NQR IN HIGH T_c-SUPERCONDUCTORS

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Results on NQR are discussed. A theory is presented determining the NQR-frequencies ν_Q for Cu(1) and Cu(2) in $YBa_2Cu_3O_{7-y}$, and also the asymmetry parameter η of the EFG tensor. The significance of the temperature-dependence ν_Q is 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 $T \to T_c$, and a strong dependence of ν_Q on oxygen content, s. $YBa_2Cu_3O_{7-y}$ for $y = 0 \to 1$.
The Knight-shift, $K = K_{orb} + K_s$, with $K_s \to 0$, for $T \to 0$, 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), $\nu_Q \sim V_{ij}, V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$. Note, the EFG is a tensor with principal axis x,y,z. The EFG characterized by the z-axis and asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. 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, one finds for the NQR-frequencies

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

In Eq. (1) Q refers to the quatrupole moment, γ_∞ to the Sternheimer antishielding factor, η to the asymmetry factor. The contributions q_{zz}^{ion} and q^{val} denote the

Table 1: 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.

	$YBa_2Cu_3O_6$	$YBa_2Cu_3O_7$
$[\frac{e^2}{2}Qq_{zz}^{ionic}(1-\gamma_\infty)]_1$	4.86MHz	−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($\sim$ 1)
$\eta_2(\eta_2^{exp})$	0.0(0)	0.07(0.01 $\div$ 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

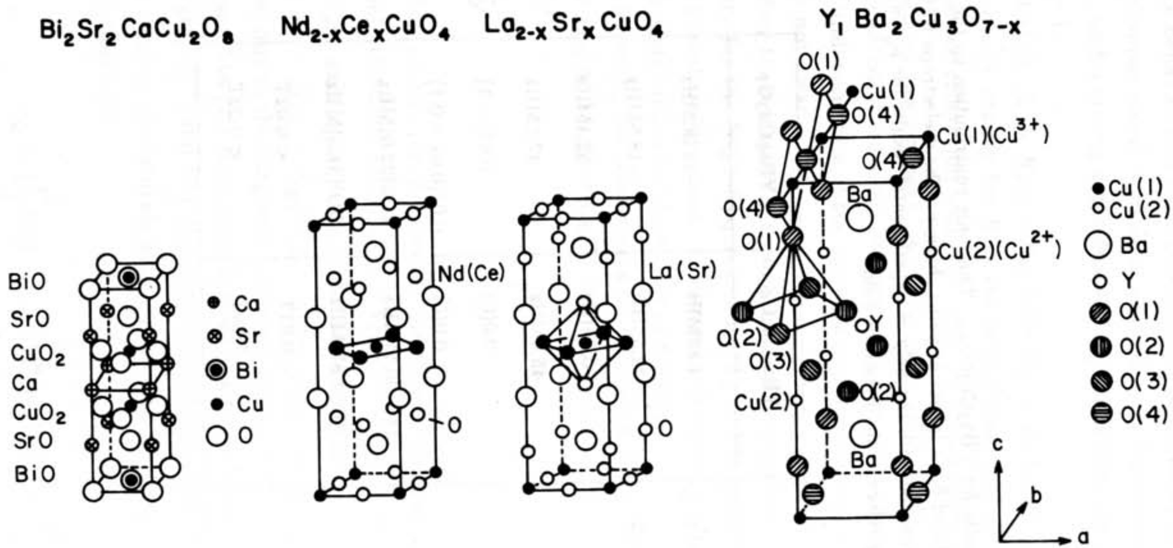

Fig. 1: Lattice structure of some high-T_c-superconductors.

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 V_{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, if high T_c compounds had strong ionic character in CuO_2-planes, then

$$q^{val} \approx 0$$

as in Cu_2O, for example. However, $q^{val} \approx 0$ disagrees strongly with experiment. Thus, we conclude $q^{val} \neq 0$ is 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). 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 (of course, $q^{val} \approx 0$, for Cu_2O). 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. In calculating q^{val}, Eq. (3) has been used. the z-axis of the EFG tensor is deduced from the largest component V_{ii} of the EFG. Also, we calculate

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

using the approximation $q_{xx}^{val} = q_{yy}^{val} = -\frac{q_{zz}^{val}}{2}$.

In order to illustrate how we determine the NQR-frequencies in detail, we discuss the determination of ν_{Q1} of Cu(1) in YBa2Cu3O6. Since Cu_2O is ionic, 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_2O. Since the atomic environment of Cu(1) in $YBa_2Cu_3O_6$ is nearly the same as of Cu in Cu_2O, we use also $q^{val} \approx 0$ in $YBa_2Cu_3O_6$. 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 $YBa_2Cu_3O_6$ is calculatd by assuming that the atomic environment of Cu(2) in La_2CuO_4 and (123)-systems is nearly the same. Thus, in lowest approximation q^{val} determined for La_2CuO_4 from

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

is also used for $YBa_2Cu_3O_6$. ($\nu_Q^{val} \equiv (1+\frac{\eta^2}{3})^{1/2} \cdot q^{val}$). 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 $YBa_2Cu_3O_7$ proceeds in the same spirit. Here, we use also Eq. (3) for calculating how differences in η_h for La_2CuO_4 and $YBa_2Cu_3O_7$ change the NQR-frequencies[2]. Note, the shift of ν_{Q2} in $YBa_2Cu_3O_7$ 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 $YBa_2Cu_3O_6$ to $\nu_{Q1} < \nu_{Q2}$ observed for $YBa_2Cu_3O_7$. Discrepancy between theory and experiment with respect to η for $YBa_2Cu_3O_7$ results from the approximation used for V_{ii}^{val}.

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.

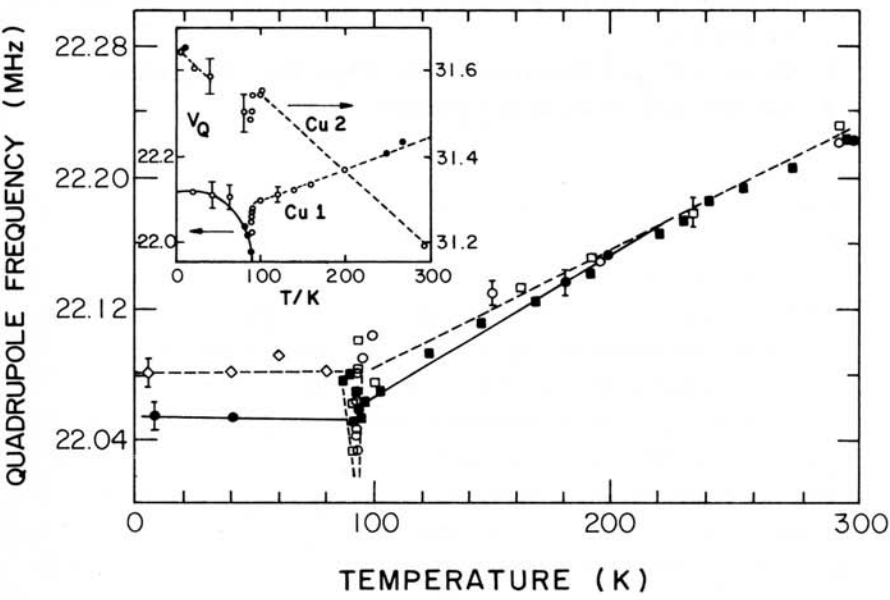

Fig. 2: Temperature-dependence of the NQR-frequency $\nu_Q(T)$ for Cu(1) and Cu(2)-sites of ^{63}Cu in YBa2Cu_3O_7. Note the drastic temperature-dependence near the superconducting transition temperature T_c. (Results refer to recent experiments by H. Riesemeier et al., and D. Brinkmann et al., to be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

Since charge- fluctuations affect EFG, $V_{ij} \rightarrow (V_{ij}/\varepsilon(\omega))$, ε denotes the dielectric constant, it might be that important physics[1,3] is revealed by this behaviour. Possibly, $\varepsilon \rightarrow \infty$ is caused by a phase transition (due to oxygen displacements, reordering or ferroelectricity(?)).

References

1 Garcia M.E., and Bennemann K.H., review to be published (1990, ed. B. Chakraverty).

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

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