Charging Effects of Vortex Core in High Temperature Superconductors Probed by Nuclear Quadrupole Interaction

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From high resolution measurements of the nuclear quadrupole frequencies we obtain experimental evidence that a vortex in high T_c superconductors (HTSC) traps a finite electric charge. In slightly overdoped $YBa_2Cu_3O_7$ the vortex is negatively charged by trapping electrons, while in underdoped $YBa_2Cu_4O_8$ it is positively charged by expelling electrons. The sign of the trapped charge is opposite to the sign predicted by the conventional BCS theory. Moreover, in both materials the deviation of the magnitude of the charge from the theory is significant. These features can be attributed to the novel electronic structure of the vortex in HTSC.

Key words: NMR; NQR; Quadrupole Interactions; Vortex Core; High-T_c Superconductors.

1. Introduction

A vortex line in the type-II superconductors can support a magnetic flux with a flux quantum $\Phi_0 = hc/2e (= 2.07 \times 10^{-7}$ Oe·cm^2) [1], which has been confirmed experimentally more than 4 decades ago. On the other hand, it is only very recent that another prominent feature, namely the possibility that a vortex of the superconductor can accumulate a finite electric charge as well, has come to be realized [2 - 5]. The vortex charge appears as a result of the chemical potential difference between the vortex core and the region away from the vortex core. It should be emphasized that the sign and magnitude of this charge is closely related to the microscopic electronic structure of the vortex, which in turn reflects all the fundamental natures of the superfluid electrons and the low energy excitation out of the condensate. Moreover, it has also been pointed out recently that the vortex charge strongly affects the dynamical properties of the vortex [6 - 10]. For instance, the origin of the vortex Hall anomaly has been attributed to the vortex charge. Though the clarification of the issue of the vortex charge serves as an important test of the predictions for the vortex electronic structure and the dynamics, it has never been examined experimentally so far. This is mainly because in conventional superconductors the magnitude of the accumulated charge within the core is very small and is extremely difficult to observe.

In this paper we report a straightforward attempt to identify the vortex charge in the high temperature superconductors (HTSC) by high resolution measurements of the nuclear quadrupole frequency ν_Q, which is very sensitive to the local charge density [11]. We show that a vortex in HTSC indeed traps a small but finite electronic charge as well. In slightly overdoped $YBa_2Cu_3O_7$ the vortex is negatively charged, while in underdoped $YBa_2Cu_4O_8$ it is positively charged. The sign of the trapped charge is opposite to the sign predicted by the conventional BCS theory. Moreover, in both materials, the accumulated charge is much larger than expected in the ordinary superconductors. We discuss several possible origins for these discrepancies.

2. Experimental

We used slightly overdoped $YBa_2Cu_3O_7$ and underdoped $YBa_2Cu_4O_8$, from which the NQR and NMR spectra are very sharp compared to those of other HTSC. The NMR spectra were obtained from powders with grains smaller than 33 μm. The grains were aligned along the c-axis by a high external field at room temperature, and then fixed with epoxy (Stycast 1266). The Cu NQR and NMR spectra were obtained by a conventional pulse spectrometer. The NMR experiments were performed under the field cooling condition at a constant field of 9.4 T by using a highly-homogeneous superconducting magnet which was stabilized to less than 1 ppm during the experiments. The measurement in the vortex state was made in the so-called Bragg-glass phase in which the quasi-long-range order of the vortex lattice is preserved.

The principle of our experiment is the following. In the measurement, only the resonance of the ^{63}Cu(2) nuclei *outside the vortex core* is detected. This is because the applied field is much smaller than H_{c2}, and hence the core region occupies a smaller area in the sample. If the vortex core traps (expels) a finite amount of electrons, the electron density outside the core should decrease (increase) from that in zero field.

To elucidate the vortex charge, a direct observation of the local carrier density is strongly required. It has been pointed out by many authors that ν_Q in HTSC's is very sensitive to the local hole density [12 - 15]. We were able to detect the change of carrier density through the change of ν_Q. In a solid, an electron distribution with spherical asymmetry such as unclosed 3d shells and noncubic surrounding ions, induces a local electric field gradient (EFG) in the vicinity of the nucleus. This EFG lifts the degeneracy of the nuclear spin levels, interacting with the nuclear quadrupole moment Q_N. The relevant information is obtained from the nuclear quadrupole resonance (NQR) in zero magnetic field and the nuclear magnetic resonance (NMR) in a finite magnetic field. For the ^{63}Cu nuclei with spin I = 3/2, the NQR resonance frequency ν_Q^{NQR} is expressed as

$$\nu_Q^{NQR} = \frac{e^2 Q_N q_{zz}}{2h}\sqrt{1+\frac{\eta^2}{3}} = \nu_Q\sqrt{1+\frac{\eta^2}{3}} \quad (1)$$

where eq_{zz} is the largest principle (z-axis) component of the EFG at the nuclear site, Q_N (= -0.211 barn for ^{63}Cu) is the quadrupole moment of copper nuclei [16].

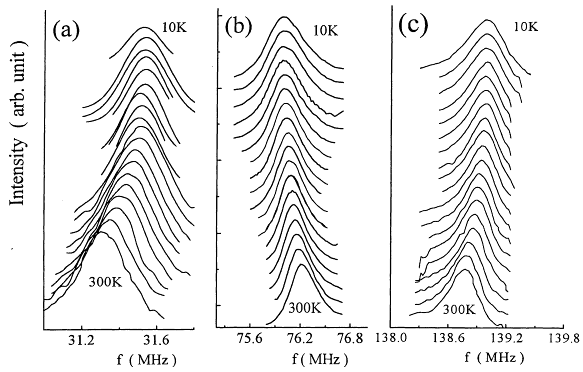

Fig. 1. The NQR spectra (a), and the the lower (b) and upper (c) NMR satellite spectra at 9.4 T of the ^{63}Cu(2) site of the $YBa_2Cu_3O_7$ at various temperatures (220 K, 200 K, 180 K and 160 k to 10 K by a 10 K step).

The asymmetry parameter η of the EFG, defined as $\eta = |(q_{xx} - q_{yy})/q_{zz}|$, is close to zero for the Cu site in the two dimensional CuO_2 planes (Cu(2) site).

In a strong magnetic field, when the Zeeman energy is much larger than the quadrupole energy, each Zeeman level is shifted by the quadrupole interactions, and thus two satellite peaks ($\pm 3/2 \leftrightarrow \pm 1/2$) appear on both sides of the central resonance peak ($\pm 1/2 \leftrightarrow \mp 1/2$). The frequency difference between the upper and the lower satellites exactly coincides with $2\nu_Q$, if the applied magnetic field is parallel to the largest principle axis of the EFG, namely, $H \parallel c$-axis in the present experimental condition.

3. Results

Figures 1 and 2 show the NQR spectra and the lower and upper satellite spectra of ^{63}Cu(2) NMR for optimally doped $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$, respectively. All data were taken with a phase coherent spin echo spectrometer. The spectra are obtained by a superposed method of the Fourier Transform spectra of the spin echo measured in a certain frequency interval. The NMR-satellite spectra are slightly-asymmetric due to the miss-alignment of some grains. Line broadenings of the NQR spectra in zero external field are not observed even below T_c in both $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$. The width of the NMR spectra becomes broader with decreasing T below T_c, partly due to the magnetic field inhomogeneity caused by the introduction of vortices, and partly due to the spatial distribution of the carrier density, which we will discuss later.

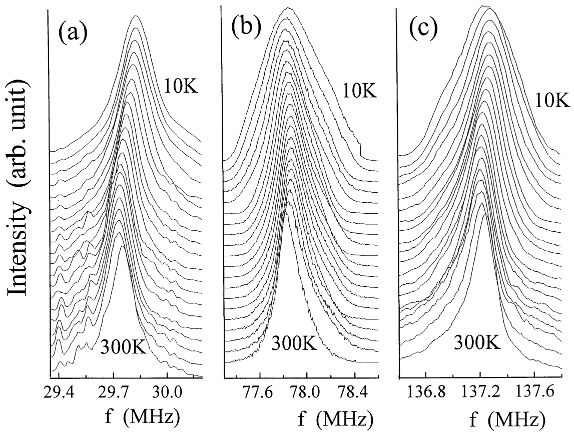

Fig. 2. The NQR spectra in zero field (a), and the lower (b) and upper (c) NMR satellite spectra at 9.4 T of the ^{63}Cu(2) site $YBa_2Cu_4O_8$ at various temperatures (300 K, 220 K, 200 K, 180 K and 160 k to 10 K by a 10 K step).

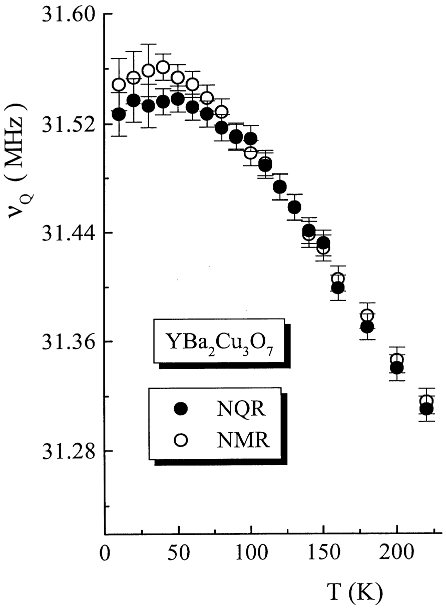

Fig. 3. The temperature dependence of ν_Q obtained from NQR and NMR of the ^{63}Cu(2) site of $YBa_2Cu_3O_7$.

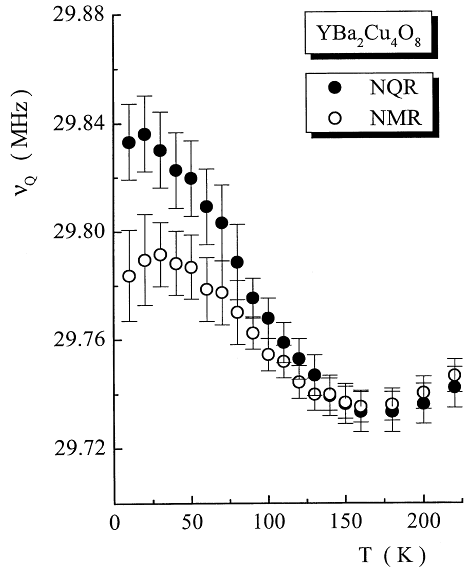

Fig. 4. The temperature dependence of ν_Q obtained from NQR and NMR of the ^{63}Cu(2) site of $YBa_2Cu_4O_8$.

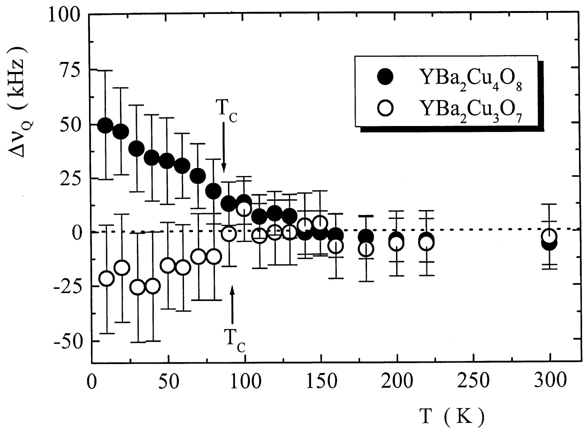

Fig. 5. The temperature dependence of $\Delta\nu_Q = \nu_Q(0) - \nu_Q(H)$ of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$. In both materials a nonzero $\Delta\nu_Q$ is clearly observed below T_c, showing that the electron density outside the core differs from that in zero field.

The temperature dependences of ν_Q obtained from NMR and NQR are shown for $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ in Figs. 3 and 4, respectively. The temperature dependences of ν_Q^{NQR} for both compounds are quite similar to those reported previously [17]. It should be noted that the procedure for obtaining ν_Q from the frequency difference between the upper and lower satellites is essentially free from the influence of the change of magnetic shift (or Knight shift). Even for the second or higher order quadrupole effect in the presence of the asymmetry η of the EFG, the satellite line shifts as much, and the corrections for $2\nu_Q$ are vanishing in the case of $H \parallel c$-axis [16]. Moreover, the magnetic effect of the asymmetric broadening (so-called Redfield pattern) due to the vortex lattice in the superconducting state is exactly cancelled in the process determining ν_Q from NMR. Thus we obtained the ν_Q values simply from the differences of the peak frequencies of the two satellite lines.

Figure 5 shows the difference between ν_Q in zero field and in the vortex state, $\Delta\nu_Q = \nu_Q(0) - \nu_Q(H)$, for $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$. The ν_Q in zero field for NQR is obtained after correction by the factor $\sqrt{1+\eta^2/3}$ in (1), although this factor is at most 0.03% of ν_Q for $\eta \approx$0.04 of the present materials. In both materials $\Delta\nu_Q$ is essentially zero above T_c, indicating no modulation of the carrier density. Meanwhile a nonvanishing $\Delta\nu_Q$ is clearly observed below T_c in both materials. While $\Delta\nu_Q \sim -25$ kHz is negative in $YBa_2Cu_3O_7$, $\Delta\nu_Q \sim 50$ kHz is positive in $YBa_2Cu_4O_8$ at T=0.

4. Discussion

We first briefly introduce the physics of the vortex charge in type-II superconductors. In the core of conventional superconductors, the distances between discrete energy levels of the quasiparticles in the Andréev bound states are merely of the order of a few mK. Thus it is sufficient to see the energy levels as forming a continuous spectrum, just as in a normal metallic state [1, 18]. Generally the chemical potential μ in the superconducting state differs from that in the normal state if an electron-hole asymmetry is present. Assuming therefore that the vortex core is a region of normal metal surrounded by the superconducting materials this difference in μ is expected to arise and should lead to a redistribution of the electrons. In order to maintain the same electrochemical potential on both sides, the charge transfer occurs between the core and the outside.

In the framework of the BCS theory, taking into account the metallic screening effect, the charge accumulated within the vortex core Q_ξ per layer normal to the magnetic field is given as

$$Q_\xi \approx \frac{2ek_F s}{\pi^3}\left(\frac{\lambda_{TF}}{\xi}\right)^2\left(\frac{\mathrm{d}\ln T_c}{\mathrm{d}\ln\mu}\right), \qquad (2)$$

where λ_{TF} the Thomas-Fermi screening length, s the interlayer distance, μ is the chemical potential and $e(>0)$ the electron charge [3]. The sign of the core charge is determined by $\mathrm{d}\ln T_c/\mathrm{d}\ln\mu$, which represents the electron-hole asymmetry. Outside the core, charges with opposite sign screen the core charge, similar to a charged particle in a metal. Far outside

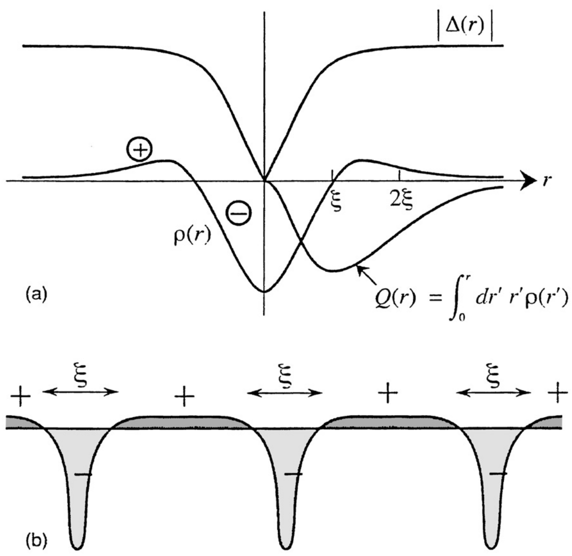

Fig. 6. (a) Schematic figure of the charge distribution around a single vortex core when the electrons are trapped within the core (negatively charged core). $\Delta(r)$ is the energy gap of superconducton, and $\rho(r)$ is the charge density. The charges accumulated inside the core are screened by charges with opposite sign. $\rho(r)$ decays gradually as r^{-4} far outside the core region. $Q(r)$ is the total charge within the distance r. $Q(r)$ goes to zero as $r \to \infty$ due to the requirement of the overall charge neutrality. (b) The charge density modulation in a strong magnetic field ($H_{c1} \ll H \ll H_{c2}$) where neighbouring vortices overlaps.

the core, these screening charges decay gradually with a power law dependence as r^{-4} (see Fig. 6(a)) [3, 9]. In strong fields ($H_{c1} \ll H \ll H_{c2}$), each vortex overlaps with its neighborhood. Then the charge density outside the core is nearly constant, and a periodic modulation of the charge density appears for a periodic vortex lattice (Fig. 6(b)). If the vortex core traps (expels) a finite amount of electrons, the electron density outside the core should decrease (increase) from that in zero field where the electron distribution is uniform, as shown in Fig. 6(b). In ordinary superconductors, $|Q_\xi|$ is estimated to be $\sim 10^{-5} - 10^{-6}e$, using $k_F \sim 1\text{Å}^{-1}$, $\lambda_{TF} \sim k_F^{-1} \sim 1$Å, $\xi \sim 100$Å and $|d\ln T_c/d\ln\mu| \approx \ln(\hbar\omega_D/k_B T_c) \sim 1 - 10$, where ω_D is the Debye frequency. Thus $|Q_\xi|$ is negligibly small and is very difficult to observe.

However, the situation in the case of HTSC's seems to be promising because ξ is extremely short compared to that of the conventional superconductors. Moreover, the strong electron correlation effects and

d-wave pairing symmetry of HTSC's are expected to change the electronic structure of the vortex dramatically [19 - 24]. In fact, recent STM measurements revealed that the vortex of HTSC's is very different from those of conventional superconductors [25 - 27]. These unusual features of HTSC are expected to enhance the charging. We will discuss this later.

We discuss here several possible origins for the nonzero $\Delta\nu_Q$. We first point out that the magnetostriction cannot be the origin of the nonzero $\Delta\nu_Q$. In fact, both the magnetostriction and ultrasonic absorption measurements showed that the local lattice distortion $\Delta\ell$ caused by the magnetostriction is negligibly small under the field cooling condition: $\Delta\ell/\ell < 10^{-8}$ below 10 T, where ℓ is the lattice constant [30]. We next consider on an in-plane charge modulation caused by a charge stripe formation [31] or the charge density wave (CDW) transition of the chain site.[32, 33]. Although the static charge ordering associated with a stripe formation in some high-T_c cuprates has been discussed, such orderings in $YBa_2Cu_3O_7$ or $YBa_2Cu_4O_8$ have never been reported. Moreover, it has been reported that in La:214 compounds the static charge stripe order gives rise to the wipe-out of NQR signals [34], implying that the static stripe order, if present, induces a large effects on quadrupole interactions. However, we have not observed a broadening of the NQR spectra (in zero field) nor any sign of the wipe-out of NQR and NMR signals in the present measurements for $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$.

Finally we mention a recent report of the broadening of the NQR line widths in the plane at low temperatures in $YBa_2Cu_3O_{7-\delta}$, which was explained in terms of the CDW formation in the chain site [33]. In the present study, in which we obtained sharper NQR lines compared to previous reports [32, 33], such line-broadenings due to electric quadrupole interaction is not observed. Thus there is no evidence of the charge modulation due to CDW- or stripe-formation in zero field in our crystals. It is also quite unlikely that the magnetic field induces the CDW- or stripe-formation. Having ruled out these various possibilities, we conclude that the nonzero values for $\Delta\nu_Q$ naturally lead to the fact that *the electron density outside the vortex core is different from that in zero field*.

We now discuss the issue of the sign and magnitude of the accumulated charge. Generally the EFG originates from two different sources, namely from the on-site distributions $q_{\text{on-site}}$ of the electrons and from

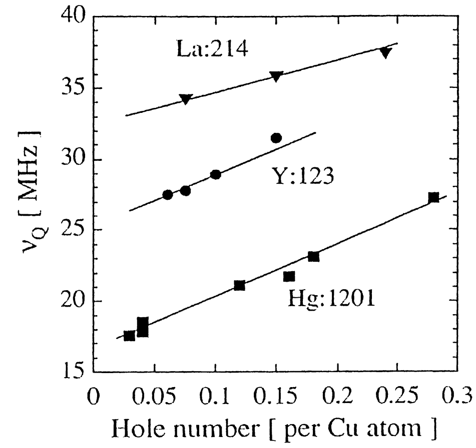

Fig. 7. Doping dependences of ν_Q on the Cu(2) site for $YBa_2Cu_3O_{7-\delta}$ [13], $La_{2-x}Sr_xCuO_4$ [14] and $HaBa_2CuO_{4+\delta}$ [15]. ν_Q is proportional to the hole number.

the surrounding ions q_{ion}, $q = q_{\text{on-site}} + q_{\text{ion}}$. Recent analysis of q on the Cu(2) site suggests that $q_{\text{on-site}}$ is mainly composed of the Cu 4p and 3d shell terms [12]. In HTSC the holes in the Cu $3d_{x^2-y^2}$ orbital play an important role for the onset of superconductivity. Figure 7 shows the doping dependence of ν_Q of the Cu(2) site for $YBa_2Cu_3O_{7-\delta}$ [13], $La_{2-x}Sr_xCuO_4$ [14], and $HgBa_2CuO_{4+\delta}$ [15]. In all materials, ν_Q increases linearly with the number of holes in the planes and can be written as

$$\nu_Q = An_{\text{hole}} + C, \tag{3}$$

where n_{hole} is the number of holes per Cu(2) atom, and A and C are constants [13 - 15]. Although C is strongly material dependent, reflecting the difference in ν_{ion}, $A \approx 20 - 30$ MHz per hole for the Cu(2) atom is essentially material independent. Thus, the precise measurement of ν_Q makes possible an accurate determination of the change of the local hole number at the Cu site. The negative $\Delta\nu_Q$ in $YBa_2Cu_3O_7$ indicates the increment of the hole density outside the core. This excess density of holes is nothing but the holes expelled from the core. Therefore the accumulated charge in the core of $YBa_2Cu_3O_7$ is negative. By the same reasoning, the positive $\Delta\nu_Q$ in $YBa_2Cu_4O_8$ indicates a positive accumulated charge. Meanwhile, since the chemical potential decreases monotonically with the number of doping holes, (1), sgnQ_ξ =sgn(d ln T_c/d ln μ), predicts that $Q_\xi > 0$ in the underdoped regime while $Q_\xi < 0$ in the overdoped regime. This is in striking contrast to the sign determined by the present experiment. The deviation of the magnitude of the charge from theory is also noteworthy. The magnitude of charges per pancake vortex, which are roughly estimated using $Q_\xi \approx \Delta\nu_Q H_{c2}/AH$ assuming $H_{c2} \sim 200$ T, are $Q_\xi \sim -0.005\,\mathrm{e}$ to $-0.02\,\mathrm{e}$ for $YBa_2Cu_3O_7$ and $Q_\xi \sim 0.01$ e to $0.05e$ for $YBa_2Cu_4O_8$. However, according to (1), Q_ξ is estimated to be $\sim 10^{-4} - 10^{-5}$ e, where we assumed $\xi \sim 30$ Å. Therefore $|Q_\xi|$ determined by the present experiments is still one or two order of magnitude larger than expected by (1). Thus *the BCS theory not only predicts the wrong sign of the charge but also underestimates* $|Q_\xi|$ *seriously*.

There are several intriguing possible origins for these discrepancies. For example, because of the extremely short ξ, the vortex core may be in the quantum limit $k_F\xi \sim 1$, where k_F is the Fermi wave number. In this limit, the description of the quasiparticles in terms of semiclassical wavepackets breaks down in contrast to conventional superconductors [20]. Furthermore, as suggested by recent theories of the vortex core based on *e.g.* the t-J or SO(5) models, the antiferromagnetic (AF) state may be energetically preferable to the metallic state in the vortex core of HTSC [21, 22, 24]. If this is indeed so, the AF correlation is expected to enhance the charging effect because it causes a large shift of μ by changing the density of states of the electrons inside the core dramatically. We note here that the present results exclude the possibility of the SO(5) insulating AF core [21, 24], in which holes should be expelled from the core and the accumulated charges are always negative; the present result yields the opposite sign for $YBa_2Cu_4O_8$ in the underdoped regime where the AF correlation is important. Therefore a detailed microscopic calculation is needed to evaluate the accumulated charge quantitatively including the sign.

In summary, from the precise ^{63}Cu-NMR and NQR measurements we have shown that a vortex in type-II superconductors can trap a finite electric charge as well as magnetic flux. In the slightly overdoped $YBa_2Cu_3O_7$ the vortex is negatively charged, while in underdoped $YBa_2Cu_4O_8$ it is positively charged. In both high T_c materials, the accumulated charges are much larger than expected in the ordinary superconductors. The sign and value of the charges indicate a novel electronic structure of the vortex in HTSC's.

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