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*Note: The content is a table with the specified columns for each field.*
Charged vortices in high-temperature superconductors probed by NMR

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We report experimental evidence that a vortex in high-temperature superconductors (HTSC) traps a finite electric charge from the high-resolution measurements of the nuclear quadrupole frequencies. In slightly overdoped YBa 2 Cu 3 O 7 the vortex is negatively charged by trapping electrons, while in underdoped YBa 2 Cu 4 O 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 charge from the theory is also significant. These unexpected features can be attributed to the electronic structure of the vortex in HTSC.

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I. INTRODUCTION

One of the most important physical properties of the vortex created in type-II superconductors is that a vortex line can support a magnetic flux with a flux quantum $\Phi_0 = \hbar c/2e \approx 2.07 \times 10^{-7}$ Oe cm$^2$. This fact 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 the total fundamental nature of the superfluid electrons and the low-energy excitation 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 high-temperature superconductors (HTSC) by high-resolution measurements of the nuclear quadrupole frequency $v_Q$, which is very sensitive to the local charge density. We show that a vortex in HTSC indeed traps a small but finite electronic charge as well. In slightly overdoped YBa 2 Cu 3 O 7 the vortex is negatively charged, while in underdoped YBa 2 Cu 4 O 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.

II. VORTEX CHARGE

We first briefly introduce the vortex charge in type-II superconductors. In the core of the conventional superconductors, the distance between each discrete energy level of the quasiparticles in the Andreev bound states is merely of the order of a few mK. Thus it is sufficient to view the energy levels as forming a continuous spectrum, just like in a normal metallic state. 1,11 Generally the chemical potential $\mu$ 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 normal metallic region surrounded by the superconducting materials, this difference in $\mu$ is expected to arise and should lead to the 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 $Q_\xi$ per layer, normal to the magnetic field is given as

$$Q_\xi = \frac{2e k_F s}{\pi^3} \left( \frac{\lambda_{TF}}{\xi} \right)^2 \left( \frac{d \ln T_c}{d \ln \mu} \right),$$

where $\lambda_{TF}$ is the Thomas-Fermi screening length, $s$ is the interlayer distance, $\mu$ is the chemical potential, and $e (> 0)$ is the electron charge. 3 The sign of the core charge is determined by $d \ln T_c/d \ln \mu$, which represents the electron-hole asymmetry. Outside the core, the charges with opposite sign screen the core charge similar to a charged particle in a metal. Far outside the core, these screening charges decay gradually with a power-law dependence as $r^{-4}$ [see Fig. 1(a)]. 3,9 In strong fields ($H_{c1} \ll H < H_{c2}$), each vortex overlaps with its neighborhood. Then the charge density outside the core is nearly constant and periodic modulation of the charge density appears for the periodic-vortex lattice [Fig. 1(b)]. In ordinary superconductors, $|Q_\xi|$ is estimated to be $\sim 10^{-5} \sim 10^{-6} e$, using $k_F \sim 1$ Å$^{-1}$, $\lambda_{TF} \sim 1$ Å, $\xi \sim 100$ Å, and $|d \ln T_c/d \ln \mu| \sim \ln(\hbar \omega_p/k_BT_c) \sim 10$, where
local carrier density is strongly required. It has been pointed out by many authors that $\nu_Q$ in HTSC is very sensitive to the local hole density.\textsuperscript{23–26} In a solid, an electron distribution with spherical asymmetry such as an unclosed 3$d$ shell and noncubic surrounding ions induce a local electric-field gradient (EFG) in the vicinity of the nuclei. 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 $^{63}\text{Cu}$ nuclei with spin $I = 3/2$, the NQR resonance frequency $\nu_Q^{NQR}$ is expressed as

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

where $eq_{zz}$ is the largest principal ($z$ axis) component of EFG at the nuclear site, $Q_N = -0.211$ barn for $^{63}\text{Cu}$ is the quadrupole moment of copper nuclei.\textsuperscript{27} The asymmetry parameter $\eta$ 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 ($\pm 1/2 \leftrightarrow \pm 1/2$) resonance peak. The frequency difference between the upper and the lower satellites exactly coincides with $2\nu_Q$ when a magnetic field is applied parallel to the largest principal axis of EFG, namely, $H || c$ axis in the present experimental condition described below. Even for the second-order or more higher-order quadrupole effect in the presence of the asymmetry $\eta$ of EFG, each satellite line is shifted as much and the corrections for $2\nu_Q$ are vanishing in the case of $H || c$ axis.\textsuperscript{27}

Generally the EFG originates from two different sources, namely, from the on-site distributions $q_{on-site}$ of the electrons and from the surrounding ions, $q_{ion} \cdot q = q_{on-site} + q_{ion}$. Recent analysis of $q$ on the Cu(2) site suggests that $q_{on-site}$ is mainly composed of the Cu 4$p$ and 3$d$ shell terms.\textsuperscript{23} In HTSC the holes in the Cu 3$d_{x^2−y^2}$ orbital play an important role for the onset of superconductivity. Figure 2 shows the doping dependence of $\nu_Q$ of the Cu(2) site for $\text{YBa}_2\text{Cu}_3\text{O}_7−\delta$, $\text{La}_{2−x}\text{Sr}_x\text{Cu}_2\text{O}_4$,\textsuperscript{23} and $\text{Haf}_2\text{CuO}_4+\delta$.\textsuperscript{26} In all materials, $\nu_Q$ increases linearly with the number of holes in the planes and can be written as

$$\nu_Q = An_{hole} + C, \quad (3)$$

where $n_{hole}$ is the number of holes per Cu(2) atom, and $A$ and $C$ are constants.\textsuperscript{24–26} Although $C$ is strongly material dependent, reflecting the difference in $\nu_{ion}$, $A \approx 20–30$ MHz per hole for the Cu(2) atom is essentially material independent. Thus, the precise measurement of $\nu_Q$ makes possible an accurate determination of the change of the local hole number at the Cu site.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(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 superconducting energy gap. $\rho(r)$ is the charge density. The charge accumulated inside the core is screened by the charges with opposite sign. $Q(r)$ 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 the strong magnetic field ($H_{11} \neq H_{22} H_{22}$) where each vortex overlaps.}
\end{figure}
III. EXPERIMENT

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 less than $H_{c2}$ and hence the core region occupies a smaller area in the sample. If the vortex core traps or expels a finite amount of electrons, the electron density outside the core should decrease from that in zero field where the electron distribution is uniform, as shown in Fig. 1b. We are able to detect the change of carrier density through the change of the value of $\nu_Q$.

In the present measurements, we used slightly overdoped YBa$_2$Cu$_3$O$_7$ and underdoped YBa$_2$Cu$_4$O$_8$ in which the NQR and NMR spectra are very sharp compared to those of other HTSC. The NMR spectra are obtained for fine-powdered samples (the grains are less than 33 $\mu$m) with uniaxial alignment. Each grain aligns to an easy axis (the c axis) in a high external field at room temperature, and is then fixed with epoxy (Stycast 1266).

The Cu-NQR and NMR spectra were obtained by a conventional pulse spectrometer. The NMR experiments were performed in a field-cooling condition under a constant field of 9.4 T by using a highly homogeneous superconducting magnet that was stabilized to less than 1 ppm during the experiment. The present measurement in the vortex state is made in the so-called Bragg-glass phase in which the quasi-long-range order of the vortex lattice is preserved. We see a slightly asymmetric shape of the NMR-satellite spectra due to the misalignment, somehow, of some grains. The line broadenings of the NQR spectra in zero external field are not observed even below $T_c$ in both YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$. 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 the vortices and partly due to the spatial distribution of carrier density, which we will discuss later.

IV. RESULTS AND DISCUSSION

Figures 3(a)–(c) show the NQR and NMR spectra of $^{63}$Cu(2) for optimally doped YBa$_2$Cu$_3$O$_7$. Figures 4(a)–(c) show the same spectra for YBa$_2$Cu$_4$O$_8$. All data were taken by utilizing a phase-coherent spin-echo spectrometer. The spectra are obtained with a superposed method of the Fourier-transform spectra of the spin echo measured at a certain frequency interval. The temperature dependencies of $\nu_Q$ obtained from NMR and NQR are shown for YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ in Figs. 5 and 6, respectively. The temperature dependencies of $\nu_Q^{NQR}$ for both YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ are quite similar to those of $\nu_Q^{NQR}$ reported previously. It should be noted that the procedure for obtaining $\nu_Q$ from the frequency difference between the upper and lower satellites is essentially free from the influence of the change of the magnetic shift (or Knight shift). Moreover, the magnetic effect of the asymmetric broadening (so-called Redfield pattern) due to the vortex lattice in the superconducting state is exactly canceled out in the process determining $\nu_Q$ from NMR. Thus, we obtained the $\nu_Q$ values simply from the difference of the peak frequencies of the two satellite lines.
We plot in Fig. 7 the difference between \( n_Q \) in zero field and in the vortex state, \( Dn_Q = n_Q(0) - n_Q(H) \), for YBa\(_2\)Cu\(_3\)O\(_7\) and YBa\(_2\)Cu\(_4\)O\(_8\). The \( n_Q \) in zero field for NQR is obtained after correction by the factor of \( a_1 h^2/3 \) in Eq. (1), although this factor is at most 0.03% of \( n_Q \) for \( h' < 0.04 \) of the present materials. In both materials \( Dn_Q \) is essentially zero above \( T_c \), indicating no modulation of the carrier density. Meanwhile a nonvanishing \( Dn_Q \) is clearly observed below \( T_c \) in both materials. While \( Dn_Q \); 25 kHz is negative in YBa\(_2\)Cu\(_3\)O\(_7\), \( Dn_Q \); 50 kHz is positive in YBa\(_2\)Cu\(_4\)O\(_8\) at \( T = 0 \).

We discuss here several possible origins for the nonzero \( Dn_Q \). We first point out that the magnetostriction cannot be the origin of the nonzero \( Dn_Q \). In fact, both the magnetostriction and ultrasonic-absorption measurements showed that the local lattice distortion \( \Delta l \) caused by the magnetostriction is negligibly small under the field-cooling condition; \( \Delta l/l < 10^{-8} \) below 10 T where \( l \) is the lattice constant. We next remark on an in-plane charge modulation caused by a charge-stripe formation\(^{30}\) or the charge density wave (CDW) transition of the chain site.\(^{31,32}\) Although the static-charge ordering associated with a stripe formation has been discussed in some of the high-\( T_c \) cuprates, such orderings have never been reported in YBa\(_2\)Cu\(_3\)O\(_7\) nor in YBa\(_2\)Cu\(_4\)O\(_8\). Moreover, it has been reported that in La:214 compounds the static-charge-stripe order gives rise to the wipeout of NQR signals,\(^{33}\) implying that the static-stripe order, if present, induces large effects on quadrupole interactions. However, we have observed neither the broadening of the NQR spectra (in zero field) nor any sign of the wipeout of NQR and NMR signals in the present measurements for YBa\(_2\)Cu\(_3\)O\(_7\) or YBa\(_2\)Cu\(_4\)O\(_8\). Finally we mention a recent report of the broadening of the NQR line widths in the plane at low temperatures in YBa\(_2\)Cu\(_3\)O\(_7\)-\( \delta \), which was explained in terms of the CDW formation in the chain site.\(^{32}\) In the present study, in which we obtained sharper NQR line widths compared to the previous reports,\(^{31,32}\) such line broadenings due to the electric-quadrupole interaction is not observed. Thus, there is no evidence of 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 formations. Having ruled out these various possibilities, we conclude that the nonzero values for \( Dn_Q \) naturally lead to the fact that the electron density outside the core differs from that in zero field.

We now discuss the issue of the sign and magnitude of the accumulated charge. The negative \( Dn_Q \) in YBa\(_2\)Cu\(_3\)O\(_7\) 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\(_2\)Cu\(_3\)O\(_7\) is negative. By the same reasoning, the positive \( Dn_Q \) in YBa\(_2\)Cu\(_4\)O\(_8\) indicates a positive accumulated charge. Meanwhile, since the chemical potential decreases monotonically with doping holes, Eq. (1), \( sgn Q_{\xi} = sgn(d \ln T_c/d \ln \mu) \), predicts that \( Q_{\xi} > 0 \) in the underdoped regime while \( Q_{\xi} < 0 \) in the overdoped regime. This is strikingly in contrast to the sign determined by the present experiment. The deviation of the magnitude of the charge from

FIG. 5. The temperature dependence of \( n_Q \) obtained from NQR and NMR for \( ^{63}\)Cu(2) site of YBa\(_2\)Cu\(_3\)O\(_7\).

FIG. 6. The temperature dependence of \( n_Q \) obtained from NQR and NMR for \( ^{63}\)Cu(2) site of YBa\(_2\)Cu\(_4\)O\(_8\).

FIG. 7. \( T \) dependence of \( \Delta n_Q = n_Q(0) - n_Q(H) \) for YBa\(_2\)Cu\(_3\)O\(_7\) and YBa\(_2\)Cu\(_4\)O\(_8\). In both materials nonzero \( \Delta n_Q \) is clearly observed below \( T_c \), showing that the electron density outside the core differs from that in zero field.
theory is also noteworthy. The magnitude of charges per pancake vortex, which are roughly estimated using \( Q_{\xi} \approx \Delta \nu_b H_c / \alpha H \) assuming \( H_c \approx 200 \text{T} \) are \( Q_{\xi} \approx -0.005e \) to \(-0.02e \) for \( \text{YBa}_2\text{Cu}_4\text{O}_7 \) and \( Q_{\xi} \approx -0.01e-0.05e \) for \( \text{YBa}_2\text{Cu}_3\text{O}_8 \). However, according to Eq. (1), \( Q_{\xi} \) is estimated to be \( \sim 10^{-4} - 10^{-7}e \) where we assumed \( \xi \approx 30 \text{Å} \). Therefore, \( |Q_{\xi}| \) determined by the present experiments are still one or two orders of magnitude larger than expected by Eq. (1). Thus the BCS theory not only predicts the wrong sign of the charge but also underestimates \( |Q_{\xi}| \) greatly.

There are several intriguing possible origins for these discrepancies. For example, because of the extremely short \( \xi \), the vortex core may be in the quantum limit and indeed so, the AF correlation is expected to enhance the microscopic calculation is needed to evaluate the accumulated charge quantitatively including the sign.

V. CONCLUSION

From the precise \(^{63}\text{Cu-NMR} \) 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 \( \text{YBa}_2\text{Cu}_4\text{O}_7 \), the vortex is negatively charged, while in underdoped \( \text{YBa}_2\text{Cu}_3\text{O}_8 \), 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 the electronic structure of the vortex in HTSC.

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