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Magnetic properties of copper cluster-spins in BaCuO_{2+x} ($x = 0$ and 0.14), investigated by magnetization and nuclear magnetic resonance measurements

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Abstract

To clarify the combined magnetic behaviour of BaCuO_{2+x} , which contains in the body-centred-cubic unit cell two $\text{Cu}_{18}\text{O}_{24}$ spherical clusters, eight Cu_6O_{12} ring clusters, and six CuO_4 lone units, we made measurements of magnetization, $^{63,65}\text{Cu}$ nuclear magnetic resonance (NMR) near 6 T, and pure quadrupole resonance (PQR) in zero field on samples with well-defined oxygen contents $x = 0$ and 0.14 . Quantitative analyses of Curie–Weiss-like susceptibility data for $\text{BaCuO}_{2.00}$ indicate that Cu spins within the Cu_6 clusters go into a ferromagnetically (FM) ordered ground state with a maximum spin $S_r = 3$ below ~ 100 K, and those within the Cu_{18} clusters into an FM-like ground state below ~ 20 K with net spin $S_s \sim 5$ that is less than the maximum possible spin $S_s = 9$. For $\text{BaCuO}_{2.14}$ the Cu spins within the Cu_6 clusters go into an FM ordered ground state at a lower temperature of ~ 30 K, and these clusters exhibit no signature of long-range magnetic ordering down to 2 K. The NMR spectra for $\text{BaCuO}_{2.00}$ observed below ~ 12 K have a trapezoidal structure that is known to be a characteristic of long-range magnetic ordering, and is consistent with the antiferromagnetic ordering of the Cu_6 clusters below $T_N = 15$ K predicted previously. On the other hand, the spectrum for $\text{BaCuO}_{2.14}$ observed in a temperature range between 1.2 and ~ 50 K has an electric quadrupole-split powder pattern structure. This provides microscopic evidence that there is no long-range magnetic ordering in $\text{BaCuO}_{2.14}$. The addition of 0.14 moles of oxygen atoms results in a large suppression of some magnetic entities. We find,

however, some anomalies in the NMR and PQR data for $\text{BaCuO}_{2.14}$ near ~ 10 K, which could be associated with short-range ordering of the paramagnetic Cu_{18} clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Clusters of atoms and ions have been widely studied in physics because they represent a form of matter that is intermediate between single atoms and bulk matter. In the copper oxides, the couplings of the magnetic moments are realized via superexchange interactions and their sign depends on the $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ bond angles [1, 2]. A linear bond superexchange leads to an antiferromagnetic (AFM) interaction, whereas a 90° bond angle produces a ferromagnetic (FM) interaction. Thus the study of the magnetic properties of spin clusters should provide a valuable insight into the physics of the superexchange interactions with intermediate bond angle.

In oxocuprate BaCuO_{2+x} ($x \approx 0$), despite its simple chemical formula (space group = $Im3m$), there are three different systems of Cu spins within which, and between which, there are complex interactions. The Cu atoms are all in square-planar CuO_4 units, most of which share edges to form $\text{Cu}_{18}\text{O}_{24}$ sphere-like clusters and Cu_6O_{12} ring-like clusters. The bcc unit cell (lattice parameter $a = 18.28$ Å) contains two of the sphere-like clusters centred on the corner and body-centre positions, and eight of the ring-like clusters located between the spheres and centred on the four body diagonals. There are also partially occupied sites that correspond to Cu_2O_{10} clusters, each of which can contain two CuO_4 units that do not share edges. In the bcc unit cell there are six of these clusters located between the spheres on the cube edges, and on parallel lines through the cube centre, but the Cu sites are only 50% occupied, giving a total of six Cu of this type, referred to as lone spins [3–5] (figure 1). Within a Cu_6 cluster the bond angle is 83° and within the Cu_{18} cluster it is 87° . This allows the nature of the superexchange interaction for angles near 90° to be studied.

Magnetization [6, 7] and neutron diffraction [6, 8] measurements on a BaCuO_{2+x} sample revealed that the lone unit Cu ions have spin $S = 1/2$, while the Cu spins within each of the Cu_6 ring and Cu_{18} sphere clusters form FM ordered ground states with net spins of $S_r = 3$ and $S_s \sim 9$, respectively. Neutron diffraction studies on a single crystal [10] confirmed long-range AFM ordering of the Cu_6 clusters below $T_N = 13$ K, as proposed by Wang *et al* [6]. There was no indication of FM ordering of the Cu_{18} clusters down to 50 mK, in disagreement with the suggestion based on the magnetic susceptibility measurements [6].

Fisher *et al* have carried out specific heat measurements on the same samples of $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$ [9] used in the present measurements. For $\text{BaCuO}_{2.00}$ they observed, in addition to a cooperative ordering anomaly associated with the AFM ordering of Cu_6 clusters at ~ 15 K, two Schottky-like anomalies having maxima at ~ 5 and ~ 0.7 K. These anomalies can be identified with magnetic ordering (not long range) of the paramagnetic (PM) net spins of the Cu_{18} clusters and most likely of the $S = 1/2$ spins of the lone units, respectively. Since for $\text{BaCuO}_{2.14}$ only the Schottky-like anomalies are observed, this suggests that the increase in the Cu oxidation increases Cu–O covalent bonding and/or produces nonmagnetic Cu^{3+} ions. The conjecture by Wang *et al* [6] that the lone spins and Cu_{18} clusters interact to form a ferromagnetic complex at ~ 5 K and, in turn, order antiferromagnetically below ~ 1 K is not supported. The magnetic properties of BaCuO_{2+x} are very sensitive to the increase in Cu oxidation.

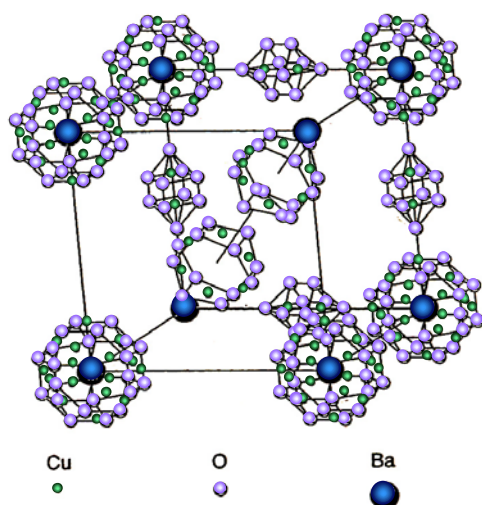


Figure 1. A perspective representation of the two types of Cu/O clusters and lone units in the bcc unit cell of BaCuO_{2+x} , cited from [6].

We have measured the magnetization M , nuclear magnetic resonance (NMR), and pure quadrupole resonance (PQR) of $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$ samples with well-defined oxygen contents in order to reveal microscopically the combined magnetic states and the effect of the Cu oxidation on them. The polycrystalline ceramics with $x = 0$ and 0.14 in this study are the same samples used in the specific heat [10] and susceptibility [6, 7] measurements. Details of the sample preparation procedure are given in [6] and [10].

2. Magnetization

The magnetization was measured in a temperature (T) range between 2 and 300 K at magnetic fields of $H = 0.5$ and 50 kOe with a superconducting quantum interference device (SQUID) magnetometer. As is shown in figure 2, the value of M/H above ~ 40 K is independent of H and, therefore, gives a measure of the magnetic susceptibility, χ . Below ~ 40 K, on the other hand, M/H depends on H and exhibits saturation behaviour at $H = 50$ kOe. We take the M/H data at 0.5 kOe as the value of χ . The inverse χ plotted in figure 3 for each of the samples does not follow the Curie–Weiss law, $1/\chi = (T - \Theta)/C$, as reported previously [8]. We evaluated the Weiss temperature Θ and effective magnetic moment $\mu_{\text{eff}} = (3k_{\text{B}}C/N_{\text{A}})^{-1/2}/\mu_{\text{B}}$ for 20 K intervals using five successive χ data points. As shown in figures 4 and 5, the value of μ_{eff} increases with decreasing temperature, accompanied by a decrease of Θ .

3. Nuclear magnetic resonance spectra

The NMR and PQR measurements were carried out with wide-band phase-coherent spin-echo spectrometers. The sample coil was made of silver wire. The resonance signal of ^{63}Cu ($I = 3/2$, $\gamma_n = 1.1285 \text{ kHz Oe}^{-1}$, $Q = -0.211 \text{ cm}^2$, natural abundance 69.09%) and ^{65}Cu ($I = 3/2$, $\gamma_n = 1.2090 \text{ kHz Oe}^{-1}$, $Q = -0.195 \text{ cm}^2$, natural abundance 30.09%) in $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$, respectively, could be observed only at temperatures below ~ 15 and ~ 50 K because of the small signal intensity. The NMR spectra observed at 75 MHz and 4.2 K in a field sweeping procedure are displayed in figure 6.

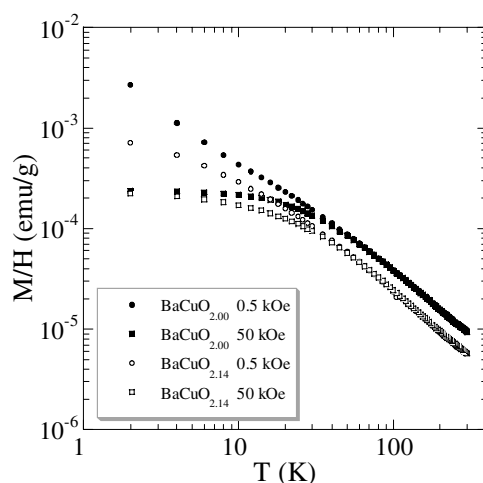


Figure 2. The temperature dependence of the magnetization divided by applied magnetic fields of 0.5 and 50 kOe for both $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$.

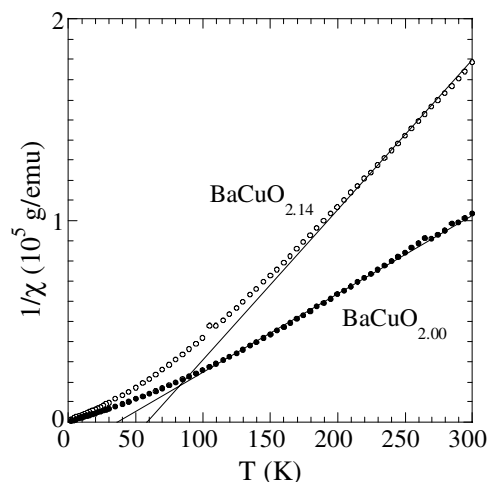


Figure 3. The inverse susceptibility plotted against temperature for $\text{BaCuO}_{2.00}$ (closed circles) and $\text{BaCuO}_{2.14}$ (open circles).

The NMR spectrum for $\text{BaCuO}_{2.14}$ has the characteristic of an electric quadrupole-split powder-pattern structure, which consists of an equally separated satellite pair and a second-order split central line [11]. In order to assign the resonance peaks, we made PQR measurements in zero field with a frequency sweep procedure in the range 20–28 MHz (figure 7(a)). From the resonance frequency at the peak intensity point of the PQR spectrum, we obtain the values of the quadrupole frequency $\nu_Q = e^2qQ/2h = 23.5$ and 21.7 MHz for ^{63}Cu and ^{65}Cu , respectively. Here, Q is the quadrupole moment and q the electric field gradient at the nucleus. As is shown in figure 8, most of the resonance peaks in the NMR spectrum could be reproduced as a superposition of two sets of resonance lines (solid curves in the figure) originating from ^{63}Cu and ^{65}Cu , with corresponding ν_Q values. In the NMR spectrum for $\text{BaCuO}_{2.14}$, however, there is an additional single resonance line between the second-order

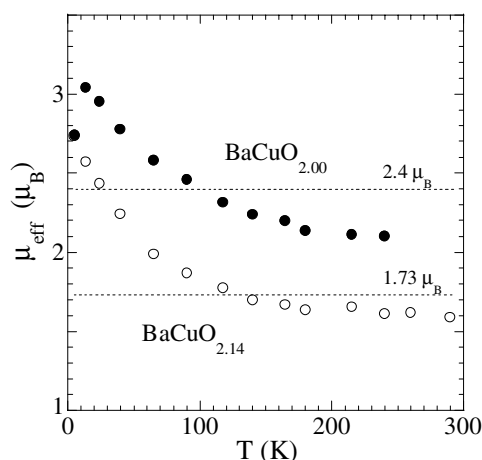


Figure 4. The temperature dependence of the effective magnetic moment for BaCuO_{2.00} (closed circles) and BaCuO_{2.14} (open circles), deduced by the procedure described in the text.

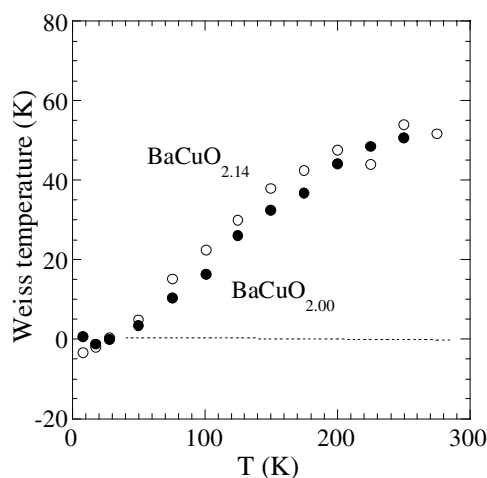


Figure 5. The temperature dependence of the Weiss temperature for BaCuO_{2.00} (closed circles) and BaCuO_{2.14} (open circles), deduced by the procedure described in the text.

quadrupole-split central peaks for each of ⁶³Cu and ⁶⁵Cu (illustrated by the coloured spectra in figure 8). The resonance shift $K = (H_0 - H_{\text{res}})/H_{\text{res}}$ of ⁶³Cu for the quadrupole-split spectrum was deduced through the spectrum analysis described above, and that for the single resonance line was defined at the peak intensity point. As is plotted by open circles in figure 9 against temperature, K of the quadrupole-split spectrum has a positive value of $\approx 0.25\%$ and is almost temperature independent. However, the negative K of the single resonance line only weakly depends on temperature (square symbols in figure 9), and exhibits a small anomaly near 12 K. It is worth noting that, as shown in figure 7(b), the PQR signal intensity at low temperatures decreases with decreasing temperature without significant linewidth broadening, and completely disappears below 2.4 K.

In contrast, the NMR spectrum for BaCuO_{2.00} shown in figure 6 has a trapezoid-like line shape without any distinguishable peaks, which is known to be a characteristic of long-range

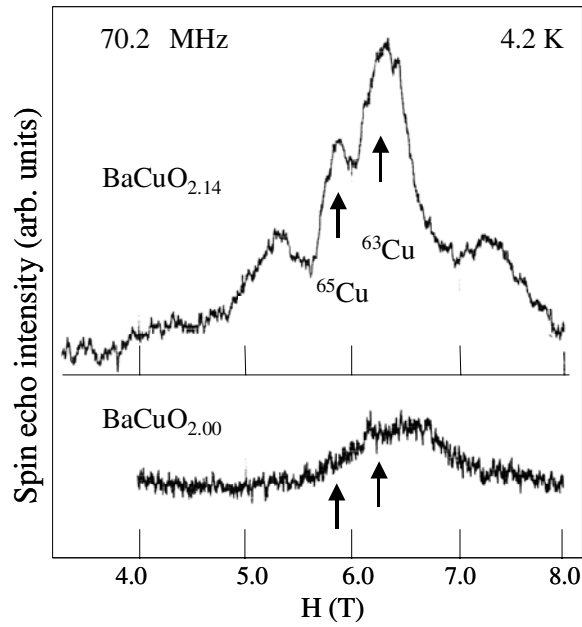


Figure 6. NMR spectra observed for $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$ at 4.2 K and 75 MHz.

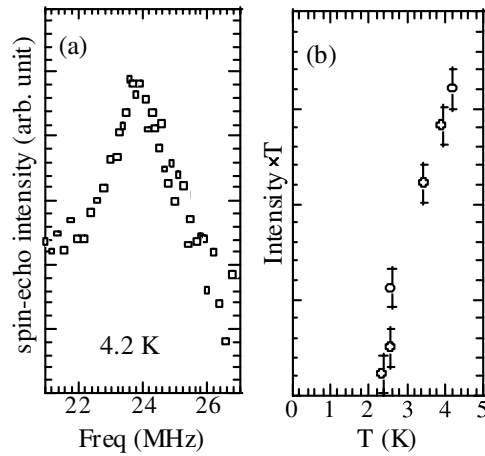


Figure 7. (a) PQR spectra observed for $\text{BaCuO}_{2.14}$ at 4.2 K, and (b) the temperature dependence of PQR intensity multiplied by temperature, IT .

magnetically ordered states. The negative K , tentatively deduced from the spectrum, increases with decreasing temperature as shown in figure 9 by the closed circles. The PQR signal for $\text{BaCuO}_{2.00}$ could not be observed within the present experimental temperature range.

4. Nuclear spin–lattice relaxation

Measurement of the nuclear spin–lattice relaxation time T_1 provides information on the dynamical property of the Cu spins. We measured T_1 at the centre position of the ^{63}Cu

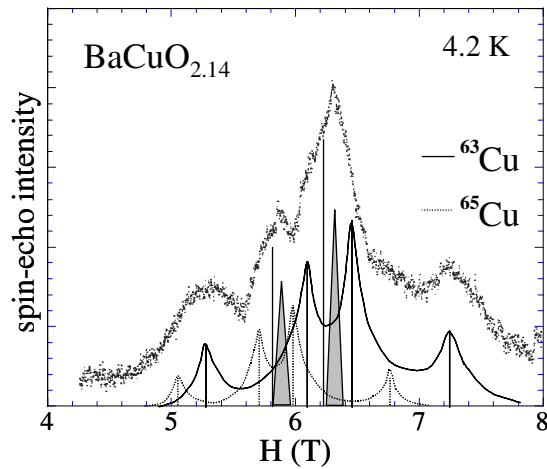


Figure 8. The decomposition of the NMR spectrum for BaCuO_{2.14} into two sets of quadrupole-split NMR lines, and a single resonance line.

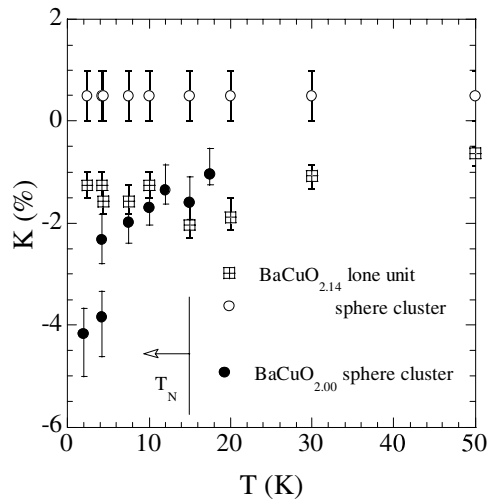


Figure 9. The temperature dependence of the ⁶³Cu resonance shift for sphere clusters (open circles) and lone units (square symbols) in BaCuO_{2.14}, and for sphere clusters (closed circles) in BaCuO_{2.00}.

NMR spectra utilizing a single rf saturation method. The theoretical magnetization recovery curve at a time t after the saturation pulse is given by [12]

$$[M(\infty) - M(t)]/M(\infty) = \sum a_i \exp[-b_i t/T_1] \quad (1)$$

where the coefficients $b_1 = 1$, $b_2 = 6$ and $a_1 = 0.1$, $a_2 = 0.9$ for the central $|1/2\rangle \leftrightarrow |-1/2\rangle$ transition. We cannot, however, reproduce the experimental recovery curves by equation (1). As mentioned above, the ⁶³Cu NMR signal at the peak position of the spectrum consists of the single resonance line and the second-order quadrupole-split central line. We assumed that the experimental magnetization M is composed of two components: M_l with a relaxation time T_1^l ; and M_s with a relaxation time T_1^s . The values of the relaxation times T_1^l and T_1^s were

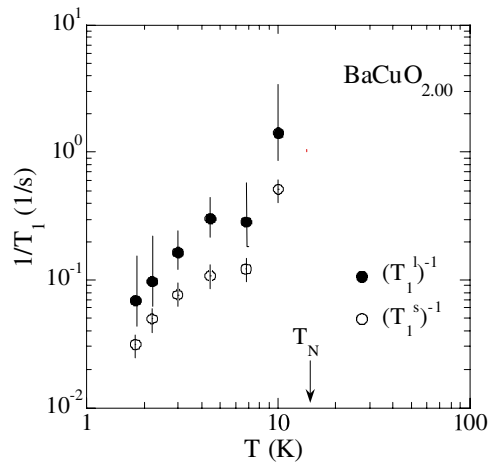


Figure 10. The temperature dependence of the rapid and slow relaxation rates $(T_1^l)^{-1}$ and $(T_1^s)^{-1}$ for $\text{BaCuO}_{2.00}$.

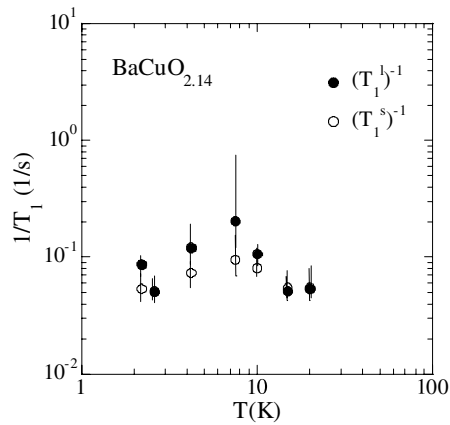


Figure 11. The temperature dependence of the rapid and slow relaxation rates $(T_1^l)^{-1}$ and $(T_1^s)^{-1}$ for $\text{BaCuO}_{2.14}$.

determined by fitting experimental $M(t)$ data with the theoretical recovery curve given by following equation:

$$[M(\infty) - M(t)]/M(\infty) = M_l \sum a_i \exp[-b_i t / T_1^l] + M_s \sum a_i \exp[-b_i t / T_1^s]. \quad (2)$$

Taking $M_s/M_l \sim 0.7$, the experimental recovery curves can be reproduced satisfactorily. The values of $(T_1^l)^{-1}$ and $(T_1^s)^{-1}$ deduced through this procedure are plotted against temperature in figures 10 and 11 for $\text{BaCuO}_{2.00}$ and $\text{BaCuO}_{2.14}$, respectively. As can be seen in the figures, $(T_1^l)^{-1}$ has almost the same temperature dependence as $(T_1^s)^{-1}$: for $\text{BaCuO}_{2.00}$, T_1^{-1} measured in the long-range AFM ordered state decreases with decreasing temperature, and is roughly proportional to T^2 ; for $\text{BaCuO}_{2.14}$, T_1^{-1} weakly depends on temperature and shows a small maximum near 7 K.

Table 1. Combined effective magnetic moments (μ_B) calculated for four possible cases compared with experimental data for of BaCuO_{2.00} and BaCuO_{2.14}.

		Intra-cluster		Inter-cluster	
	Cu ₆ cluster	PM	FM ($S_r = 3$)	FM ($S_r = 3$)	Long-range AFM
	Cu ₁₈ cluster	PM	PM	FM ($S_r = 3$)	IPM
	μ_{eff} (cal)	1.73	2.5	3.5	3.3 μ_B
BaCuO _{2.00}	μ_{eff} (exp)		2.1 (300 K)	3.1 (15 K)	2.7 (2 K)
BaCuO _{2.14}	μ_{eff} (exp)	1.6 (300 K)		2.7 (2 K)	

5. Discussion

The magnetic susceptibility χ at high temperatures exhibits linear Curie–Weiss-type behaviour with a positive Weiss temperature $\Theta = 50$ K (figure 3), which indicates that the dominant interactions are ferromagnetic. With decreasing temperature below ~ 200 K, the χ data begin to deviate from the linear relation, which is consistent with the data reported by Wang *et al* [6].

In the PM state of BaCuO_{2+x}, χ of the unit cell is a sum of contributions from the two spherical clusters, eight ring clusters, and six lone units:

$$\chi(T) = 2\chi_s(T) + 8\chi_r(T) + 6\chi_l(T). \quad (3)$$

We calculated the value of the combined effective magnetic moments μ_{eff} per unit cell for four possible cases: (1) Cu spins are all in the PM state with $S = 1/2$; (2) Cu spins within Cu₆ clusters are in the FM ground state with $S_r = 3$; (3) Cu spins within Cu₁₈ clusters are also in the FM ground state with $S_s = 9$. (4) net spins of Cu₆ ring clusters are in the long-range AFM ordered state. The results are tabulated in table 1.

The experimental value of $\mu_{\text{eff}} = 1.6 \mu_B$ for BaCuO_{2.14} near room temperature is close to $1.73 \mu_B$ for free Cu²⁺ ions, indicating that at room temperature there is no magnetic ordering within either intra-clusters or inter-clusters. With decreasing temperature, the experimental μ_{eff} shows a monotonic increase and at ~ 20 K exceeds a value $2.4 \mu_B$ that is expected for the formation of a FM ground state for the Cu spins within the Cu₆ ring clusters with $S_r = 3$. The maximum $\mu_{\text{eff}} = 2.3 \mu_B$ near 2 K with $\Theta = -3.5$ K is assumed to be associated with the increase in the ferromagnetic coupling within the Cu₁₈ ring clusters and the increase in the AFM coupling between the net spins of the ring clusters. No indication of long-range magnetic ordering in the χ data for BaCuO_{2.14} down to 1.2 K is consistent with the specific heat [10] and magnetization measurements.

The stoichiometric oxocuprate BaCuO_{2.00} has a larger effective moment $\mu_{\text{eff}} = 2.1 \mu_B$ at 300 K in comparison with BaCuO_{2.14}. We conclude that Cu spins within the Cu₆ ring clusters of BaCuO_{2.00} are in a state near the FM ordered ground state even at rather high temperatures. With a lowering of the temperature, μ_{eff} increases and takes a maximum value of $3.1 \mu_B$ near ~ 15 K followed by a significant decrease. This can be explained reasonably by the long-range AFM ordering of the spins of the Cu₆ clusters predicted previously [6]. The calculation of the combined effective moment of the clusters based on equation (3) indicates that the experimental maximum value of $3.1 \mu_B$ is realized when the Cu spins within the Cu₁₈ sphere clusters go into a FM-like ordered state with net spin of $S_s \sim 5$, in addition to the FM ordered ground state of the Cu₆ ring clusters. The net spin of $S_s \sim 5$ that is smaller than the maximum possible spin $S_s = 9$ was also reported previously in the data analysis of the neutron diffraction pattern observed at 10 kOe and 0.05 K [9]. This could be explained if three lone spins ($S = 1/2$) adjacent to each sphere cluster were coupled to the sphere cluster to form a ferrimagnetic complex proposed by Wang *et al* [6]. However, the two Schottky-like anomalies having maxima at ~ 5 and ~ 0.7 K

observed in the specific heat of $\text{BaCuO}_{2.00}$ [10] do not support this conjecture because the anomalies can be identified with the magnetic ordering (not long range) of the PM net spins of Cu_{18} clusters and, most likely, the lone units, respectively. Thus we conclude that the ground state of the Cu_{18} clusters has net spins of $S_s \sim 5$ with a complex spin structure associated with the nature of the superexchange interaction for the $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ with bond angle 87° .

In the unit cell of BaCuO_{2+x} , there are three crystallographically inequivalent Cu sites: $\text{Cu}_{18}\text{O}_{24}$ sphere clusters, Cu_6O_{12} ring clusters, and CuO_4 lone units. In the Cu_{18} sphere and Cu_6 ring clusters, the Cu atoms are all in square-planar CuO_4 units and, therefore, the NMR spectrum originating from these clusters is considered to have the electric quadrupole-split structure with quadrupole frequencies $\nu_Q = e^2qQ/2h$ that are not far from the values observed for many of the copper oxides (for example, ν_Q of ^{63}Cu in high- T_C superconducting oxides [13]). In the long-range AFM ordered state of the Cu_6 clusters, the NMR frequency of ^{63}Cu originating from the ring clusters would be largely shifted making observation of the signal difficult. On the other hand, the NMR spectrum originating from the sphere clusters would be only broadened through the transferred hyperfine interactions with the adjacent ring clusters. From the number of the Cu nuclei in the unit cell (36 Cu in sphere clusters, 48 Cu in ring clusters, and 6 Cu in the lone units), the NMR signal intensity originating from the lone units is smaller than those from the sphere and ring clusters.

The ^{63}Cu NMR for PM $\text{BaCuO}_{2.14}$ consists of two spectra as seen in figure 8: an electric quadrupole-split powder-pattern spectrum with $\nu_Q = 23.5$ MHz; and a single resonance line with $\nu_Q \sim 0$. We assign the quadrupole-split spectrum to the Cu nuclei in the Cu_{18} sphere cluster because the ν_Q value has a reasonable magnitude for a square-planar CuO_4 unit and, in the long-range AFM ordered state of $\text{BaCuO}_{2.00}$, each of the quadrupole-split lines is not shifted but broadened with a trapezoidal shape (figure 6). The single resonance line in figure 8 is assigned to the Cu nuclei in lone units because of the relatively small signal intensity. Lack of distinguishable quadrupole splitting could be expected from its rather small local crystal asymmetry.

As is plotted by open circles in figure 9, the ^{63}Cu resonance shift for the sphere clusters of $\text{BaCuO}_{2.14}$ is positive (0.5%) and nearly independent of temperature. K for the sphere clusters is considered to be dominated by the orbital contribution, and the transferred hyperfine coupling with the adjacent ring clusters is considered to be small enough. On the other hand, the negative Knight shift for the lone units weakly depends on temperature (square symbols in figure 9). Above ~ 40 K, K versus χ plots shown in figure 12 are roughly on a straight line, and the slope of the line gives an estimate of hyperfine field $H_{\text{hf}} = N\mu_B K/\chi \simeq -3.0$ kOe/ μ_B .

The weak temperature dependent behaviour of the nuclear spin-lattice relaxation rate T_1^{-1} for both the lone units and sphere clusters of $\text{BaCuO}_{2.14}$ (figure 11) is consistent with the lack of long-range magnetic ordering. The small temperature independence of T_1^{-1} is indicative of a dominant relaxation process to the fluctuations of local magnetic moments [14]. T_1^{-1} for $\text{BaCuO}_{2.00}$ measured in the long-range AFM state largely decreases with decreasing temperature (figure 10). This is caused by the suppression of the spin fluctuations associated with the long-range AFM ordering of the Cu_6 ring clusters [15].

For $\text{BaCuO}_{2.14}$, the specific heat [10] and the present magnetization measurements on $\text{BaCuO}_{2.14}$ showed that the system is PM down to 0.35 K without any long-range magnetic ordering. The observation of well separated NMR lines for $\text{BaCuO}_{2.14}$ down to 1.7 K is consistent with the specific heat and magnetization measurements. However, we find in the NMR and PQR data some anomalous behaviour:

- (1) a negative K for the lone unit exhibits a small peak near 15 K (square symbols in figure 9), and in the K versus χ plots below ~ 15 K there is a deviation from a straight line;
- (2) T_1^{-1} shows a small anomaly near 8 K followed by small decrease;

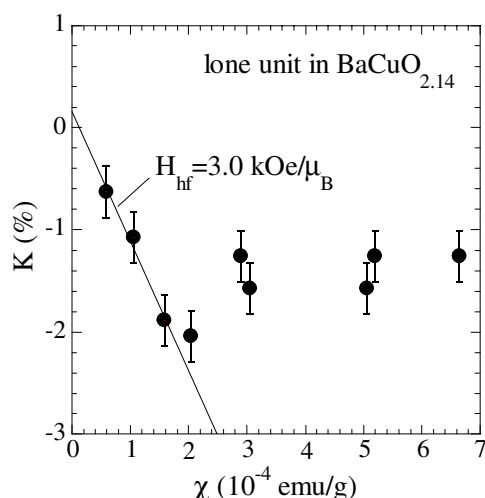


Figure 12. ⁶³Cu Knight shift versus χ plots for lone units of BaCuO_{2.14}.

- (3) the PQR signal intensity in zero field originating from the Cu₁₈ clusters decreases with decreasing temperature and completely disappears below 2.4 K as shown in figure 7(b), although the NMR signal intensity observed at ~ 6 T does not vary with temperature down to 1.7 K.

These results indicate that (short-range) magnetic ordering appears in BaCuO_{2.14} at low temperatures. Fisher *et al* observed for BaCuO_{2.14} a Schottky-like specific heat anomaly at low temperatures. The application of the magnetic field moves the threshold of the anomaly toward higher temperature. We conclude that the NMR and PQR anomalies observed for BaCuO_{2.14} are closely related to the short-range ordering of PM net spins of the Cu₁₈ sphere clusters.

6. Conclusion

We have carried out magnetization, ^{63,65}Cu NMR, and PQR measurements for BaCuO_{2+x} with well-defined oxygen contents $x = 0$ and 0.14. Quantitative analyses of the Curie–Weiss-like χ data for BaCuO_{2.00} indicate that Cu spins within the Cu₆ clusters go into an FM ordered ground state with a maximum spin $S_r = 3$ below ~ 100 K, and those within the Cu₁₈ clusters into an FM-like ground state below ~ 20 K with net spin $S_s \sim 5$ less than the maximum possible spins $S_s = 9$. The net spins of ring clusters order antiferromagnetically below $T_N = 15$ K. For BaCuO_{2.14} the Cu spins within the Cu₆ clusters go into the FM ordered ground state at a lower temperature of ~ 30 K. No signature of long-range magnetic ordering appears in the χ data down to 2 K. The NMR spectrum for BaCuO_{2.14} observed in the temperature range between 1.2 and ~ 50 K has an electric quadrupole-split powder-pattern structure, and is assigned to the Cu nuclei in the sphere clusters. This provides evidence that there is no long-range magnetic ordering in BaCuO_{2.14}. The NMR spectra for BaCuO_{2.00} observed below ~ 12 K has a trapezoidal structure that is consistent with the AFM ordering of the Cu₆ clusters below $T_N = 15$ K. The addition of 0.14 moles of oxygen atoms results in a large suppression of some magnetic entities. We find, however, several anomalies in the NMR and PQR data for BaCuO_{2.14} near ~ 10 K, which could be associated with a short-range ordering of PM Cu₁₈ clusters.

Acknowledgment

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