Why is the Cu(2) Asymmetry Parameter of NQR Spectra in HTSC so Small? *

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Z. Naturforsch. **49a,** 385–388 (1994); received August 17, 1993

An explanation has been proposed for the unusual behaviour of the asymmetry parameter of NQR spectra of Cu(2) in layered cuprates. When holes are introduced into the plane, Zhang-Rice singlets (ZRS) appear which have a strong vibronic coupling to tetragonal and orthorhombic modes. The equation for the adiabatic potential has been derived. It is shown that its minimum, corresponding to orthorhombic distortions of the oxygen plaquette around the Cu(2) ions, changes under doping to tetragonal character due to the singlet exchange coupling between copper and oxygen holes. A strong interaction of ZRS via the phonon field has been found.

Key words: NQR, Singlet correlation, Adiabatic potential, Tetragonal mode, Phonon coupling.

I. Introduction

The aim of this paper is to discuss the question why the asymmetry parameter of NQR spectra of Cu(2) in HTSC is so small. For example in $YBa_2Cu_4O_8$ $\eta = 0.04 \pm 0.04$ [1], and in $YBa_2Cu_3O_7$ $\eta = 0.01 \pm 0.01$ [2–5]. Careful measurements of the asymmetry parameter at the Cu(2) sites in $YBa_2Cu_3O_7$ were done by Riesemeier et al. [6] and η was determined to be $\eta < 0.01$. This is unexpected because in all these materials the crystal lattice are not tetragonal. According to calculations [7], [8], and [9] the asymmetry parameter η should be equal to 0.07, 0.07, and 0.1, respectively. Four important contributions determine the electric field gradient at the Cu(2) site in HTSC materials [10]. i) The valence contribution from $3\,d_{x^2-y^2}$ Cu(2) orbitals, ii) the copper core 3 p, 3 d overlap with oxygens, iii) the charge transfer or covalency and iv) the lattice contribution. The contributions i), ii), and iii) are dominated by the oxygen atoms near the Cu(2) position. In this paper we shall show that hole doping of the plane causes singlet coupling between $Cu^{2+}(2)$ and O^- spins, which leads to a new local equilibrium of the oxygen atoms around Cu(2) with tetragonal symmetry during the singlet lifetime. As a result, the main contribution to the asymmetry parameter goes to zero. Only a residual contribution from the lattice remains, but that is relatively small.

II. Undoped Case

Let us start from the Jahn-Teller problem for Cu^{2+} ($3\,d^9$). The Hamiltonian can be written as [11]

$$H_0 = V(U_\Theta Q_\Theta + U_\varepsilon Q_\varepsilon) + \frac{M\omega^2}{2}(Q_\varepsilon^2 + Q_\Theta^2) + \delta_t U_\Theta + \delta_r U_\varepsilon . \qquad (1)$$

Here V is the vibronic coupling constant, $U_\Theta = -X^{\Theta,\Theta} + X^{\varepsilon,\varepsilon}$ and $U_\varepsilon = X^{\Theta,\varepsilon} + X^{\varepsilon,\Theta}$ are combinations of Hubbard operators $X^{p,q}$, Q_Θ, and Q_ε are normal coordinates of the vibrations of the oxygen plaquette with respect to the copper atom, δ_t and δ_r are parameters which describe the tetragonal and orthorhombic crystal field at the copper ion. Typical values of parameters for Cu^{2+} are [11]

$$V = -0.8\ \text{eV/Å}, \quad M\omega^2 = 4\ \text{eV/Å}^2,$$
$$\delta_t = -0.5\ \text{eV}, \qquad \delta_r = 0.1\ \text{eV}. \qquad (2)$$

The adiabatic potential

$$H_0 = \frac{M\omega^2}{2}(Q_\varepsilon^2 + Q_\Theta^2) \pm [(VQ_\Theta + \delta_t)^2 + (VQ_\varepsilon + \delta_\varepsilon)^2]^{1/2} \qquad (3)$$

in polar coordinates ($Q_\Theta = \varrho \cos \phi$, $Q_\varepsilon = \varrho \sin \phi$) has it's minimum at $\varrho \approx 0.2$ Å and $Q_\varepsilon = 0.04$ Å. This means that there is a static orthorhombic distortion of

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* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

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oxygen ions surrounding Cu^{2+}, this distortion leading to an asymmetry parameter $\eta \approx 0.1$.

III. Vibronic Coupling in Copper-Oxygen Singlet States

Now we introduce a hole into the system. By the Hamiltonian

$$\begin{aligned} H^{(1)}_{\text{hop}} = & -2 \sum_{\sigma} (t_{\varepsilon} d^{+}_{\varepsilon\sigma} P_{\varepsilon\sigma} - t_{\Theta} d^{+}_{\Theta\sigma} P_{\Theta\sigma}) \\ & - \sum_{\sigma} [t'_{\varepsilon} d^{+}_{\varepsilon\sigma} P_{\varepsilon\sigma} - t'_{\Theta} d^{+}_{\Theta\sigma} P_{\Theta\sigma}] Q_{\Theta} \\ & - \sum_{\sigma} [t'_{\varepsilon} d^{+}_{\varepsilon\sigma} P_{\varepsilon\sigma} - t'_{\Theta} d^{+}_{\Theta\sigma} P_{\Theta\sigma}] Q_{\varepsilon} + \text{h.c.} \end{aligned} \tag{4}$$

hopping processes between copper and oxygen are taken into account. Here $t_{\varepsilon} = \frac{\sqrt{3}}{2} t_{\sigma}$ and $t_{\Theta} = \frac{1}{2} t_{\sigma}$ are the transfer integrals, t'_{ε} and t'_{Θ} are the derivatives $t'_{\varepsilon} = \partial t_{\varepsilon}/\partial R$ and $t'_{\Theta} = \partial t_{\Theta}/\partial R$. R is the interatomic copper-oxygen distance, d^{+}_{Θ} and d^{+}_{ε} are the hole creation operators of copper states, P_{ε} and P_{Θ} are combinations of annihilation operators for oxygen holes,

$$\begin{aligned} P_{\varepsilon\sigma} &= \tfrac{1}{2} (p^{(1)}_{\sigma} - p^{(2)}_{\sigma} - p^{(3)}_{\sigma} + p^{(4)}_{\sigma}), \\ P_{\Theta\sigma} &= \tfrac{1}{2} (p^{(1)}_{\sigma} + p^{(2)}_{\sigma} - p^{(3)}_{\sigma} - p^{(4)}_{\sigma}). \end{aligned} \tag{5}$$

Oxygen holes can jump to neighbouring oxygen sites,

$$H^{(2)}_{\text{hop}} = \sum_{ij} t^{xy}_{ij} p^{i+}_{\sigma} p^{j}_{\sigma} + \text{h.c.}, \tag{6}$$

The parameter which describes this process is t^{xy}. For simplicity we ignore corrections which are caused by vibrations since our calculation has found these corrections to be relatively small.

Hamiltonian (1) acts within the basis $|\varepsilon\rangle$ and $|\Theta\rangle$ states, which correspond to the lower Hubbard band only. Furthermore Hamiltonian (3) contains terms which describe hopping firstly between the lower oxygen and the upper copper Hubbard band, and secondly between the lower copper and upper oxygen bands. These terms yield in second order perturbation theory an effective Hamiltonian which acts in the Hilbert space of the lower Hubbard band states $|\varepsilon\rangle$, $|\Theta\rangle$, $|P_{\varepsilon}\rangle$ and $|P_{\Theta}\rangle$ only,

$$\begin{aligned} H^{(1)}_{\text{eff}} = & [J_{\varepsilon\varepsilon} + (J'_{\varepsilon\varepsilon} + V'_{pd}) Q_{\Theta}] \Psi^{+}_{\varepsilon\varepsilon} \Psi_{\varepsilon\varepsilon} \\ & + [J_{\Theta\Theta} + (J'_{\Theta\Theta} + V'_{pd}) Q_{\Theta}] \Psi^{+}_{\Theta\Theta} \Psi_{\Theta\Theta} \\ & + [J_{\varepsilon\Theta} + J'_{\varepsilon\Theta} Q_{\Theta}) (\Psi^{+}_{\varepsilon\varepsilon} \Psi_{\Theta\Theta} + \Psi^{+}_{\Theta\Theta} \Psi_{\varepsilon\varepsilon}) \\ & + [J'_{\varepsilon\varepsilon} (\Psi^{+}_{\varepsilon\varepsilon} \Psi_{\varepsilon\Theta} + \Psi^{+}_{\varepsilon\Theta} \Psi_{\varepsilon\varepsilon}) \\ & + J'_{\varepsilon\Theta} (\Psi^{+}_{\varepsilon\varepsilon} \Psi_{\Theta\varepsilon} + \Psi^{+}_{\Theta\varepsilon} \Psi_{\varepsilon\varepsilon}) \\ & + J'_{\Theta\Theta} (\Psi^{+}_{\Theta\Theta} \Psi_{\varepsilon\Theta} + \Psi^{+}_{\Theta\varepsilon} \Psi_{\Theta\Theta}) \\ & + J'_{\Theta\varepsilon} (\Psi^{+}_{\varepsilon\Theta} \Psi_{\Theta\Theta} + \Psi^{+}_{\Theta\Theta} \Psi_{\varepsilon\Theta})] \frac{Q_{\varepsilon}}{2}. \end{aligned} \tag{7}$$

Here $\Psi^{+}_{\alpha\beta}$ are creation operators of copper oxygen hole singlets, as given by

$$\begin{aligned} \Psi^{+}_{\varepsilon\Theta} &= \frac{1}{\sqrt{2}} (X^{\varepsilon\uparrow,0} P^{+}_{\Theta\downarrow} - X^{\varepsilon\downarrow,0} P^{+}_{\Theta\uparrow}), \\ \Psi^{+}_{\Theta\varepsilon} &= \frac{1}{\sqrt{2}} (X^{\Theta\uparrow,0} P^{+}_{\varepsilon\downarrow} - X^{\Theta\downarrow,0} P^{+}_{\varepsilon\uparrow}), \end{aligned} \tag{8}$$

The values $J_{\alpha\beta}$ are determined by two contributions, namely via the upper Hubbard band (contribution of $A_{\alpha\beta}$ type) and through the upper oxygen band ($P_{\gamma\delta}$ contributions):

$$J_{\alpha\beta} = A_{\alpha\beta} + P_{\alpha\beta}. \tag{9}$$

The expressions for $A_{\alpha\beta}$ are given by

$$\begin{aligned} A_{\varepsilon\varepsilon} &= -t^{2}_{\sigma} \left[\frac{6}{I_{\varepsilon\varepsilon} - 2V_{pd} - \Delta_{\varepsilon}} + \frac{1}{I_{\varepsilon\Theta} + K_{\varepsilon\Theta} - 2V_{pd} - \Delta_{\Theta}} \right], \\ A_{\Theta\Theta} &= -t^{2}_{\sigma} \left[\frac{2}{I_{\Theta\Theta} - 2V_{pd} - \Delta_{\Theta}} + \frac{3}{I_{\varepsilon\Theta} + K_{\varepsilon\Theta} - 2V_{pd} - \Delta_{\varepsilon}} \right], \\ A_{\Theta\varepsilon} &= \frac{\sqrt{3}}{2} t^{2}_{\sigma} \left[\frac{1}{I_{\varepsilon\Theta} + K_{\varepsilon\Theta} - 2V_{pd} - \Delta_{\Theta}} \right. \\ & \qquad \left. + \frac{1}{I_{\varepsilon\Theta} + K_{\varepsilon\Theta} - 2V_{pd} - \Delta_{\varepsilon}} \right], \end{aligned} \tag{10}$$

where $I_{\alpha\beta}$ and $K_{\alpha\beta}$ are the Coulomb and exchange integrals of copper states, Δ_{ε} and Δ_{Θ} are the charge transfer energies and V_{pd} is the energy of the Coulomb repulsion of copper and oxygen holes. The values $P_{\gamma\delta}$ are given by

$$\begin{aligned} P_{\varepsilon\varepsilon} &= -t^{2}_{\sigma} \frac{1.5}{U_{pp} + \Delta_{\varepsilon}}, \\ P_{\Theta\Theta} &= -t^{2}_{\sigma} \frac{0.5}{U_{pp} + \Delta_{\Theta}}, \\ P_{\Theta\varepsilon} &= \frac{\sqrt{3}}{2} t^{2}_{\sigma} \left[\frac{1}{U_{pp} + \Delta_{\varepsilon}} + \frac{1}{U_{pp} + \Delta_{\Theta}} \right], \end{aligned} \tag{11}$$

where U_{pp} is the energy of the Coulomb repulsion of two oxygen holes at the same site. The expression for $J'_{\alpha\beta}$ are obtained from $J_{\alpha\beta}$ by replacing t^{2}_{σ} with $t_{\sigma} t'_{\sigma}$.

IV. Equation for the Adiabatic Potential

Now we are going to determine the adiabatic potential. First we need a numerical estimate for all parameters which appear in (6). We start from typical values for layered cuprates [12] in eV:

$$\begin{aligned} &\Delta_\varepsilon = 2, \quad \Delta_\Theta = 1, \quad V_{pd} = 1, \quad U_{pp} = 6, \\ &I_{\varepsilon\varepsilon} = 9, \quad I_{\Theta\Theta} = 9, \quad I_{\varepsilon\Theta} + K_{\varepsilon\Theta} = 8, \\ &t_\sigma = 1.2, \quad t'_\sigma = -0.9/\text{Å}, \quad t^{xy} = 0.6\,. \end{aligned} \tag{12}$$

After some calculations, which were described in the text, we obtain

$$J_{\varepsilon\varepsilon} = -2.3, \quad J_{\Theta\Theta} = -1.7, \quad J_{\varepsilon\Theta} = 0.9 \tag{13}$$

in eV and

$$J'_{\varepsilon\varepsilon} = 2.0, \quad J'_{\Theta\Theta} = 1.4, \quad J'_{\varepsilon\Theta} = -0.8, \quad V'_{pd} = -0.5 \tag{14}$$

in eV/Å. The secular equation for the adiabatic potential can be written on the basis of (1) and (7) as

$$\begin{vmatrix} V_1 & VQ_\varepsilon + \delta_\mathrm{r} + 0.5 J'_{\varepsilon\Theta} Q_\varepsilon & 0.5 J'_{\varepsilon\varepsilon} Q_\varepsilon & J_{\varepsilon\Theta} + J'_{\varepsilon\Theta} Q_\Theta \\ VQ_\varepsilon + \delta_\mathrm{r} + 0.5 J\ '_{\varepsilon\Theta} Q_\varepsilon & -VQ_\Theta - \delta_\mathrm{t} - 2t^{xy} - E & 0 & 0.5 J'_{\Theta\Theta} Q_\varepsilon \\ 0.5 J'_{\varepsilon\varepsilon} Q_\varepsilon & 0 & VQ_\Theta + \delta_\mathrm{t} + 2t^{xy} - E & VQ_\varepsilon + \delta_\mathrm{r} + 0.5 J'_{\Theta\varepsilon} Q_\varepsilon \\ J_{\varepsilon\Theta} + J'_{\varepsilon\Theta} Q_\Theta & 0.5 J'_{\Theta\Theta} Q_\varepsilon & VQ_\varepsilon + \delta_\mathrm{r} + 0.5 J'_{\Theta\varepsilon} Q_\varepsilon & V_2 \end{vmatrix}$$

$$+ \frac{M\omega^2}{2}(Q_\Theta^2 + Q_\varepsilon^2) + V_{pd} = 0\,, \tag{15}$$

where V_1 and V_2 are given by

$$\begin{aligned} V_1 &= VQ_\Theta + \delta_\mathrm{t} + J_{\varepsilon\varepsilon} - 2t^{xy} + (J'_{\varepsilon\varepsilon} + V'_{pd})\, Q_\Theta - E\,, \\ V_2 &= -VQ_\Theta + \delta_\mathrm{t} + J_{\Theta\Theta} - 2t^{xy} + (J'_{\Theta\Theta} + V'_{pd})\, Q_\Theta - E\,. \end{aligned} \tag{16}$$

The numerical solution of this equation yields an energy minimum at $\varrho = 0.3$ Å and $\phi \approx \pm\pi$. In this case the orthorhombic distortion is absent ($Q_\varepsilon = 0$) and consequently $\eta \to 0$.

V. Conclusion

We have shown that the so-called Zhang-Rice singlets (ZRS) [13] possess a strong coupling with the tetragonal mode Q_Θ. Due to this coupling the asymmetry parameter of the Cu(2) NQR spectra goes to zero. At the same time we have found an additional stabilization factor for the formation of ZRS. It arises from the coupling of the lower singlet states $\Psi_{\varepsilon\varepsilon}$ to the excited states $\Psi_{\varepsilon\Theta}$, $\Psi_{\Theta\varepsilon}$, and $\Psi_{\Theta\Theta}$. According to our calculations on the basis of (15) this stabilization is about -0.5 eV. Finally we like to remak that the ZRS at different sites of the crystal lattice have a rather strong interaction via the elastic field. Using the theory of interaction of inpurity centers via a phonon field [14] or via elastic media [15] we have calculated the interaction energy as

$$\begin{aligned} \mathscr{H}_{ij} = -\frac{d^i d^j}{8\pi\tilde{\varrho}\, r_{ij}^3} \Bigg[& 4\left(\frac{1}{c_t^2} - \frac{2}{c_l^2}\right) \\ & - 6\left(\frac{3}{c_t^2} - \frac{4}{c_l^2}\right) \frac{x_{ij}^2 + y_{ij}^2}{r_{ij}^2} \\ & + 15\left(\frac{1}{c_t^2} - \frac{1}{c_l^2}\right) \frac{(x_{ij}^2 + y_{ij}^2)^2}{r_{ij}^4} \Bigg] \psi_i^+ \psi_i \psi_j^+ \psi_j\,. \end{aligned} \tag{17}$$

Here c_t and c_l are the transverse and longitudinal sound velocities, respectively, $\tilde{\varrho}$ is the crystal density, and d^i is a parameter of the deformation potential ($d^i \approx RJ'_{\varepsilon\varepsilon}$). We use here for simplicity the abbreviated description of the singlet state $\Psi = \Psi_{\varepsilon\varepsilon}$. Expression (17) reveals that ZRS attract each other in the plane as well as between the planes. Both of these interactions are stronger than the superexchange between the Cu(2) spins. We have found $Q_\Theta < 0$ for ZRS. This means that the copper oxygen distance R decreases with doping. This effect is opposite to the influence on the chains which are extended by doping. Probably this competition between the tetragonal contraction in the plane and the orthorhombic elongation in the chain is responsible for the unusual behaviour of the b axis in $YBa_2Cu_3O_x$. According to [16] the b axis increases from $x = 6.5$ to 6.8, but at larger doping if decreases.

Acknowledgements

The title question of this paper is due to Prof. M. Teplov. I am very grateful to him. I am deeply indebted to Prof. D. Brinkmann, Dr. R. Markendorf, Dr. M. Mali, Dr. J. Roos, and R. Stern for useful discussions. This work is supported by the Russian Government program "High Temperature Superconductivity" No. 91001 and the Schweizerischer Nationalfonds.

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