Charge-inhomogeneity doping relations in YBa$_2$Cu$_3$O$_y$ detected by angle-dependent nuclear quadrupole resonance

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The origin of charge inhomogeneity in YBa$_2$Cu$_3$O$_y$ is investigated using an experimental method designed to determine the nuclear quadrupole resonance (NQR) asymmetry parameter $\eta$ for very wide NQR lines at different positions on the line. The method is based on the measurement of the echo intensity as a function of the angle between the radio frequency field $\mathbf{H}_1$ and the principal axis of the electric field gradient. Static charge inhomogeneity deduced from $\eta>0$ is found in this compound, but only in conjunction with oxygen deficiency. This limits considerably the possible forms of charge inhomogeneity in bulk YBa$_2$Cu$_3$O$_y$.

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The discussion on the mechanism for high-temperature superconductivity (HTSC) is focused these days on the presence or absence of charge and spin inhomogeneity in the CuO$_2$ planes. Such inhomogeneity can lead to a one-dimensional boundary, possibly in the form of stripes, between “hole-rich” and “hole-poor” regions and, allegedly, to superconductivity. Indeed, it is now established by both surface and bulk techniques that most of the underdoped cuprates phase separate into “hole-rich” and “hole-poor” regions. For example, there is a consensus derived from surface sensitive scanning tunneling microscopy (STM) experiments on underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ that the planes are inhomogeneous. A different example is La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) where the evidence for phase separation is derived from experiments sensitive to both magnetic fluctuation, such as muon spin relaxation ($\mu$SR), and charge fluctuations such as nuclear quadrupole resonance (NQR). Even in very underdoped YBa$_2$Cu$_3$O$_y$ (YBCO) phase separation is observed; neutron scattering from phonons related to charge inhomogeneity is found in doping levels up to YBCO$_{6.5}$ and $\mu$SR detects a spin glass phase for a similar doping range. However, the origin of this phase separation is still not clear; it is coming from competing phases in the CuO$_2$ plane, or does it simply stem from the quenched disorder introduced by doping?

A possible way to address this question is to apply NQR to YBCO$_y$ since in this compound one can distinguish between different in-plane coppers [Cu(2)] resonance lines, and associate each line with a local environment. However, a standard NQR based determination of charge homogeneity is not available to date due to the complicated and very wide spectrum of underdoped YBCO (which will be reviewed below). The purpose of this work is to overcome the NQR problems and to shed light on the evolution of charge homogeneity in the bulk of YBCO close to optimal doping. For this purpose we developed a new experimental technique based on the measurement of the Cu(2) NQR echo intensity as a function of the angle between the radio frequency (rf) field, $\mathbf{H}_1$, and the principal axis of the electric field gradient (EFG) at the copper site. We call this angle-dependent NQR technique ADNQR.

Standard NQR is based on the fact that nuclei with spin $I>1/2$ can be viewed as positively charged oval objects. As a result, their energy inside a solid depends on their orientation in the electrostatic potential $V(r)$ generated by the other nuclear and electronic charges. When the nuclear poles are close to positive charges their energy is high, and when the poles are close to negative charges the energy is low. The energy difference between different orientations is determined by the EFG tensor $V_{ij}=\partial^2V/\partial x_i\partial x_j$ at the position of the Cu nuclei. The directions can be chosen so that $V_{ij}$ is diagonal. These directions are known as the principal axis of the EFG. Due to the Laplace equation $(V_{xx}+V_{yy}+V_{zz}=0)$ the NQR Hamiltonian is determined by only two parameters, $\nu_q$ and $\eta$, and is given by

$$\mathcal{H}_q = \frac{\hbar}{6}[3I_x^2 - I^2 + \eta(I_x^2 - I_y^2)],$$

where $\nu_q$ is a frequency scale proportional to the EFG $V_{zz}$ and

$$\eta = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

is a dimensionless number. It is customary to choose the directions so that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, and therefore $0 \leq \eta \leq 1$. For the spin 3/2 Cu nuclei this Hamiltonian has only one resonance frequency given by

$$f = \nu_q \sqrt{1 + \frac{\eta^2}{3}}.$$
situation is demonstrated in Fig. 1 obtained using a toy model. The parameters of this model are chosen for clarity only and have no implications on the physical situation in YBCO. A plane of a square lattice with total charge $Q$ is sandwiched between two similar planes with total charge $-Q/2$ each. The electric field produced by each ion is screened with a screening length of two lattice sites. The charge in the central plane is distributed in the form of a line along one of the principal axes of the EFG. The pulse length is optimized at $\theta=90^\circ$ and kept constant throughout the sample rotation. The inset shows the experimental configuration.

$$\lambda = \frac{1}{2\sqrt{3} + \eta^2} \left[ \left(9 + \eta^2 + 6\eta \cos(2\phi)\right) \sin^2(\theta) + \left[2\eta \cos(\theta)^2\right]^{1/2} \right],$$

and $M_0$ is a constant.

We apply the ADNQR experiment to oriented powder of YBa$_2$Cu$_3$O$_y$ with $\mathbf{e}\parallel \hat{z}$. In such powders the $\mathbf{a}$ and $\mathbf{b}$ directions are mixed. In this case $M$ is obtained from Eq. (4) by averaging over $\phi$, namely,

$$M(\eta, \theta, \phi) = \frac{1}{2\pi} \int_0^{2\pi} M(\eta, \theta, \phi) d\phi.$$  

This averaging must be done numerically, and the expected $M(\eta, \theta, M(\eta, 90^\circ))$ for various values of $\eta$ is presented in Fig. 2. The pulse length ($t_{\pi/2}$) is optimized at $\theta=90^\circ$ and is kept constant throughout the rotation of the sample with respect to the coil.

The ADNQR technique has three major strengths: (1) It allows the determination of $\eta$ even for a wide NQR spectrum and at every point on the spectrum, thus providing a great advantage over nuclear magnetic resonance (NMR), which can determine $\eta$ only from the entire spectrum with no local resolution; (2) unlike NMR, where one needs to fit the spectrum to five different parameters out of which only one is $\eta$, ADNQR is sensitive only to $\eta$; and (3) it allows the determination of $\eta$ without the application of a static magnetic field and can be used even in the superconducting state. The weakness of ADNQR is that it is very insensitive at small $\eta$'s as demonstrated in Fig. 2.

Before presenting the ADNQR results it is essential to review the NQR frequency assignments in YBCO. In the (a), (b), and (c) panels of Fig. 3 we show the NQR lines at a temperature of 100 K for three different samples with $y$
It is simplest to review the enriched $y=6.678$ spectrum in panel (b) first. This spectrum exhibits three peaks at $f = 28.1$, $29.2$, and $30.8$ MHz (none of which are from the $^{65}\text{Cu}$ isotope). The peaks are classified in terms of the number of oxygen surrounding the chain copper [Cu(1)] neighboring the detected Cu(2). The higher the oxygen coordination of the Cu(1), the higher the frequency. In other words, the peak in $f = 30.8$ MHz is from Cu(2) adjacent to a Cu(1) in a fully oxygenated environment [Cu(2)$_4$], the peak in $f = 28.1$ MHz is from Cu(2) near a Cu(1) in a fully oxygen deficient environment [Cu(2)$_2$], and finally, the peak in $f = 29.2$ MHz is from Cu(2) whose neighboring Cu(1) is missing one oxygen [Cu(2)$_3$].

The main features in the spectrum of the natural YBCO$_7$ (without enrichment) depicted in panel (a) are two resonance peaks at $f = 31.55$ and $29.3$ MHz. In addition, each peak has two shoulders to the left ($31$ MHz/$28.7$ MHz) and right ($32$ MHz/$29.7$ MHz) of the biggest peak. The origin of the right shoulder is not clear. The left shoulder is associated again with a partially oxygen deficient environment [mostly Cu(2)$_3$]. This spectrum, including the shoulders, resembles the spectrum obtained by others$^{13,14}$ where the lines are identified as the plane-copper isotopes [$^{65}\text{Cu}(2)$] and [$^{63}\text{Cu}(2)$]. The ratio between the peak intensity of the two isotopes is the one expected from their natural abundance, indicating that our spectrometer functions properly.

It is important to mention that the Cu(1) can also contribute intensity to the Cu(2) signal$^{14}$. This is demonstrated in panel (c) for YBCO$_{6.08}$. In this antiferromagnetic sample the Cu(2) signal is at $f = 90$ MHz$^{15}$ and in panel (c) only the two isotopes of Cu(1) can be seen$^{14}$. This panel clarifies our careful choice of oxygenation level of the underdoped compound. The Cu(2) peaks of the $y=6.678$ sample are not contaminated by the Cu(1) signal.

The ADNQR experiments in the YBCO$_7$ sample were done on the $^{63}\text{Cu}(2)$ peak and the two shoulders. In YBCO$_{6.678}$ we investigated the peaks of all different local environments. The frequencies where ADNQR was applied are marked by arrows in panels (a) and (b). The ADNQR experiments were also done at $T = 100$ K temperature using an automated sample rotor. To improve $H_1$ homogeneity we used a spherical coil.

The ADNQR results for YBCO$_7$ and YBCO$_{6.678}$ in the $\theta = 0$–$180$ range are depicted in Fig. 4. In all cases the intensities at $\theta = 0$ and $180$ are lower than at $\theta = 90$, as it should be. It is also clear that the intensity as a function of angular...
deviation from $\theta = 90^\circ$ drops faster for the Cu(2)$_4$ in both dopings. This is a model-independent observation of the fact that $\eta$ is smallest for Cu(2)$_4$. The fit of Eq. (6) to the experimental data is demonstrated by the solid lines. In the fit we allow a common finite base line for a given sample, in order to account for some unknown amount of misalignment. We found 24% and 17% misaligned crystallines in the YBCO$_7$ and YBCO$_{6.678}$, respectively. This misalignment is typical. The best fit for YBCO$_7$ peak gives $\eta = 0.01 \pm 0.01$.

The best fit for YBCO$_7$ peak gives $\eta = 0 \pm 0.15$ for the Cu(2)$_4$ in the YBCO$_{6.678}$ sample ($f = 30.8$ MHz). In contrast, in oxygen deficient environments in both YBCO$_7$ and YBCO$_{6.678}$ $\eta = 0.6$. This is the major finding of our work.

The data from YBCO$_{6.678}$ are evidence for charge anisotropy in a highly doped YBCO. As mentioned before, to date, static charge/spin inhomogeneity has been detected in YBCO by neutron scattering and muSR only up to $y \leq 6.35$. However, the possibility of electronic phase separation, reflected by $\eta > 0$, is found (within our experimental sensitivity) only in conjunction with quenched disorder. This means that Cu(2)$_4$ cannot reside on a static boundary between two phases of different charge concentration, like the boundary generated by our toy model. This result is in accordance with recent STM measurements. We thus conclude that in YBCO charge inhomogeneity stems from quenched disorder.

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