NQR IN HIGH T_c-SUPERCONDUCTORS

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Results on NQR in $YBa_2Cu_3O_{7-y}$ are discussed.

1. Introduction

High-T_c-superconductors like $La_{2-x}Sr_xCuO_4$, $YBa(Cu_{1x}M_x)_3O_{4-y}$, $Nd_{2-x}Ce_xCuO_4$, $Bi_2Sr_2CaCu_2O_8$ remain a puzzle. In these systems superconductivity occurs in the CuO_2-planes. However, what is the mechanism for superconductivity (singlet Cooper-pairs)? Are charge (or spin-) fluctuations involved, what is the origin of anti-ferromagnetism ($T_N(n_h)$ in La_2CuO_4, in Nd_2CuO_4)? What is a good theory for the strongly correlated electronic systems (electronic–, atomic–structure)? NMR (Knight-shift $K \sim Im\chi(q,\omega)$), NQR ($\nu_Q(T) \sim$ EFG), and spin-lattice relaxation (reflects Cu-spin dynamics) are good tools to probe (local) electronic structure (charge fluctuations $\leftrightarrow$ EFG, $\cdots$), interplay of magnetism and superconductivity, role of holes at Cu–, O–sites, and oxygen distribution (s. $YBa_2Cu_3O_{7-y}$). In particular, temperature dependence of $\nu_Q(T)$, Knight-shift, and spin-lattice relaxation T_1^{-1} reflect the elementary excitations, the coupling of charge-fluctuations and spin-fluctuations, and the induced CuO-bond-length changes. Regarding the experimental situation one notes the following[1]: (a) Similar behaviour of ν_Q, K, T_1^{-1} in all high-T_c superconductors, (b) BCS-like behaviour, of superconductivity presumably singlet

Cooper-pairs, no precursor (Cooper-pairs) behaviour above T_c, (c) Anomalous behaviour of $\nu_Q(T)$ for $T \rightarrow T_c$, and a strong dependence of ν_Q on oxygen content, s. $YBa_2Cu_3O_{7-y}$ for $y = 0 \rightarrow 1$.
The Knight-shift, $K = K_{orb} + K_s$, with $K_s \rightarrow 0$, for $T \rightarrow 0$, below T_c exhibits strong anisotropy, mainly for K_{orb} the orbital contribution to K.
The Spin-lattice relaxation with $T_1^{-1} \propto \sum_q \chi''(q,\omega)$ reflects sensitively electronic correlations and has no peak below T_c as in BCS-theory. Furthermore, T_1^{-1} is strongly enhanced at Cu-sites, but not at O-sites (due to electronic correlation).A theoretical understanding of the temperature-dependence of the various quantities is presently not clear.

Regarding the situation in theory, a typical example is the discussion of an electronic theory for the NQR-frequencies $\nu_Q(T)$ in $YBa_2Cu_3O_{7-y}$ (for $y = 0, y = 1$) for the Cu(1) and Cu(2) atoms. As shown in the table, ν_{Q1}, ν_{Q2} depend sensitively on the hole distribution for d-orbitals at Cu-sites.

In the following we concentrate on discussing the determination of the NQR-frequencies ν_{Q1} and ν_{Q2} of Cu(1) and Cu(2) atoms in $YBa_2Cu_3O_{7-y}$, for $y = 0$ and $y = 1$.[2]

2. Theory

NQR frequencies result from the coupling of Nuclear Quadrupole Moment to Electric Field Gradient (EFG), $\nu_Q \sim q_{ij}, q_{ij} = \frac{\partial^2 q}{\partial x_i \partial x_j}$. Note, the EFG is a tensor with principal axis x,y,z. The EFG are characterized by p_{zz} and asymmetry parameter $\eta = (q_{xx} - q_{yy})/q_{zz}$. Note, B_{Hf} (hyperfine field may shift NQR frequencies) due to the magnetic moments $\mu(Cu)$. EFG acts at Cu(1), Cu(2) sites, s. Fig. 1, and has (1.) ionic contribution due to lattice of ion-charges, treated like point-charges, ν_Q^{ion}, and (2.) electronic contribution due to the deformation of the d-electron shell in the orbitals $3d_{x^2-y^2}$, etc. at Cu-sites, ν_Q^{el}. Thus, if the principal axes of both contributions are the same, one finds for the NQR-frequencies (nuclear spin of Cu I = 3/2)

$$\nu_Q = \{\frac{e^2}{2} Q(1-\gamma_\infty) q_{zz}^{ion} + q^{val}\}(1 + \frac{\eta^2}{3})^{1/2} \qquad (1)$$

In Eq. (1) Q refers to the quatrupole moment, γ_∞ to the Sternheimer anti-shielding factor, η to the asymmetry factor. The contributions q_{zz}^{ion} and q^{val} denote the EFG contribution due to the lattice of ionic point charges (calculated using Evjen-method) and due to the incomplete, distorted d-shell at Cu-sites.

The z-axis is obtained from the component q_{ii} which is largest. The electronic contribution to ν_Q is given by

$$q^{val} = \frac{1}{2}(1-R)e^2 Q q_{zz}^{val} \tag{2}$$

with (A=const.)

$$q_{zz}^{val} = A < r^{-3} >_{3d} \{n_h(3d_{3z^2-r^2}) - n_h(3d_{x^2-y^2}) - n_h(3d_{xy}) + \frac{1}{2}n_h(3d_{xz}) - \frac{1}{2}n_h(3d_{yz})\} \tag{3}$$

The derivation of this important equation is straightforward[1,2]. Eq.(3) exhibits the sensitive dependence of the NQR-frequencies on the d-hole distribution. $n_h(3d_{xy})$ denotes the number of holes in the $3d_{xy}$ orbital of Cu(1) or Cu(2), etc.

Note, since experiment demonstrates the presence of holes in the d-shell of Cu, one expects q^{val} to be an important contribution to EFG or ν_Q in high T_c-compounds.

In the following we calculate ν_{Q1} and ν_{Q2} in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ using Eq. (1) - (3). First, we asume a given charge distribution for calculating the ν_Q^{ion}, and then we calculate through q^{val} the corrections to the ionic model. The assumed charge configurations are: Y^{3+}, Ba^{2+} for both compounds, and $O(2)^{2-}$, $O(3)^{2-}$, $Cu(1)^{+}$, $Cu(2)^{2+}$, $O(4)^{2-}$ for $YBa_2Cu_3O_6$, whereas $O(2)^{1.95-}$, $O(3)^{1.95-}$, $Cu(1)^{2.4+}$, $Cu(2)^{2.1+}$, $O(4)^{2-}$, $O(1)^{1.8-}$ for $YBa_2Cu_3O_7$. For this we use also experimental results for ν_Q in Cu_2O with Cu^{+} and La_2CuO_4 with Cu^{++}. Thus, we substitute for ν_Q in Eq. (1) the experimental result, calculate ν_Q^{ion} (1. term in Eq. (1)) for point charge lattice using as usually the Evjen method[2], substituting the result into Eq. (1), and deduce then (solving Eq. (1) for the unknown q^{val}) ν_Q^{val} or q^{val} for Cu_2O and La_2CuO_4. After this procedure, we calculate the corrections for q^{val} in $YBa_2Cu_3O_{7-y}$ by taking into account the different atomic- and electronic structure of this high T_c-compound. Details are discussed by Garcia et al.[2]. Combining this with the direct calculation of ν_Q^{ion}, we obtain results for ν_{Q1} and ν_{Q2} in (123)-systems which are given in the table. Also, we calculate

$$\eta = (q_{xx} - q_{yy})/q_{zz} \tag{4}$$

using the approximation $q_{xx}^{val} = q_{yy}^{val} = -\frac{q_{zz}^{val}}{2}$, i.e. assuming that the Laplace equation holds at the Cu nucleus, which is reasonable for d-electrons. In order to illustrate how we determine the NQR-frequencies in detail, we discuss the determination of ν_{Q1} of Cu(1) in YBa2Cu$_3$O$_6$. Since Cu$_2$O is ionic with Cu$^+$, we expect $q^{val} \approx 0$. Actually, calculating $\nu_Q^{ion} = (e^2Q/2)(1-\gamma_\infty)q_{zz}^{ion}$ by using the Evjen method for the calculation of the EFG due to the lattice of ionic charges, we find in agreement with experiment that $\nu_{Q1} \approx \nu_Q^{ion}$ in Cu$_2$O. Since the atomic environment of Cu(1) in YBa$_2$Cu$_3$O$_6$ is nearly the same as of Cu in Cu$_2$O, we use also $q^{val} \approx 0$ in YBa$_2$Cu$_3$O$_6$. In addition we calculate ν_Q^{ion} using the Evjen method. Then, assuming that γ_∞ is the same in both compounds, one gets

$$\nu_{Q1}(123) \approx \nu_Q(Cu_2O)\ \{q_{zz}^{ion}(123)/q_{zz}^{ion}(Cu_2O)\}$$

Substituting the experimental result for $\nu_Q(Cu_2O)$ and the results for q_{zz}^{ion} we obtain

$$\nu_{Q1}(123) = 31.5MHz\ (exp: 30.1)$$

Furthermore, one gets $\eta_1 = 0$ and $z \| c$.

The other NQR frequencies are similarly determined. ν_{Q2} for Cu^{++}(2) in YBa$_2$Cu$_3$O$_6$ is calculatd by assuming that the atomic environment of Cu(2) in La$_2$CuO$_4$ and (123)-systems is nearly the same. Thus, in lowest approximation q^{val} determined for La$_2$CuO$_4$ from

$$\nu_{Q2}^{val} = \nu_{Q2}^{exp}(La_2CuO_4) - \nu_{Q2}^{ion}La_2CuO_4)$$

is also used for YBa$_2$Cu$_3$O$_6$. Then, using Tight-binding theory we correct q^{val} for (123)-compound, due to Cu-O bond-length differences. This correction changes ν_{Q2} from 29.6 MHz to 22 MHz, which agrees well with the experimental result. The calculation of ν_{Q1} and ν_{Q2} in YBa$_2$Cu$_3$O$_7$ proceeds in the same spirit. Here, we use also Eq. (3) for calculating how differences in η_h for La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$ change the NQR-frequencies[2]. Note, the shift of ν_{Q2} in YBa$_2$Cu$_3$O$_7$ expected for $B_{Hf} \neq 0$ is neglected. This is presumably justified, since effectively $B_{Hf}^{eff} \to 0$ due to fluctuations of the Cu-magnetic moments.

Note, the theory explains well the transition from $\nu_{Q1} > \nu_{Q2}$ in YBa$_2$Cu$_3$O$_6$ to $\nu_{Q1} < \nu_{Q2}$ observed for YBa$_2$Cu$_3$O$_7$. Discrepancy between theory and

experiment with respect to η for $YBa_2Cu_3O_7$ results from the approximation used for q_{ii}^{val}.

From ^{17}O nuclear-magnetic-resonance experiments on $YBa_2Cu_3O_7$, the EFG on the different oxygen atoms have been obtained[4]. In the same work, a charge configuration in which only Cu^{2+} and $O^{13/7-}$ appear has been proposed in order to calculate the field gradients.

Although a good agreement with experiment is obtained, this charge distribution is incompatible with the NQR results for Cu, since it gives $\eta_1 \cong 0.3$ whereas experiment give values close to $\eta_1 \cong 1$. We have calculated the ionic EFG with our assumed charge distribution. Although the value of γ_∞ is not known for oxygen, we can deduce it from the equation for the total field gradient applied to O(4)

$$\vec{q} = (q_{x'x'}^{ion}, V_{y'y'}^{ion}, V_{z'z'}^{ion})(1 - \gamma_\infty) + (V_{x'x'}^{val}, V_{y'y'}^{val}, V_{z'z'}^{val})$$

Since we have supposed $O(4)^{2-}$, it should hold

$$1 = \gamma_\infty = \frac{V_{x'x'}}{V_{xx}^{ion}} = \frac{V_{y'y'}}{V_{y'y'}^{ion}} = \frac{V_{z'z'}}{V_{z'z'}^{ion}}$$

We get

$$\frac{V_{x'x'}}{V_{x'x'}^{ion}} = 15.4 \; ; \frac{V_{y'y'}}{V_{y'y'}^{ion}} = 13.78 \quad \frac{V_{z'z'}}{V_{z'z'}^{ion}} = 14.3$$

In order to calculate the EFG for the other oxygens, we take for $1 - \gamma_\infty$ the average of those three previous values.

The results for the EFG (ionic) are given in Table II. Note, there is agreement between our calculated values and the experimental results regarding the x, y, and z principal axis. Furthermore, our values are close to the experimental ones, and the z-principal axis lies along the Cu-O bond axis that induces us to think that the small quantity of holes on the oxygens will occupy the orbitals involved in the Cu-O covalent bonding. The equation for q_{zz}^{val} in case of p-orbital (analogous to Eq. (3)) is

$$q_{zz}^{val} = B < r^{-3} >_{2p} \{n_h(2p_z) - \frac{1}{2}n_h(2p_x) - \frac{1}{2}n_h(2p_y)\}$$

Assuming, like Takigawa et al.[4] $< r^{-3} >_{2p} (1 - R) = 3.63$, which is 70% of the atomic $< r^{-3} >_{2p}$ one gets:

$$q^{val}(O(2)) = (\ \ 0.133, -0.066, -0.066)$$
$$q^{val}(O(3)) = (-0.066,\ \ 0.133, -0.066)$$
$$q^{val}(O(1)) = (-0.066,\ \ 0.133,\ \ 0.066)$$

With these values we calculate the total EFG, which are given in Table II.

The agreement with the experimental results is reasonable as one can see from the asymmetry parameters

$$n_1^{exp} = 0.4,\ \ n_1^{calc} = 0.44,\ \ n_2^{exp} = 0.21,\ \ n_2^{calc} = 0.11$$
$$n_3^{exp} = 0.24,\ \ n_3^{calc} = 0.12,\ \ n_4^{exp} = 0.31,\ \ n_4^{calc} = 0.36$$

The disagreement of n_2^{calc} and n_3^{calc} with the experimental values may be due to our assumption that the holes only occupy the orbital along the Cu-O bond-axis. There are also some covalency between the oxygens O(2) and O(3), which could reduce the value of q_{zz}^{val} and consequently q_{zz}^{tot}, increasing the asymmetry parameters for O(2) and O(3).

The temperature dependence[3], s. Fig. 2, of $\nu_{Qi}(T)$ is presently not well understood. Note, in particular $\nu_{Q1} \to 0$ for $T \to T_c$, which is rather anomalous. Since charge- fluctuations affect EFG, $q_{ij} \to (q_{ij}/\varepsilon(\omega))$, ε denotes the dielectric constant, it might be that important physics[1,3] is revealed by this behaviour. Possibly, $\varepsilon \to \infty$ is caused by a phase transition (due to oxygen displacements, reordering or ferroelectricity(?)).

References

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2 Garcia M.E., and Bennemann, K.H., Phys. Rev. B40, (1989).

3 Riesemeier, H. et al., to be published.

4 Takigawa, M., Hammel, P.C., Meffner, R.M., Z. Fisk., Ott, K.C., and Thompson, J.D., Phys. Rev. Lett. 63, 1865 (1989).

Table I: NQR results for $YBa_2Cu_3O_{7-y}$. The ionic contribution to the NQR-frequencies is calculated for a lattice of point charges. The d-electrons EFG contribution q^{val} is estimated with the help of experimental results for ν_Q in Cu_2O and La_2CuO_4. B_{Hf} refers to the hyperfine field.

	$YBa_2Cu_3O_6$	$YBa_2Cu_3O_7$
$[\frac{e^2}{2}Qq_{zz}^{ionic}(1-\gamma_\infty)]_1$	31.5MHz	−32.36MHz
$[\frac{e^2}{2}Qq_{zz}^{ionic}(1-\gamma_\infty)]_2$	−22.5MHz	−18.9MHz
$(q^{val})_1$	0.0MHz	52.1MHz
$(q^{val})_2$	45.4MHz	47.1MHz
$\eta_1(\eta_1^{exp})$	0.0(0)	0.67(∼ 1)
$\eta_2(\eta_2^{exp})$	0.0(0)	0.07(0.01 ÷ 0.1)
$\nu_{Q1}(\nu_{Q1}^{exp})$	31.5(30.1)MHz	21.2(22.0)MHz
$\nu_{Q2}(\nu_{Q2}^{exp})$	22.87(22.87)MHz	28.0(31.5)MHz
$(B_{Hf})_1$	< 0.01T	< 0.02T
$(B_{Hf})_2$	7.66T	< 0.02T

Table II: Calculated and experimental values of EFG for the different oxygen sites in $YBa_2Cu_3O_7$. Results are given in MHz.

	O(1)	O(2)
ionic EFG	(-0.41, 1.58, -1.17)	(0.98, -0.54, -0.43)
total EFG	(-0.47, 1.71, -1.23)	(1.11, -0.61, -0.49)
exp. EFG	(-0.484, 1.629, -1.145)	(0.986, -0.598, -0.387)

	O(3)	O(4)
ionic EFG	(-0.36, 0.83, -0.47)	(-0.35, -0.76, 1.1)
total EFG	(-0.42, 0.96, -0.53)	(-0.35, -0.76, 1.1)
exp. EFG	(-0.368, 0.966, -0.598)	(-0.375, -0.721, 1.096)

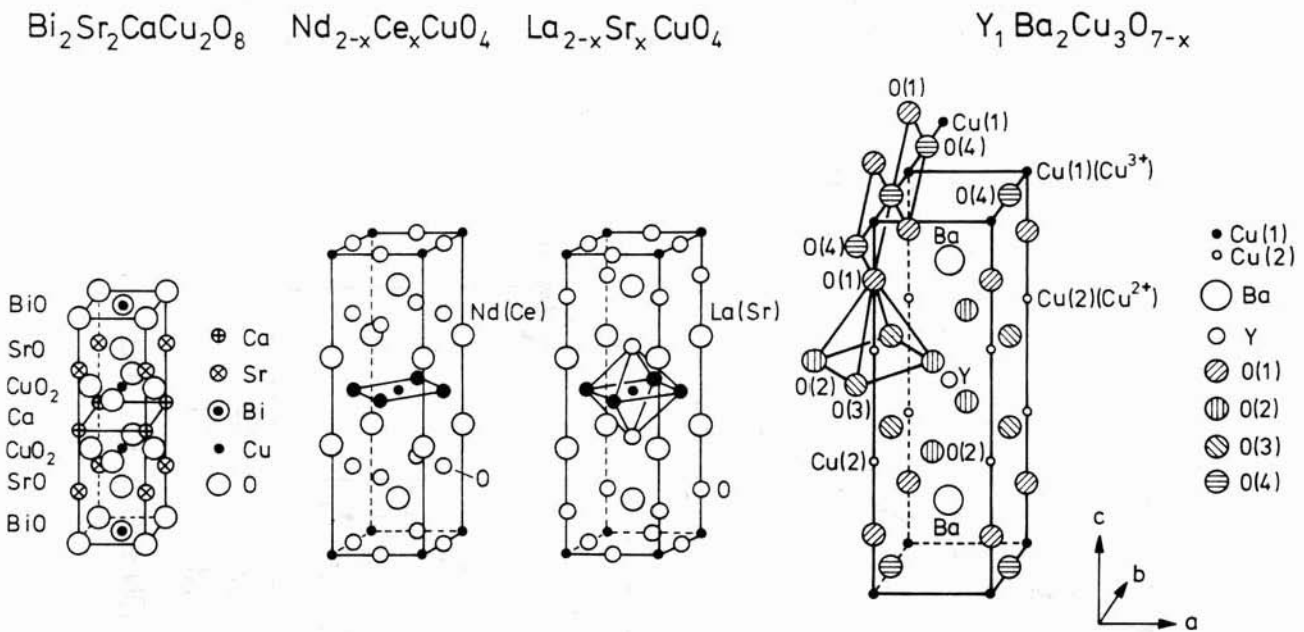

Fig. 1: Lattice structure of some high-T_c-superconductors.

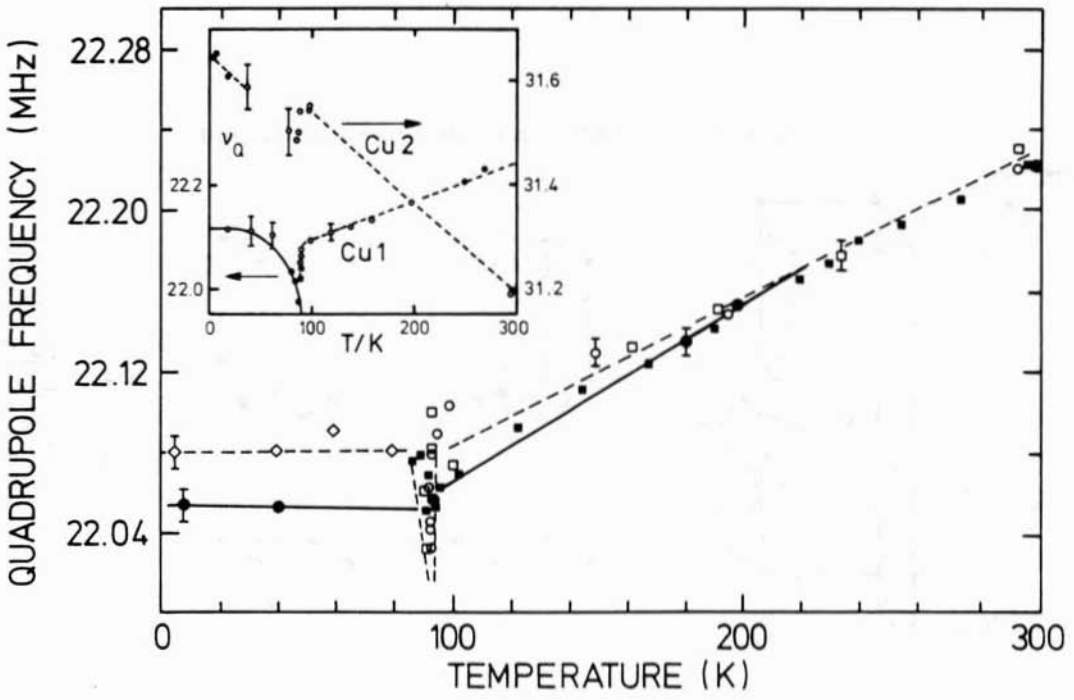

Fig. 2: Temperature-dependence of the NQR-frequency $\nu_Q(T)$ for Cu(1) and Cu(2)-sites of ^{63}Cu in $YBa2Cu_3O_7$. Note the drastic temperature-dependence near the superconducting transition temperature T_c. (Results refer to recent experiments by H. Riesemeier et al., and D. Brinkmann et al., to be published.)