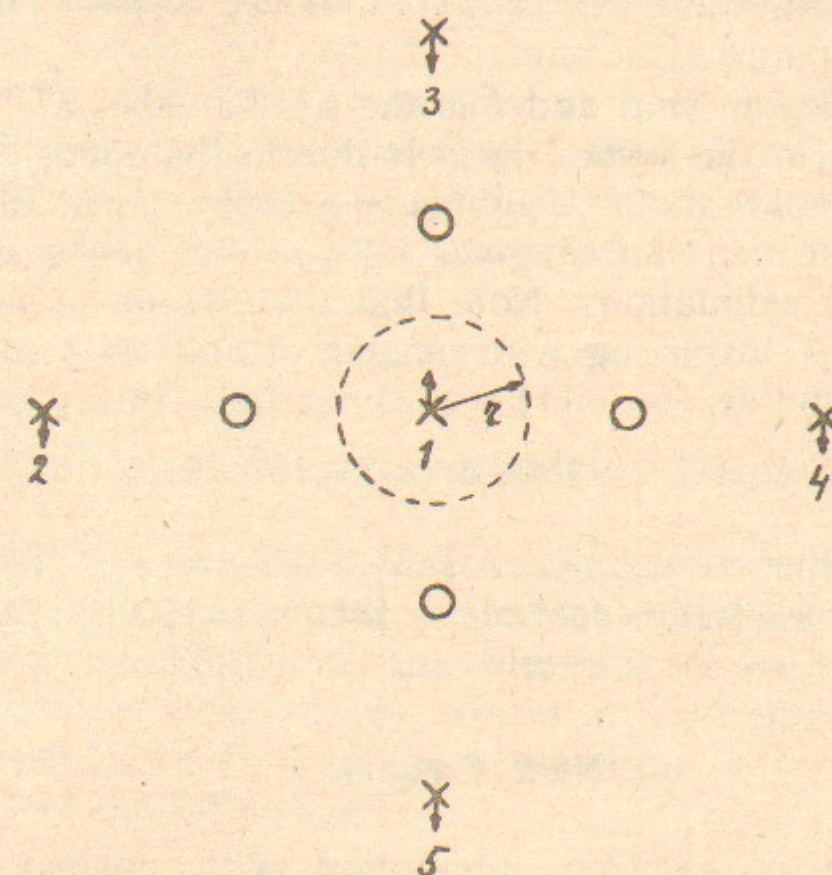
Now we should find contribution of oxygen 2*p*-electron into copper *s*-wave. At first sight situation is similar to 3*d*—2*p* hopping, i. e. it is enough to introduce matrix element of 2*p*—4*s* hopping. However, it is not so. The point is that 3*d*-copper and 2*p*-oxygen wave functions are localized well enough and therefore overlapping is small: $\langle 3d_{x^2-y^2} | 2p_x \rangle \sim 0.06$. In this situation it is reasonable to introduce effective hopping matrix element (see, e. g. [13]) and to work with these states as with orthogonal states. In the case of 4*s*-orbital the size of wave function is larger than the distance between Cu and O. Here another way is more adequate. It is necessary to draw a sphere around copper and expand oxygen wave function in spherical harmonics on this sphere (see Figure). Then we should match these harmonics with corresponding copper wave functions, e. g. with 4*s* and 4*p*. Of course, this procedure is reasonable only if matching coefficients do not depend strongly on sphere radius *r* when *r* varies in some reasonable interval (say, $r = 1.5 \div 2.5a_B$). One could say that there is a region of dual description of wave function. Coefficients of oxygen orbitals expansion in 4*s* and 4*p* copper orbitals for different values of *r* are presented at the Table. It is seen that duality condition is fulfilled at least for 2*p*-orbital which is the most important.

Table
Coefficients of Expansion of Oxygen 2*p*, 2*s*-orbitals
in 4*p*, 4*s* copper orbitals for different values
of matching radius *r*. Cu—O distance is $3.6a_B$.

<i>r/a_B</i>	4 <i>s</i>			4 <i>p</i>		
	1.5	2.	2.5	1.5	2.	2.5
2 <i>p_σ</i>	-0.43	-0.40	-0.44	0.71	0.68	0.74
2 <i>p_π</i>	—	—	—	0.26	0.26	0.31
2 <i>s_σ</i>	0.13	0.15	0.22	-0.31	-0.36	-0.49

Note that oxygen orbitals are obtained by Hartree—Fock method in spherically averaged crystal field of the lattice [4]. Atomic correlations change them very little. Contribution of higher harmonics of crystal field influences on expansion coefficients presented in Table at the level of $\leq 10\%$. The situation for copper orbitals is

more complicated. Here we use Brueckner orbitals 4*s* and 4*p* in copper atom (configurations 3*d*¹⁰4*s* or 3*d*¹⁰4*p*) as a basis set instead of Hartree—Fock orbitals. Brueckner orbitals include dominating intra-atomic correlation corrections (their contributions to *a*_{4*s*} and *a*_{4*p*} are $\sim 20\%$) and essentially better reproduce hyperfine structure of atomic levels (see e. g. Ref. [11]). We use atomic orbitals instead of ion orbitals because hyperfine constants are known from experiment just for neutral atom. Validity of use of atomic orbitals in copper ion is based on the fact that wave functions of ion are proportional to atomic wave functions at the $r \leq 2a_B$. The reason of



CuO₂—plane, O is oxygen atom, X is copper atom, arrows show directions of spins.

proportionality is that at $r < 2a_B$ the difference in potential and in energy between ion and atom is negligible: $\Delta U, \Delta E \ll U$. The normalization coefficient is determined by matching with oxygen wave function in any case. In this situation it does not matter what functions are used. It is only necessary to use the corresponding hyperfine constants. For example, we can use functions 5*s* and 5*p* instead of 4*s* and 4*p*.

Basing on values presented at Table we take the following expansion coefficients of oxygen 2*p* and 2*s*-orbitals in 4*s* and 4*p* copper orbitals (for distance between Cu and O equal $3.6a_B$):

$$\begin{aligned}\beta_{\sigma}(2p, 4s) &= -0.40, & \beta_{\sigma}(2p, 4p) &= 0.68, \\ \beta_{\sigma}(2s, 4s) &= 0.15, & \beta_{\pi}(2p, 4p) &= 0.26, \\ & & \beta_{\sigma}(2s, 4p) &= -0.36.\end{aligned}\quad (12)$$

Now we can calculate the total magnetic field at the copper nucleus I including both the interaction with $|x-y^2\rangle$ hole localized at copper I (formulae (7), (10)) and with electron spins of the neighbours:

$$\langle W_M \rangle = \left\{ \left(\frac{2}{7} + 0.21 \right) a_{3d} - 4\alpha^2 \left[a_{4s} \beta_{\sigma}^2(2p, 4s) + \frac{1}{5} a_{4p} \beta_{\sigma}^2(2p, 4p) \right] \right\} \vec{s} \cdot \vec{I}. \quad (13)$$

Here \vec{s} is the electron spin and \vec{I} is the nuclear spin at the copper I . The sign minus in the second term is due to the opposite orientation of the electron spins at the neighbouring copper ions. In the antiferromagnetic state experiment gives $\langle 2s_z \rangle = 0.5$ [14], which agrees with theoretical estimations. Note that the change of normalization of $3d$ -orbital due to mixing with oxygen orbitals is also included in $\langle s \rangle$. Using formulae (5), (11) — (13) we find NMR frequency

$$\nu_L = (597 - 166 - 5) \langle s_z \rangle = 107 \text{ MHz}. \quad (14)$$

First term is the contribution of a_{3d} , second: a_{4s} , third: a_{4p} . The value (14) agrees with experiment [3]: $\nu_L = 100.1(1)$ MHz. Remind that the frequencies are presented for isotope ^{65}Cu .

NQR Frequency

Hamiltonian of electron interaction with nuclear quadrupole moment is of the form (see e. g. Ref. [8]):

$$W_Q = -b \frac{1}{Q} \sum_m \sqrt{\frac{4\pi}{5}} Y_{2m} \left(\frac{\vec{r}}{r} \right) Q_{2m}^* \quad (15)$$

$$b = e^2 Q \left\langle \frac{1}{r^3} \right\rangle.$$

Here $Q = 2Q_{20}$ is nuclear quadrupole moment, \vec{r} is the electron coordinate, e is the electron charge. Constants b can be found from the experimental data [9] on hyperfine structure of copper atom in configurations $3d^9 4s^2$, $3d^{10} 4p_{3/2}$:

$$\begin{aligned}b_{3d} &= 311 \text{ MHz}, \\ b_{4p} &= -65 \text{ MHz}.\end{aligned}\quad (16)$$

The values are presented for isotope ^{65}Cu . Note that b_{3d} corresponds to $3d$ -hole and therefore it has the sign opposite to Eq. (15). Calculation with Hartree—Fock wave functions give value b_{3d} which is by 3% larger than the experimental one and b_{4p} which is 53% smaller than the experimental value. The reason of disagreement is well known. It is many-body intra-atomic effects (see e. g. Ref. [15]). However it is not essential for our work since we use «experimental» values (16) which include intra-atomic correlations. According to Eq. (11) the probability of hole presence in x^2-y^2 copper state equals $1-4\alpha^2 \approx 0.835$. Therefore $|x^2-y^2\rangle$ hole contribution to the quadrupole splitting of levels with nuclear spin projections $|I_z| = 3/2$ and $|I_z| = 1/2$ is equal to

$$E_{3/2} - E_{1/2} = \frac{2}{7} b_{3d} (1-4\alpha^2) = 74 \text{ MHz}. \quad (17)$$

This is the main but not unique contribution to the quadrupole splitting.

We have mentioned above that oxygen orbitals have noticeable p -wave component at the copper ion, which also lead to quadrupole splitting of nuclear levels. Expansion coefficients for orbitals of O^{2-} ion from CuO_2 -sheet in $4p$ copper orbital are presented in Eq. (12). Similar coefficients for O^{2-} in the octahedron vertex ($\text{Cu}-\text{O}$ distance $4.59a_B$) are the following:

$$\begin{aligned}\tilde{\beta}_{\sigma}(2p, 4p) &= 0.35, \\ \tilde{\beta}_{\pi}(2p, 4p) &= 0.10, \\ \tilde{\beta}_{\sigma}(2s, 4p) &= -0.10.\end{aligned}\quad (18)$$

Using formulae (15), (16), (18) we can calculate the contribution to quadrupole splitting, which is due to penetration of oxygen electrons to copper:

$$\begin{aligned}\frac{8}{5} b_{4p} [\beta_{\sigma}^2(2p, 4p) + \beta_{\sigma}^2(2s, 4p) - \beta_{\pi}^2(2p, 4p) - \tilde{\beta}_{\sigma}^2(2p, 4p) - \\ - \tilde{\beta}_{\sigma}^2(2s, 4p) + \tilde{\beta}_{\pi}^2(2p, 4p)] = -42 \text{ MHz}.\end{aligned}\quad (19)$$

Finally, there is contribution of quadrupole crystal field of nearest ions enhanced by antishielding factor. For copper ion this fac-

tor is about 19 [15]. In the approximation of point-like nucleus this contribution equals -37 MHz. However, calculation with realistic density distribution gives much smaller value: -8 MHz. Moreover this contribution is in fact included in equation (19). The point is that we use «experimental» atomic value b_{4p} . In atom both region inside $3d$ -shell and external region contribute to b_{4p} . Atomic calculation (with taking into account antishielding polarization) shows that about 20–25% of contribution to b_{4p} is given by configurations with $4p$ -electron position at $r > 2a_B$. In crystal there is no sense to describe these configurations by formula (19). Therefore we should exclude 20–25% from contribution (19) and add contribution of long-range crystall field (-8 MHz). But these corrections compensate one another. Therefore, quadrupole splitting of Cu levels with $|I_z| = 3/2$ and $|I_z| = 1/2$ is equal to sum of contributions (17) and (19):

$$\nu_Q = E_{3/2} - E_{1/2} = 74 - 42 = 32 \text{ MHz.} \quad (20)$$

This value agrees with experimental one [3]: $\nu_Q = 29.5$ MHz.

Authors are grateful to N.K. Moroz for useful discussions.

REFERENCES

1. Amnon Aharony *et al.* Phys. Rev. Lett., 60 (1988) 1330.
2. R.J. Birgeneau *et al.* Phys. Rev. B38 (1988) 744; B38 (1988) 6614; Hideki Yoshida *et al.* J. Phys. Soc. Jap., 57 (1988) 3686.
3. K. Kumagai and Y. Nakamura. Physica, C157 (1989) 307.
4. V.V. Flambaum and O.P. Sushkov. Physica, C159 (1989) 586.
5. J.C. Fuggle *et al.* Phys. Rev., B37 (1988) 123.
6. W.E. Pickett. Rev. Mod. Phys., 61 (1989) 433.
7. G.A. Sawatzky. in Proc. IBM Int. School Mater. Sci. and Techn. on «Earlier and Recent Aspects of Superconductivity», 1989, Italy.
8. I.I. Sobelman. Introduction to the Theory of Atomic Spectra (Moscow, 1963).
9. Josef Ney. Zeit. Phys., 196 (1966) 53; W. Fisher, H. Huhnermann and K.-J. Kollath. Zeit. Phys., 194 (1966) 417; 200 (1967) 458.
10. I. Lindgren, J. Lindgren and A.-M. Martensson. Z. Phys., A279 (1976) 113.
11. V.A. Dzuba, V.V. Flambaum, P.G. Silvestrov and O.P. Sushkov. J. Phys., B17 (1984) 1953; 18 (1985) 597; 20 (1987) 1399.
12. Ch.E. Moore, Atomic Energy Levels, v.2 (Washington, DC, US Govt. Printing Office, 1971).
13. L.F. Matheiss. Phys. Rev., 132 (1970) 3918.
14. D. Vakhin *et al.* Phys. Rev. Lett. 58 (1987) 2802.
15. A.J. Freeman and R.E. Watson. in Magnetism, v.2, Part A, p.168, Ed. G.T. Rado and H. Suhl (Academic press, N.Y. and London, 1965).

V.V. Flambaum and O.P. Sushkov

Frequencies of Nuclear Resonances for Copper and Electronic Wave Function of Antiferromagnetic La_2CuO_4

О.П. Сушков, В.В. Фламбаум

Частоты ядерных резонансов для меди и электронная волновая функция антиферромагнитного состояния La_2CuO_4

Ответственный за выпуск С.Г. Попов

Работа поступила 4 октября 1989 г.

Подписано в печать 18.X 1989 г. МН 10419

Формат бумаги 60×90 1/16 Объем 1,4 печ.л., 1.1 уч.-изд.л.

Тираж 190 экз. Бесплатно. Заказ № 138

Набрано в автоматизированной системе на базе фотонаборного автомата ФА1000 и ЭВМ «Электроника» и отпечатано на ротапринтере Института ядерной физики СО АН СССР, Новосибирск, 630090, пр. академика Лаврентьева, 11.