^{63}Cu-NMR/NQR studies on apical-F bi-layered cuprates Ba$_2$CaCu$_2$O$_4$F$_2$ and Ba$_2$CaCu$_2$O$_4$(F$_{1.6}$O$_{0.4}$)

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ABSTRACT

We report ^{63}Cu-NMR/NQR on the bi-layered high-T_c copper oxide Ba$_2$CaCu$_2$O$_4$F$_2$, which is expected to be a Mott insulator in an ideal case of a nominal content of fluorine, and less fluorinated Ba$_2$CaCu$_2$O$_4$(F$_{1.6}$O$_{0.4}$) to clear the doping mechanism in apical-fluorine multilayered system Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$F$_2$, where n is the number of the layers in a unit cell. In the case of $n=3$ and, especially, $n=4$, the origin of carrier doping has been attributed to a *self-doping* mechanism based on the nominal stoichiometry; electrons are transferred between the inner CuO$_2$ plane (IP) and the outer one (OP), keeping Cu^{+2} on average. It is revealed that Ba$_2$CaCu$_2$O$_4$F$_2$ is an underdoped superconductor with *hole carriers*, doped by an inevitable deviation from the nominal content of apical fluorines. This result suggests that hole carriers are doped in the same manner for the case of $n=3$ and 4, and that we should reconsider the self-doping mechanism as the carrier source in the apical-fluorine system.

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1. Introduction

Multilayered copper oxides Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$F$_2$, where n is the number of layers in a unit cell, are known as a relatively new family of cuprates [1–3]. Copper oxides having more than three layers comprise inequivalent types of CuO$_2$ layers, an outer CuO$_2$ plane (OP) in a fivefold pyramidal coordination, and an inner plane (IP) in a fourfold square coordination. In an ideal case of a nominal content of fluorine, the apical sites of the OP are fully occupied by F^{-1}, and hence the formal Cu valence is just 2+. Eventually, it is expected that the apical-fluorine system Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$F$_2$ could act as a Mott insulator; however, they exhibit SC. The occurrence of the SC in the case of $n=4$ has been attributed to a *self-doping* model, in which charge carriers are transferred between the IP and the OP; this was first proposed based on ARPES (angle resolved photoemission spectroscopy) [4] and a band calculation [5]. Our previous NMR study supported the *self-doping* mechanism on the basis of the results for $n=3$ and 4, assuming that the Cu-valence is only 2+ when the apical sites of OP are fully occupied by F^{-1} [6]. Since then, bi-layered Ba$_2$CaCu$_2$O$_4$F$_2$ (the $n=2$ compound(#1)), which has only OP and no IP, has also been synthesized; it exhibits SC with $T_c=73$ K. The above mentioned *self-doping* mechanism cannot apply to this compound because it has no IPs. Therefore, NMR studies on the

$n=2$ compound(#1) and less fluorinated Ba$_2$CaCu$_2$O$_4$(F$_{1.6}$O$_{0.4}$) (the $n=2$ compound(#2)) will provide us with an opportunity to obtain a better understanding of whether the *self-doping* mechanism occurs in the apical-fluorine system.

In this paper, we report Cu-NMR/NQR studies on the $n=2$ compound(#1) and (#2), which reveal that SC in the $n=2$ compound(#1) occurs due to *hole carriers* doped in association with a possible replacement of O^{-2} for F^{-1}. This result suggests that even in the case of $n=3$ and 4 hole carriers are unexpectedly introduced into both the OP and the IP by an deviation from the nominal stoichiometry, i.e., Cu^{+2} on average realizes only in the case of the nominal stoichiometry under the total neutrality. Therefore, we need to reconsider the possibility of the *self-doping* mechanism as a carrier source in the apical-fluorine system.

Polycrystalline powder samples used in this study were prepared by a high-pressure synthesis technique, as described elsewhere [1–3]. Powder X-ray diffraction measurements indicate that these compounds almost entirely comprise a single phase. The superconducting transition temperature T_c was determined to be 73 and 105 K for the $n=2$ compound(#1) and the $n=2$ compound(#2), respectively, by onsets of diamagnetism using a dc SQUID magnetometer. For NMR measurements, the powder samples, which were aligned along the c-axis at an external field of $H\sim16$ T, were fixed using stycast 1266 epoxy. The NMR experiments were performed by the conventional spin-echo method in a temperature (T) range of 1.5–300 K with H perpendicular to the c-axis.

2. Results and discussion

Ba$_2$CaCu$_2$O$_4$F$_2$, which has two OPs in a unit cell, exhibits SC below $T_c = 73$ K. For the ideal case where all the apical sites of the OP are occupied by F^{-1}, the formal Cu valence should be just Cu^{+2}. Therefore, a Mott insulating state should be expected as in other undoped CuO$_2$ systems. However, off-stoichiometry, a deviation from the nominal content of F^{-1}, can introduce hole carriers into the OPs. The investigation of two kinds of bi-layered samples, the nominal stoichiometries of which are Ba$_2$CaCu$_2$O$_4$F$_2$ (the $n = 2$ compound(#1)) and Ba$_2$CaCu$_2$O$_4$(F$_{1.6}$O$_{0.4}$) (the $n = 2$ compound(#2)), provides an understanding of the origin of carrier-doping and the SC properties of multilayered copper oxides with apical fluorines.

Fig. 1(a) shows the ^{63}Cu-NMR spectrum for the $n = 2$ compound(#1) at 20 K with H perpendicular to the c-axis at a fixed frequency of 174.2 MHz. Its largest peak at around $^{63}K = 0$ arises from a central peak ($I = -\frac{1}{2} \Leftrightarrow \frac{1}{2}$ transition) for ^{63}Cu. Generally, the Hamiltonian for Cu nuclear spin with $I = \frac{3}{2}$ is described by the Zeeman interaction due to a magnetic field H and the nuclear quadrupole interaction (NQI) as follows:

$$\mathscr{H} = \mathscr{H}_Z + \mathscr{H}_Q = -\gamma_N \hbar \boldsymbol{I} \cdot \boldsymbol{H} + \frac{eV_{zz}Q}{4I(2I-1)}((3I_z^2 - I(I+1))), \quad (1)$$

where γ_N is the Cu nuclear gyromagnetic ratio and H is perpendicular to the c-axis. Note that the quadrupole frequency $v_Q = 3eQV_{zz}/2hI(2I-1)$, where Q is the nuclear quadrupole moment and V_{zz}, the electric field gradient (EFG) at the Cu
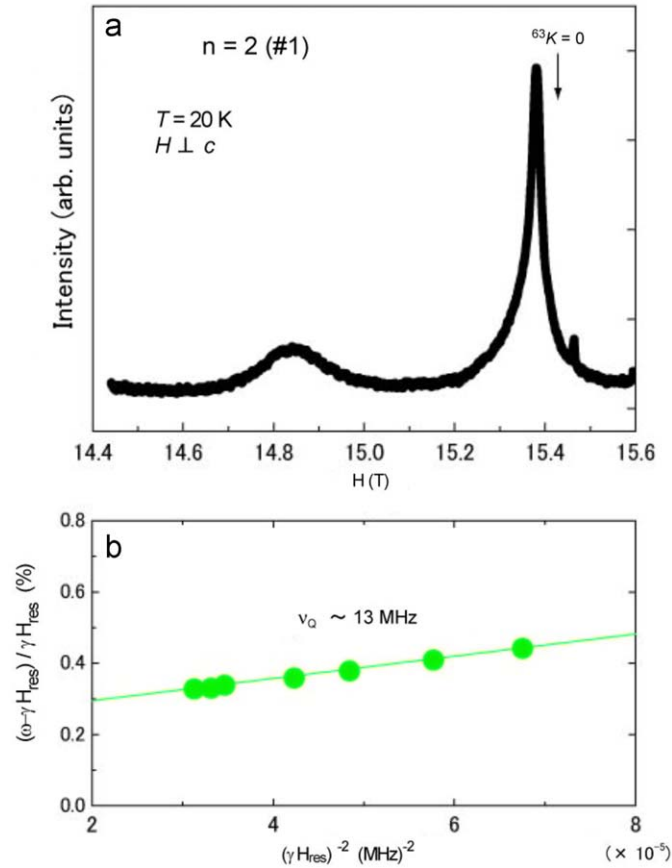
nuclear site. When we consider the second-order NQI for Eq. (1) under the condition of $\mathscr{H}_Z \gg \mathscr{H}_Q$, an NMR frequency ω_0^{2nd} at this central peak is given by

$$\frac{\omega_0^{2nd} - \gamma_N H_{res}}{\gamma_N H_{res}} = K_\perp + \frac{3v_Q^2}{16(1+K_\perp)} \frac{1}{(\gamma_N H_{res})^2}, \quad (2)$$

where H_{res} is an NMR resonance field and $K_\perp$, the Knight shift with H perpendicular to the c-axis. Fig. 1(b) shows a plot of $(\omega_0^{2nd} - \gamma_N H_{res})/\gamma_N H_{res}$ vs. $(1/\gamma_N H_{res})^2$, which enables us to estimate $^{63}v_{QQ} \sim 13$ MHz from a slope in this plot. The NMR frequencies ω_0^{1st} for two satellite peaks ($\pm\frac{1}{2} \Leftrightarrow \pm\frac{3}{2}$) due to the first-order NQI are given by

$$\frac{\omega_0^{1st} - \gamma_N H_{res}}{\gamma_N H_{res}} = K_\perp \mp \frac{v_Q}{2} \frac{1}{\gamma_N H_{res}}. \quad (3)$$

The peak at $H = 14.85$ T in Fig. 1 arises from the ($-\frac{1}{2} \Leftrightarrow -\frac{3}{2}$) transition of ^{63}Cu, confirming $^{63}v_{QQ} \sim 13$–14 MHz. However, the most accurate measurement of $^{63}v_{QQ}$ comes from NQR spectra. Figs. 2(a) and (b) show the Cu-NQR spectra for the $n = 2$ compound(1) and (#2), indicating $^{63}v_{QQ} = 13.7$ and 15.7 MHz, respectively. These values are comparable to $^{63}v_{QQ} = 15$–17 MHz for hole-doped HgBa$_2$CaCu$_2$O$_y$ (Hg-1212), which includes two OPs in a fivefold pyramidal coordination of oxygen [7]. Note that these values of $^{63}v_{QQ}$ for hole-doped OP are larger than those of electron-doped copper oxides. For example, $^{63}v_{QQ}$ for electron-doped Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ is reduced to ≤ 0.5 MHz, smaller than $^{63}v_{QQ} = 14$ MHz of the non-doped Nd$_2$CuO$_4$ by more than an order of magnitude. This is because electron-doping into the Cu-3d orbit decreases the on-site electronic term in the EFG that is
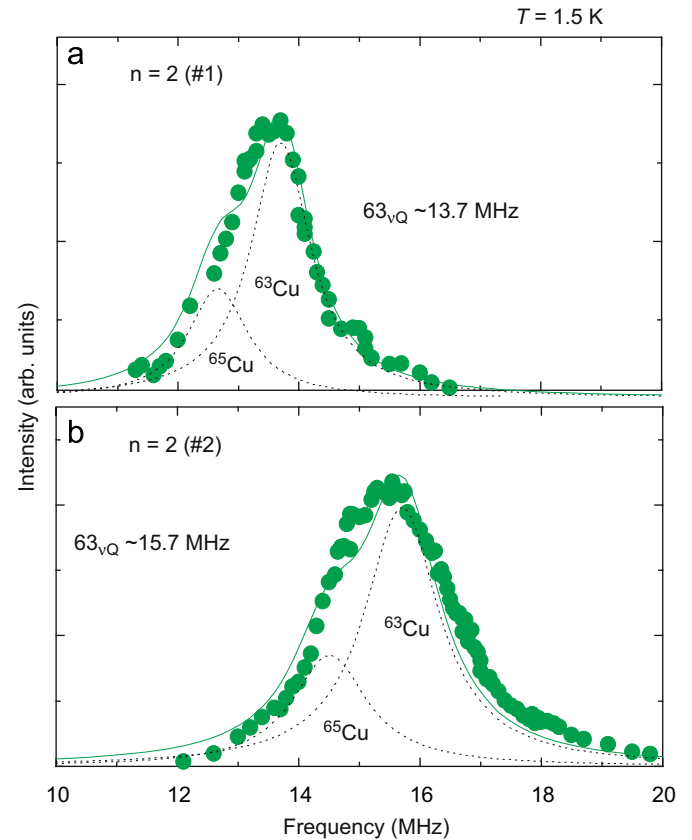

Fig. 1. (Color online) (a) ^{63}Cu-NMR spectrum for the $n = 2$ compound(#1) at $T = 20$ K with H perpendicular to the c-axis. The right and left peaks correspond to a central peak ($-\frac{1}{2} \Leftrightarrow \frac{1}{2}$ transition) and one of the satellite peaks ($-\frac{1}{2} \Leftrightarrow -\frac{3}{2}$ transition), respectively. (b) A plot of $(\omega_0^{2nd} - \gamma_N H_{res})/\gamma_N H_{res}$ as a function of $(1/\gamma_N H_{res})^2$ for the central peak. A slope in this plot gives rise to $^{63}v_{QQ}$ (see text).

Fig. 2. (Color online) Cu-NQR spectra for the (a) $n = 2$ compound(#1) and (b) $n = 2$ compound(#2), where the respective $^{63}v_{QQ}$ were estimated to be 13.7 and 15.7 MHz. An increase in the hole-doping level for the $n = 2$ compound(#2) increases $^{63}v_{QQ}$ to 15.7 MHz. The solid curves indicate the simulated results arising from two NQR spectra from ^{63}Cu and ^{65}Cu.