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Evidence for Antiferromagnetic Order in $Bi_2Sr_2CuO_6$ Phase with Stoichiometric Cation Composition

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We have succeeded in synthesizing the insulating phase of $Bi_2Sr_2CuO_{6+\delta}$ (Bi2201) with the stoichiometric cation composition by use of a heat treatment technique in an evacuated tube with titanium powders. The excess oxygen content δ and the average valence of Bi were determined electrochemically by the coulometric titration method. The value of δ in the insulating phase was found to be 0.02. The hole concentration h was also estimated with values of δ and the average valence of Bi in Bi2201. As a result, temperature dependence of resistivity and h dependence of Tc and Meissner volume fraction indicated behaviors similar to those of other high-Tc systems. The antiferromagnetic order of Cu^{2+} spins in the insulating Bi2201 phase has been confirmed by nuclear magnetic resonance. Thus, we can obtain the three distinct electronic states observed in high-Tc oxides, i.e., over-doped metallic, superconducting, and antiferromagnetic phases in Bi2201 compounds by changing only the oxygen content. The static parameters of the hyperfine field and the electric field gradient at Cu sites in $Bi_2Sr_2CuO_{6.02}$ were found to be almost comparable to those of other antiferromagnetic phases of high-Tc oxides. © 1997 Academic Press

1. INTRODUCTION

It is well known that high-Tc superconductivity can be achieved if adequate contents of carriers are introduced into the insulating cuprate oxides with antiferromagnetic long-range order in the so-called CuO_2 plane (see, for example, (1)). At a certain critical doping concentration, the system undergoes an insulator-to-metal transition and superconductivity emerges. As the hole concentration increases, the value of Tc increases and reaches a maximum (2). With further increase of carrier concentration, the superconductivity vanishes with decreasing Tc. Then, we can observe normal metallic ground state which is known as the over-doped states in a few compounds such as $La_{2-x}Sr_xCuO_4$ (2) and $Tl_2Ba_2CuO_6$ (3). Some of these transitions of electronic states have been observed in all high-Tc compounds, although all of three states, insulating antiferromagnetic, superconducting, and over-doped metallic states, could be obtained in a few materials in which carrier contents were varied by substitution of different cations such as the $La_{2-x}Sr_xCuO_4$ system. To elucidate the effect of carriers more clearly, it can be worthy to synthesize a compound in which all three states can be realized by changing only the oxygen content. Unfortunately, this attempt has not been successful among high-Tc oxides such as $YBa_2Cu_3O_{6+\delta}$ or $Tl_2Ba_2CuO_6$; the over-doped metallic and the antiferromagnetic phases could not be synthesized in the former and the latter cases, respectively.

The effect of substitution in the Bi–Sr–Cu–O system was also investigated by several workers (4–8). In our previous work (9, 10) on $Bi_2Sr_2CuO_{6+\delta}$ (Bi2201), we found that Bi2201 compounds with the stoichiometric cation composition were able to be synthesized with the heat treatment under oxygen pressures of about 30 bar. This compound, whose excess oxygen content, δ, was found to be about 0.5, showed metallic conductivity down to 4.2 K. By the heat treatment in flowing inert gas such as nitrogen at around 650°C, we could obtain the superconducting phase, of which the value of δ was about 0.1 and that of Tc was about 15 K. We could not decrease, however, the value of δ in the Bi2201 compound less than 0.12 by firing under inert gas at higher temperature than 700°C due to the decomposition of the sample. This fact indicates that the Bi2201 phase should be thermodynamically unstable at higher temperatures in this atmosphere. Thus, we tried successfully to synthesize the single phase of the Bi2201 compound with a lower value of δ by the heat treatment at lower temperature under lower oxygen partial pressure.

The antiferromagnetic phase of high-Tc cuprates has been described successfully by the two-dimensional Heisenberg model with the Néel temperature near room temperature (11). Recently, Goto *et al.* have reported on the magnetic character of antiferromagnetic phase in $TlBa_2(Ca,Y)Cu_2O_7$ system (12). They concluded that the magnetic properties at Cu sites were nearly the same as in antiferromagnetic phases of other high-Tc oxides. It was also found, however, that the character of the block layer and the spin dynamics of CuO_2 plane were quite different

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from those in $YBa_2Cu_3O_6$ and La_2CuO_4. On the other hand, there have been a few reports on the antiferromagnetic phase in Bi-based compounds (13–15). Particularly, Bi2201 compounds have not been investigated as often in this viewpoint (16) because of the nonavailability of the single phase with stoichiometric cation composition.

In this paper, we report on the synthesis of $Bi_2Sr_2CuO_{6+\delta}$ phase for $\delta \cong 0$ with the stoichiometric cation composition. The temperature dependence of the resistivity is presented for Bi2201 compounds with various oxygen contents. The hole concentration h was estimated using the result of the chemical analysis on the value of δ and the average valence of Bi. As a result, h dependencies of Tc and of Meissner volume fraction are also presented. Finally, we demonstrate the existence of the long-range antiferromagnetic order in $Bi_2Sr_2CuO_{6+\delta}$ phase for $\delta \cong 0$ at 1.3 K by the nuclear magnetic resonance under zero magnetic field. By a brief discussion, static parameters of the antiferromagnetic Bi2201 phase are compared with those in other high-Tc materials.

2. EXPERIMENTAL

The chemical formula of all samples investigated here can be written by $Bi_2Sr_2CuO_{6+\delta}$ with stoichiometric cation composition. All samples were synthesized by the solid state reaction as follows. The raw materials of Bi_2O_3, $Sr(NO_3)_2$, and CuO with 99.99% purity with stoichiometric cation composition were mixed thoroughly, pelletized, and heated in air at 700°C for 1 day. Then, the sample was again ground and exposed to heat treatment at 840°C under high oxygen pressures of 30 bar for 2 days. After this treatment, we could obtain a single phase of $Bi_2Sr_2CuO_{6+\delta}$, in which the value of δ is about 0.5 as mentioned below. Detailed procedures of this synthesis can be found in our previous work (9). In order to reduce the oxygen content, we succeedingly exposed it to one of following heat treatments: (I) firing in flowing N_2 gas for 2 days in the range from 650 to 700°C, (II) firing with the titanium powder as a reductant in an evacuated silica tube for 2 days at 350°C. In this tube, the sample and the titanium powder were separated and were heated at different temperatures as shown in Fig. 1.

X-ray diffraction (XRD) measurements were performed by using the monochromatic Cu*Kα* X-ray for the characterization of the obtained samples.

The oxygen content and the average valence of bismuth were measured electrochemically by the coulometric titration method. This method was first applied for high-Tc Bi-based oxides by Kurusu *et al.* (17) in order to distinguish the valences of copper and bismuth. In this method, we used the following two reducing reagents; copper (I) chloride CuCl for the determination of the oxygen content and iron (II) chloride $FeCl_2$ for that of the average valence of Bi. We followed procedures similar to those of Kurusu *et al.* One should refer to their report (17) for details.

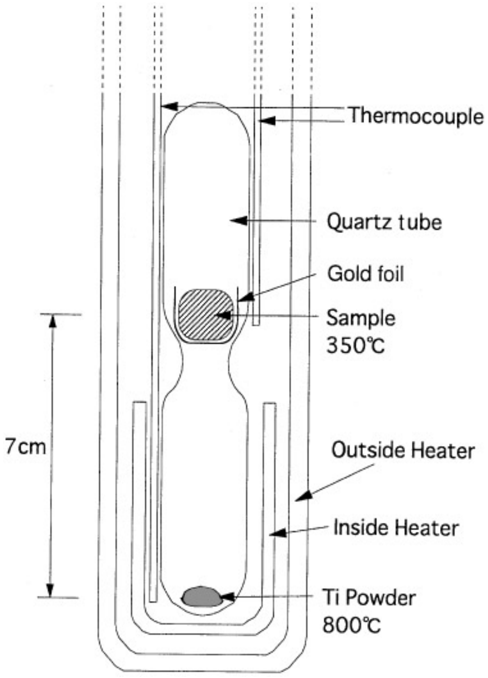

FIG. 1. Schematic view of the sample and the furnace in heat treatment (II). The sample and the titanium powder were separated and heated at different temperatures.

Magnetic susceptibility measurements were performed with the superconducting quantum interference device (SQUID) magnetometer in the magnetic field of 10 Oe and 10 kOe for powdered samples. Also, magnetic susceptibility at high temperatures between 300 and 700 K was obtained by the magnetic balance in the field of 5 kOe.

The electric resistivity measurements on sintered samples were carried out by the conventional four probe method from 4.2 K to the room temperature in a heating rate of 0.1–0.5 K/min.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) experiments were performed by the spin–echo pulse sequence mode using a homemade pulsed spectrometer. NMR and NQR spectra for ^{63}Cu and ^{65}Cu were taken under zero external magnetic field by plotting the spin–echo amplitude versus frequency with a time separation between exiting and refocusing pulses, τ, of 40 μsec.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

XRD patterns of $Bi_2Sr_2CuO_{6+\delta}$ compounds are shown in Fig. 2. By the heat treatment under 30 bar oxygen pressures, as previously reported (9), we obtained the single phase of $Bi_2Sr_2CuO_{6+\delta}$ sample whose XRD pattern is shown in Fig. 2a. The value of δ in this sample was determined to be 0.48 using the coulometric titration method. By exposing this

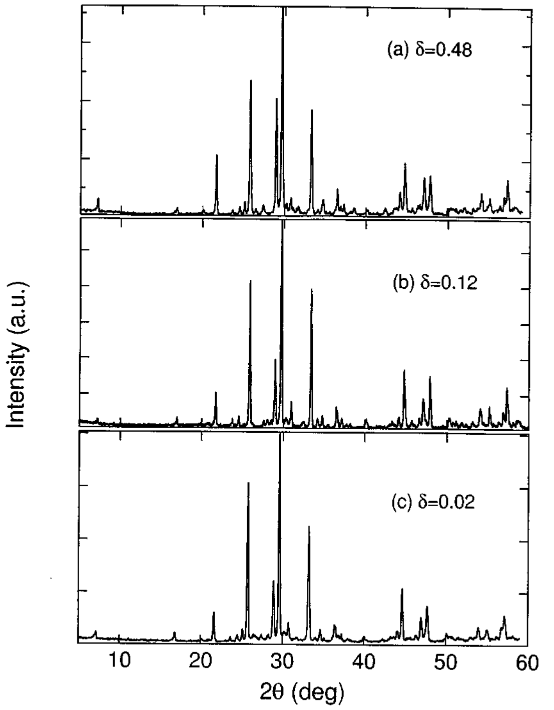

FIG. 2. XRD patterns for $Bi_2Sr_2CuO_{6+\delta}$ compounds with δ of (a) 0.48, (b) 0.12, and (c) 0.02.

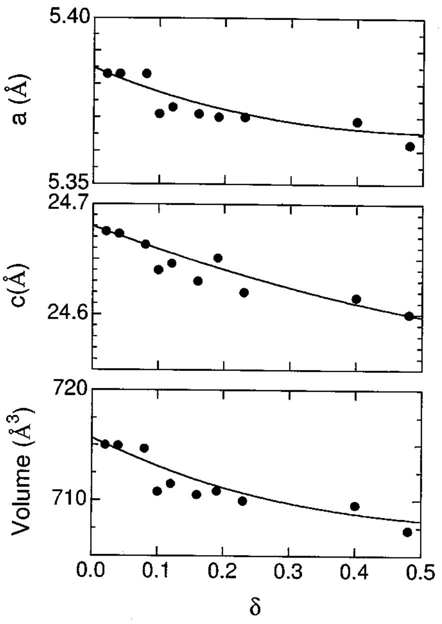

FIG. 3. Excess oxygen content, δ, dependence of lattice parameters for $Bi_2Sr_2CuO_{6+\delta}$ compounds. Solid lines are guides.

sample to the heat treatment (I) at 700°C, we obtained the superconducting phase of $Bi_2Sr_2CuO_{6.12}$ as shown in Fig. 2b. We also obtained the Bi2201 compounds with δ from 0.48 to 0.12 using the treatment (I) by controlling the temperature at which compounds were heated from 600 to 700°C. It has been, however, impossible to decrease the value of δ less than 0.12 using the treatment (I) even at higher temperature than 700°C due to the decomposition of the sample. To obtain the single phase of Bi2201 compound with lower value of δ, the compound was exposed to heat treatment (II). The titanium powder (0.5 $\Delta\delta$ mol per 1 mol of Bi2201) was enclosed in a silica tube because TiO_2 was found to be formed after the reaction, where $\Delta\delta$ represents the difference in δ before and after heat treatment. From the value of the standard free energy of formation for TiO_2 at 800°C (18), we can estimate the partial oxygen pressure in the quartz tube to be less than 10^{-30} Torr. Furthermore, the sample was heated at relatively low temperature (350°C) in order to avoid the rapid reduction and to keep the stability of Bi2201 phase. The XRD pattern for the sample obtained by the treatment (II) is shown in Fig. 2c. The value of δ of this sample was found to be 0.02 by the coulometric titration method. Thus, we have succeeded in varying the value of δ in Bi2201 compounds from 0.48 to 0.02 using the heat treatment (I) and (II). Figure 3 shows the oxygen content dependence of lattice parameters on the basis of a pseudo-tetragonal unit cell in which the modulated structure is ignored. One can notice that both *a* and *c* lattice constants and the volume of the unit cell increase with decreasing the oxygen content. This behavior is similar to those of other high-Tc oxides. The modulation period can also be estimated from the value of 2θ at satellite peaks in XRD patterns. In this estimation, we assume that the modulations exist along [0*kl*] direction as well as in the $Bi_{2+x}Sr_{2-x}CuO_y$ system (8, 19). As a result, it was noticeable that the modulated structure also varied continuously with decreasing oxygen content. In addition, for $\delta = 0.02$, we found that the direction was along [0*k*0] and that the period was almost 5.0 times as long as *b* lattice constants, implying that the modulation is nearly commensurate. The origin of modulated structure in Bi cuprate has been attributed to the existence of excess oxygen in the Bi–O layer (20, 21). This explanation is consistent with the fact that the excess oxygen content affects the period and/or the direction of the modulation in these Bi2201 compounds. It does not agree, however, with the existence of the modulation in the $Bi_2Sr_2CuO_{6.02}$ compound from which the excess oxygen has almost been removed. Thus, we may conclude that only the incommensurateness of the modulation is caused by the excess oxygen. The origin of the modulation is still unclear, although we may regard the origin as the intrinsic mismatching between the Bi–O rock salt layer and the Cu–O_2 layer.

3.2. *Resistivity*

Figure 4 shows the temperature dependence of the resistivity for Bi2201 compounds with various oxygen contents.

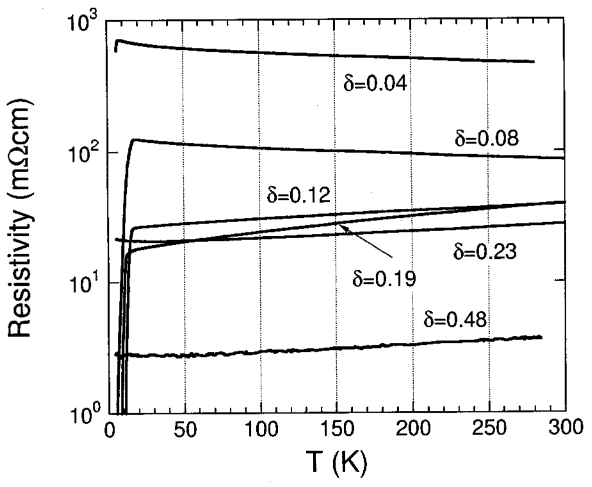

FIG. 4. Temperature dependence of the resistivity for $Bi_2Sr_2CuO_{6+\delta}$ compounds with various oxygen contents.

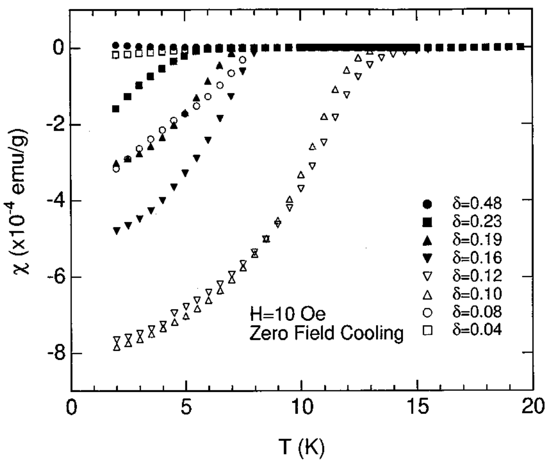

FIG. 5. Temperature dependence of the magnetic susceptibility for $Bi_2Sr_2CuO_{6+\delta}$ compounds with various oxygen contents. Metallic, superconducting, and semiconducting behaviors can be observed by changing the oxygen content.

For the sample with the value of δ more than 0.23, the temperature dependence of the resistivity shows the metallic behavior down to 4.2 K. The superconducting transition was observed around 10 K for the sample with δ ranging from 0.19 to 0.08. The resistivity above Tc of these superconducting phases shows T-linear dependence as previously reported (22–24). Moreover, the over-doped metallic sample with δ of 0.48 indicates the dependence of a higher power of T, neat T^2, at low temperature, which is typical behavior in an ordinary Fermi liquid. This crossover from T-linear to T^2-dependence has been observed also in $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201) compounds (25). On the other hand, the resistivity of the sample with δ of 0.04 shows the semiconducting behavior. Although the decrease of the resistivity was observed at low temperature, the superconducting fraction was possibly small as shown in the result of the magnetic susceptibility measurement. Moreover, we could not measure the resistivity of the sample with δ of 0.02 because its resistivity was too high to be detected with our apparatus at the room temperature. As mentioned below, this sample shows no Meissner effect down to 2 K. Consequently, in these Bi2201 compounds, we could synthesize all the metallic, superconducting, and insulating phases by changing only the oxygen content.

3.3. Magnetic Susceptibility

The temperature dependence of the magnetic susceptibility around Tc for Bi2201 compounds is shown in Fig. 5. Corresponding to the resistivity data, the superconducting transition was observed for the samples with δ from 0.19 to 0.08. The values of both Tc and Meissner volume fraction, *f*, for these samples are plotted against the excess oxygen content δ in Fig. 6a. Meissner volume fraction for $\delta = 0.12$ corresponds to about 40% of that for the powdered $YBa_2Cu_3O_7$ sample. The value of 2δ is not, however, exactly equal to the nominal hole concentration due to the mixed valence of Bi^{3+} and Bi^{5+}. The coulometric titration method

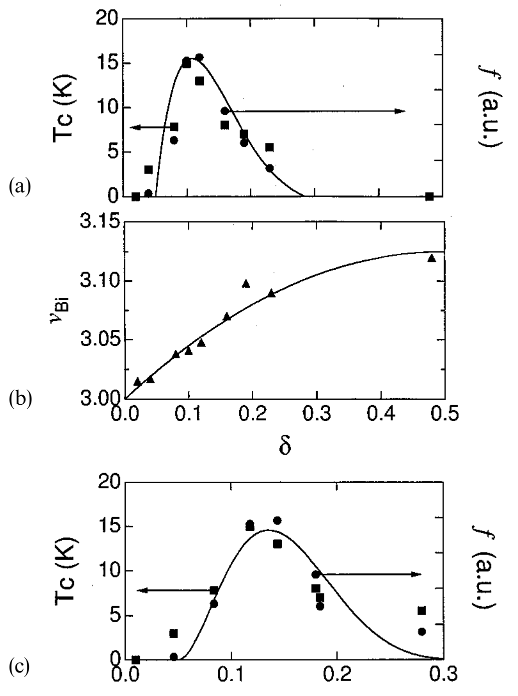

FIG. 6. (a) Excess oxygen content, δ, dependence of Tc and Meissner volume fraction, *f* and (b) the average valence of Bi, ν_{Bi}. The average hole concentration per unit cell can be estimated from values of δ and ν_{Bi} as a result of the charge neutrality. Thus, (c) the values of Tc and *f* are also plotted as a function of *h*.

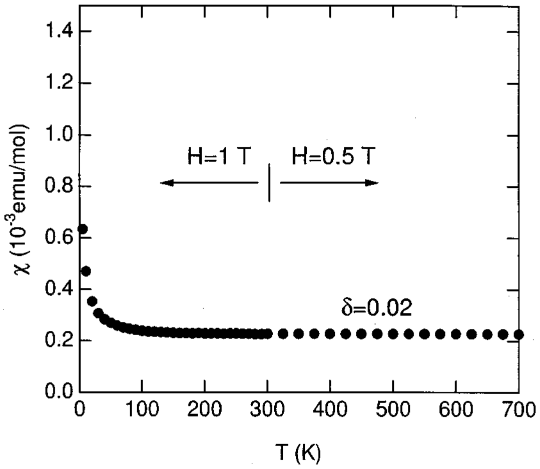

FIG. 7. Temperature dependence of the magnetic susceptibility for $Bi_2Sr_2CuO_{6.02}$ compound from 2 to 700 K. Measurement was performed under the field of 1 T by SQUID and in the field of 0.5 T by the magnetic balance, below and above 300 K, respectively.

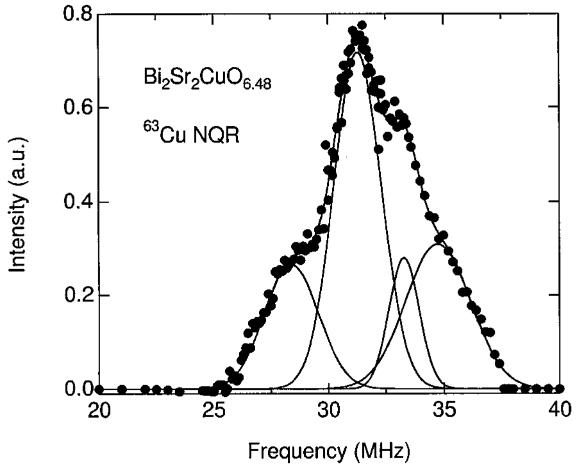

FIG. 8. Typical copper NQR spectrum for $Bi_2Sr_2CuO_{6.48}$ compound measured at 1.3 K. NQR component for ^{65}Cu is removed by numerical analysis.

has also enabled us to determine the average valence of Bi, ν_{Bi}. The oxygen content dependence of ν_{Bi} is shown in Fig. 6b. It is to be noted that the value of ν_{Bi} systematically increases with the oxygen content. As a result, using the charge neutrality we can calculate the average of hole concentration, h, given by $h = 2\delta - 2(\nu_{Bi} - 3)$. Thus, values of Tc and f can be plotted in Fig. 6c as a function of h for Bi2201 compounds. Notice that h dependence of Tc and fractions are similar to those of other high-Tc oxides except the maximum value of Tc.

In order to clarify magnetic properties of the insulating $Bi_2Sr_2CuO_{6.02}$ compound, we measured the magnetic susceptibility, χ, from 2 to 700 K as shown in Fig. 7. Measurements were performed by SQUID and magnetic balance techniques below and above 300 K, respectively. The magnitude of χ is almost temperature independent in contrast to that in the case of La_2CuO_4 in which the χ–T curve showed the peak at about 350 K due to the three-dimensional long range antiferromagnetic order (26). The disappearance of the cusp in the χ–T curve for $Bi_2Sr_2CuO_{6.02}$ should be attributed to the strong two-dimensional behavior of CuO_2 plane as reported in several experiments.

3.4. *NQR and NMR*

As shown in Fig. 8, Cu NQR spectrum was observed under zero magnetic field for the over-doped metallic sample of $Bi_2Sr_2CuO_{6.48}$. The NQR component for ^{65}Cu is removed by numerical analysis. The spectrum with NQR frequency (ν_Q) around 31 MHz can be decomposed into at least four broad peaks, although all Cu sites are equivalent in the ideal Bi2201 structure without the modulation. We can consider two reasons why several broad components were observed as follows. One is that ν_Q depends on the number of oxygen coordination around the Cu site. For example, because of different oxygen coordination caused by the excess oxygen, two resonance peaks were observed in the over-doped Tl2201 compound (27) without the modulation and with the similar structure as of Bi2201 compound. Hence, Cu sites in over-doped Bi2201 compound were probably coordinated with several different numbers of oxygen owing to about one excess oxygen per two unit cells. The other reason is that the random potential at Cu sites should be induced by the modulated structure in the Bi–O layer. In fact, broader NQR spectrum, whose width is about 10 MHz, has been observed in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) compounds (28) in contrast to that in $YBa_2Cu_3O_7$ (29, 30).

As seen in Fig. 9, Cu NQR spectrum was also measured in the superconducting $Bi_2Sr_2CuO_{6.12}$ compound of which the ν_Q shifted to a lower and narrower frequency range between 24 and 37 MHz compared with that of $Bi_2Sr_2CuO_{6.48}$ sample. This oxygen content dependence of ν_Q was also observed in Tl2201 compounds (27).

In Fig. 10, we show the NMR spectrum for the insulating sample of $Bi_2Sr_2CuO_{6.02}$ at 1.3 K. One can note broad resonance lines located in the frequency region between 80 and 100 MHz. The reason for the broad spectrum can also be attributed to the above-mentioned reasons to NQR measurements for the over-doped Bi2201 compound. The result could be interpreted not only by electric quadrupole interactions but also by the antiferromagnetic order of Cu^{2+} spins as investigated on $YBa_2Cu_3O_6$ and La_2CuO_4 (31, 32). Six lines, however, should be observed for the single copper site, including two isotopes of ^{63}Cu and ^{65}Cu, under the hyperfine field with the quadrupole interaction. Therefore, assuming that the spectrum consisted of one

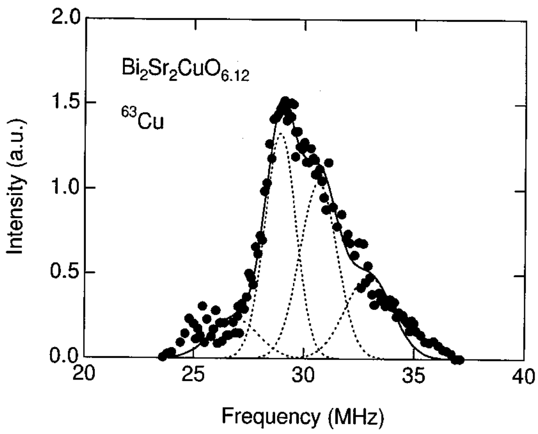

FIG. 9. Typical copper NQR spectrum for $Bi_2Sr_2CuO_{6.12}$ compound measured at 1.3 K. NQR component for ^{65}Cu is removed by numerical analysis.

component, we analyzed the spectrum using third-order perturbation theory of hyperfine interactions with parameters of ν_Q of ^{63}Cu frequency $^{63}\nu_Q$, the hyperfine field H_{hf} and the angle θ between the principal axis of the electronic field gradient (EFG). Here, the axial symmetry of the EFG η was considered to be 0. The solid line in Fig. 10 indicates the spectrum profile produced by the parameters of $H_{hf} = 76.12$ kOe, $^{63}\nu_Q = 29$ MHz, and $\theta = 70°$. The spectrum could be fitted by other profiles with different values of $^{63}\nu_Q$ and θ, although the value of H_{hf} was almost the same in those profiles. As a result, we obtained the parameters $H_{hf} \sim 76$ kOe, $^{63}\nu_Q = 22 \sim 30$ MHz, and $\theta = 65 \sim 90$ degree as shown in Table 1. Static parameters obtained with NMR experiments for other cuprate are also given in Table 1 for the comparison. As a result, these parameters were found to be comparable to those of other antiferromagnetic cuprate.

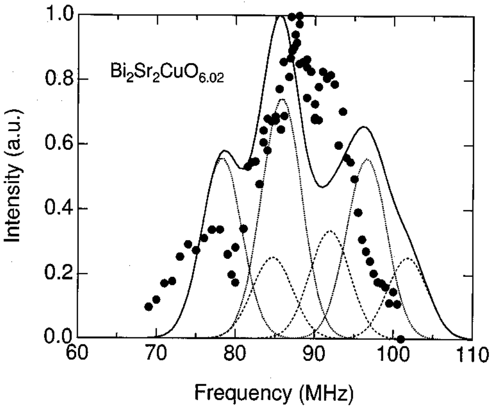

FIG. 10. AF–NMR spectrum of Cu site for $Bi_2Sr_2CuO_{6.02}$ compound measured at 1.3 K under zero magnetic field. Fitted lines are obtained by third-order perturbation theory of hyperfine interaction with parameters $H_{hf} = 76.12$ kOe, $^{63}\nu_Q = 29$ MHz, and $\theta = 70°$. Dotted lines and broken lines correspond to components for ^{63}Cu and ^{65}Cu, respectively.

TABLE 1

Values of H_{hf}, $^{63}\nu_Q$, θ, and $|A–4B|$ for $Bi_2Sr_2CuO_{6.02}$ and Antiferromagnetic Phases of Other High-Tc Oxides

Compound	H_{hf} (kOe)	$^{63}\nu_Q$ (MHz)	θ (degree)	$\lvert A–4B\rvert$ (kOe/μ_B)
$Bi_2Sr_2CuO_{6.02}$	~76	$22 \sim 30$	$65 \sim 90$	109 (127[d])
$TlBa_2YCu_2O_7$[a]	86.2	20.44(±1.3)	81(±9)	144[d]
$YBa_2Cu_3O_6$[b]	79.65	22.87	90(±10)	132.8[d]
La_2CuO_4[c]	81.86	31.9	79	136.4[d]

[a] Ref. (12).
[b] Ref. (31).
[c] Ref. (32).
[d] Result of the value of $\mu_{Cu} = 0.6$ which is obtained by theoretical estimation (Refs. (12) and (33)).

We could not obtain the exact value of the hyperfine coupling constant $A–4B$, in which A and B represent the on-site and transferred hyperfine coupling constants, because of the lack of Knight shift data at various temperatures. Nevertheless, we could estimate the absolute value using the static magnetic moment. Experimental results of the magnetic moment in antiferromagnetic Bi2201 phase have not yet been obtained, so we used the value of the Bi2212 compound. Recently, an antiferromagnetic-ordered state in $Bi_2Sr_2PrCu_2O_8$, which was obtained by substituting Pr^{3+} for Ca^{2+} in the Bi2212 superconductor, was observed by Moudden *et al.* (15) using the neutron scattering experiment. They found that the magnetic moment of Cu was 0.7 ± 0.1 μ_B and that it was comparable with other cuprate antiferromagnets such as La_2CuO_4 and $YBa_2Cu_3O_6$. Assuming that the moment of Cu, μ_{Cu}, in Bi2201 phase is almost the same value as in Bi2212 phase, we can estimate the absolute value of hyperfine coupling constant $|A–4B|$ written by $|H_{hf}/\mu_{Cu}|$ to be 109 kOe/μ_B. Hence, this value is naturally similar to those of other antiferromagnetic phases of high-Tc oxides. Thus, we have confirmed the existence of long-range magnetic order in the insulating Bi2201 compound and that the static magnetic parameters of CuO_2 planes are almost the same as those of other antiferromagnetic phases in high-Tc oxides. Consequently, the nature of antiferromagnetic order of Cu–3*d* spins is universal for most high-Tc oxides. For more quantitative discussion, spin dynamics in the Bi2201 compound must be clarified by the measurement of the nuclear spin relaxation rate, which is now in progress.

4. SUMMARY

We have succeeded in synthesizing the insulating $Bi_2Sr_2CuO_{6+\delta}$ with the stoichiometric cation composition by heat treatment with titanium powder. The excess oxygen content

δ in this sample was measured by the coulometric titration method and found to be 0.02. The hole concentration h was also estimated with values of δ and the average valence of Bi in Bi2201. As a result, temperature dependence of resistivity for various values of δ and h dependence of Tc and Meissner volume fraction showed almost the same behavior as those in other high-Tc oxides. From the analysis of the NMR spectrum of Cu(2) site, we confirmed the antiferromagnetic order of Cu^{2+} spins. Therefore, we could synthesize the three electronic states of insulating, superconducting, and over-doped metallic phases in Bi2201 compounds by changing only oxygen content. The static parameters of the hyperfine field and the electric field gradient at Cu sites in $Bi_2Sr_2CuO_{6.02}$ were found to be almost comparable to those of other antiferromagnetic phases of high-Tc oxides.

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