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Magnetic neutron diffraction from the magnetic clusters in single crystal $BaCuO_{2+x}$

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Magnetic-neutron-diffraction studies of a single crystal of $BaCuO_{2+x}$ confirm the antiferromagnetic structure of the ringlike Cu_6 clusters with ground-state spin $S=3$ proposed by Wang *et al.* [Science **264**, 402 (1994)]. No indication of a spontaneous ferromagnetic (or simple antiferromagnetic) ordering of the spherelike Cu_{18} $S=9$ clusters were observed down to a temperature of 50 mK, in disagreement with the suggestion based on magnetic-susceptibility measurements performed down to 2 K. However, diffraction scans under applied magnetic fields up to 3 T, at temperatures of 0.05 and 4.2 K align the sphere clusters ferromagnetically. The magnetic-field-induced ferromagnetic-diffraction pattern is consistent with the form factor of the Cu_{18} spherelike cluster. Frustration in the coupling with nearest neighbors leads to a paramagnetic behavior or a complex magnetic structure (noncollinear and/or incommensurate) of the spherelike clusters, consistent with our findings. [S0163-1829(98)07401-3]

I. INTRODUCTION

$BaCuO_{2+x}$ $(x\approx 0)$ is a body-centered-cubic oxocuprate (space group $Im3m$, $a=18.28$ Å at room temperature) with a unique structure that incorporates Cu/O polygons[1,2] forming three distinct spin systems all of which consist of $S=\frac{1}{2}$ spins (Cu^{2+}).[3–5] Each unit cell contains two $Cu_{18}O_{24}$ sphere clusters, eight Cu_6O_{12} ring clusters, and six lone CuO_4 units (see Fig. 1). Within a Cu_6 cluster the Cu-O-Cu bond angle is 83° and within the Cu_{18} cluster it is 87°. Whereas a linear Cu-O-Cu superexchange leads to an antiferromagnetic (AF) interaction as in the layered cuprates,[6] the nearly 90° bond angle leads to ferromagnetic coupling between the two Cu^{2+} ions.[7] This ferromagnetic superexchange is expected to be weaker than the AF one ($J\approx 1500$ K), since it involves the exchange between two oxygen wave functions being a perturbation of higher order than the linear bond coupling. $BaCuO_2$ is observed as an impurity phase in the preparation of $T_c=90$ K superconducting $YBa_2Cu_3O_7$.

Employing magnetization and neutron-diffraction measurements on polycrystalline samples we have shown[3–5] that $BaCuO_{2+x}$ exhibits a combination of magnetic behaviors. At low temperatures (below ~40 K) the Cu_6 and Cu_{18} clusters are in ferromagnetic ground states with maximum spins $S_r=3$ and $S_s=9$, respectively. Below a Néel temperature $T_N\approx 15$ K, the Cu_6 rings order antiferromagnetically whereas the Cu_{18} spheres, which are internally ferromagnetically ordered, remain paramagnetic at least down to 2 K. In the magnetization analyses it was assumed that each Cu_{18} cluster is antiferromagnetically coupled to three lone Cu. Also, from an extrapolation of the inverse susceptibility versus temperature above 2 K, it was predicted that these Cu_{18} clusters might undergo ferromagnetic long-range order below ~1 K.[3,4]

Recently, there has been a growing interest in the physics of copper-oxide chains and *ladders* with superexchange coupling of varying Cu-O-Cu bond angles as a way to gain insight into mechanisms that drive the layered compounds superconducting.[8] The clusters in the $BaCuO_2$ consist of cyclic chains that are either *ring-like* or *ladder-like* when interconnected into the Cu_{18} sphere cluster.

We have undertaken the present low-temperature neutron-diffraction study of a single crystal, to identify the spherelike clusters and to determine their ground state, and also to examine the validity of the magnetic structure proposed previously.[3,5] The magnetic structure of this complicated system consisting of 90 Cu^{2+} spins in each unit cell was proposed on the basis of two magnetic reflections observed with polycrystalline samples and on indirect magnetic-susceptibility analysis.

II. EXPERIMENTAL DETAILS

The single crystal in this study, grown in a CuO flux, was embedded in polycrystalline material that was prepared under He environment with $x\sim 0$ as described elsewhere.[3] The

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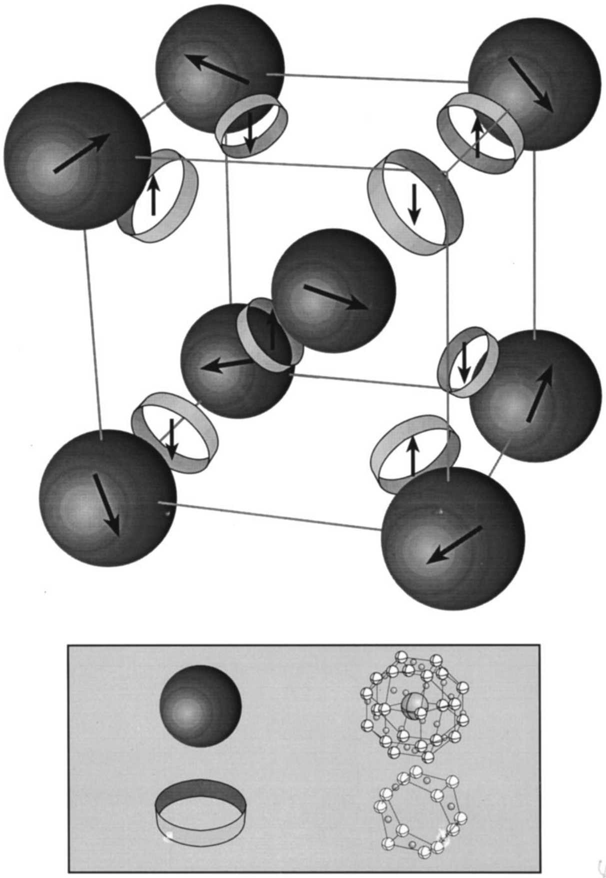

FIG. 1. Perspective representation of the two types of Cu-O clusters in the bcc unit cell of $BaCuO_{2+x}$. The $Cu_{18}O_{24}$ spherelike clusters are located at $[0\,0\,0]$ and at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ (not shown); the Cu_6O_{12} ringlike clusters are located at $[\frac{1}{4}\frac{1}{4}\frac{1}{4}]$ and the remaining seven equivalent positions with their axis of highest symmetry along the corresponding body diagonal. Lone spins are located along principal directions adjacent to the spheres. Both clusters consist of closed one-dimensional strips of CuO_4 edge-sharing squares. Below $T_N = 12$ K the eight ringlike clusters with a total spin $S = 3$ order antiferromagnetically whereas the spherelike clusters with a total spin $S = 9$ remain paramagnetic. By the AF symmetry the magnetic interaction of the ring clusters with the sphere clusters cancels out.

contribution to Bragg reflections from the polycrystalline material surrounding the crystal was not detectable with our instrument due to the minute amounts present. Neutron-diffraction measurements were carried out on the HB-1 triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. A beam of wavelength $\lambda = 2.443$ Å was selected by Bragg reflection from the (002) planes of a highly oriented pyrolytic graphite (HOPG) monochromator crystal. HOPG crystals were also used as an analyzer crystal and as a filter to remove short wavelength contamination in the beam due to higher-order reflections. The $BaCuO_{2+x}$ single crystal, with mosaic spread of 1.3°, was mounted with the (110) and (001) scattering vectors in the scattering plane of the spectrometer. The crystal was wrapped in aluminum foil, with part of the foil clamped to a copper heat sink, which was connected to the mixing chamber of an Oxford 200 dilution refrigerator. The refrigerator was designed for neutron-scattering experiments with a base temperature of 50 mK and vacuum cans and radiation shields with aluminum windows around the sample, and with no liquid nitrogen or helium in the beam path. No changes in temperature were observed upon exposure of the sample to the neutron beam. The temperature of the sample was measured using two ruthenium oxide sensors, screwed to the base of the copper heat sink. The accuracy of the temperature measurements is estimated at 5%. The magnetic field was generated by a superconducting coil with a maximum field of 5 T, which was used in persistent mode operation during measurements. The magnetic field was aligned along the $(1\,\overline{1}\,0)$ crystallographic direction.

III. RESULTS AND DISCUSSION

A. Antiferromagnetic rings

At room temperature the reflections allowed by the bcc crystal structure of $BaCuO_{2+x}$ are of the type $h+k+l=\text{even}$.[2] However below $T_N \sim 12$ K, due to the antiferromagnetic (AF) ordering of the rings, new sets of reflections of the type (odd,odd,odd) and (even,even,odd) are allowed. The AF order is such that the spins internal to each ring are ferromagnetically aligned, and the nearest-neighbor Cu_6 rings are antiferromagnetically ordered preserving the chemical unit cell, but altering its symmetry. Figure 2(a) shows scans along the $(h\,h\,h)$ direction at 77 and at 4.2 K with the prominent emergence of the $(1\,1\,1)$ magnetic reflection. The widths of the AF reflections are resolution limited, suggestive of correlation lengths that exceed 300 Å. The absence of the $(3\,3\,3)$ reflection at 4.2 K is due to the fact that the magnetic structure factor is vanishingly small at this momentum transfer, as is shown below. The magnetic structure factor for the antiferromagnetically ordered rings can be written generally as[3,5]

$$F = p_0 \mu f(\mathbf{Q}) \sum_{i=1}^{8} F_i(Q) \sigma_i \exp(i \mathbf{r}_i^0 \cdot \mathbf{Q}), \tag{1}$$

where $p_0 = 0.27 \times 10^{-12}$ cm, μ and $f(\mathbf{Q})$ are, respectively, the ordered magnetic moment and the magnetic form factor of an individual Cu^{2+} ion on the ring, and $\sigma_i = \pm 1$ are the relative directions of the ordered moments on adjacent rings. The structure factor of each ring is given by $F_i = \Sigma_{j=1}^{6} \exp(i\mathbf{r}_{i,j} \cdot \mathbf{Q})$, where $\mathbf{r}_{i,j}$ is the relative position of spin j in ring i with respect to the center point of the ring $\mathbf{r}_i^0$. The $\mathbf{r}_{i,j}$'s are of three types $[\pm\epsilon, \pm\epsilon, 0]$, $[0, \pm\epsilon, \pm\epsilon]$, and $[\pm\epsilon, 0, \pm\epsilon]$, where $\epsilon \approx 0.1008$. The plus or minus signs in the parentheses are chosen so that each $\mathbf{r}_{i,j}$ is orthogonal to the axis of highest symmetry of a ring. For the (odd,odd,odd) magnetic reflections the structure factor is given by

$$\begin{aligned} F = 16 p_0 \mu f(\mathbf{Q}) \cdot \{ & \cos[2\pi h \epsilon] \cos[2\pi k \epsilon] \\ & + \cos[2\pi k \epsilon] \cos[2\pi l \epsilon] + \cos[2\pi l \epsilon] \cos[2\pi h \epsilon] \}. \end{aligned} \tag{2}$$

Based on Eq. (2) (and including the Lorentz factor and the Cu^{2+} spin form factor[9]) the calculated relative intensities of the $(1\,1\,1)$, $(3\,3\,3)$, and $(5\,5\,5)$ reflections are, respectively, 1 : 0.005 : 0.205, compared to the relative experimental integrated intensity values 1 : 0 : 0.215. Assuming that the

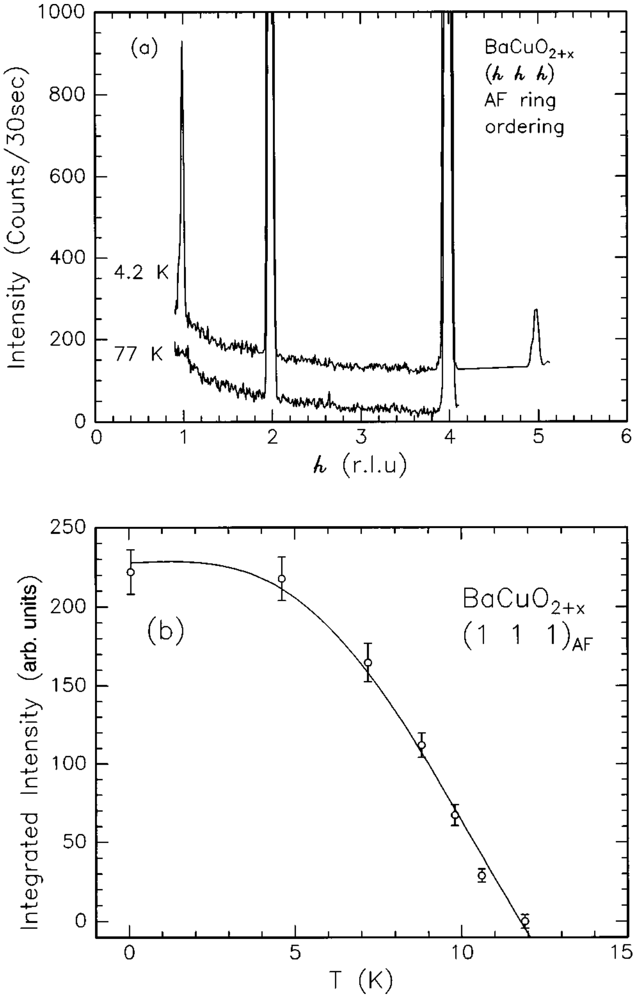

FIG. 2. (a) Diffraction pattern of single crystal $BaCuO_{2+x}$ along the $(h\,h\,h)$ direction at $T=4.2$ and at 77 K. The (odd,odd,odd) reflections are not allowed by the crystallographic structure as is evidenced at high temperatures. The emergence of the (1 1 1) and (5 5 5) reflections at low temperatures is due to the antiferromagnetic ordering of the Cu_6 rings. The absence of the (3 3 3) reflection is due to the vanishingly small magnetic structure factor given in Eq. (2). (b) The temperature dependence of the (1 1 1) reflection, indicating a Néel temperature $T_N=12$ K.

direction of the magnetic moment within each ring is along the (0 0 1) direction (i.e., collinear arrangement of the moments), the calculated value for the average ordered moment per Cu^{2+} is $0.8\pm0.1\mu_B$. This value is somewhat smaller than the one extracted for the corresponding polycrystalline sample.[3] Accurate estimates of the ordered magnetic moment with a single crystal are in general difficult to make due to secondary extinctions and crystal shape dependence of absorption.

Figure 2(b) shows the order parameter as a function of temperature indicating that the antiferromagnetic transition occurs at 12±1 K. This Néel temperature is comparable to those reported by Wang *et al.*,[3] and is consistent with ESR studies,[12] other neutron-diffraction measurements of a polycrystalline sample,[13] and with specific-heat measurements.[10]

B. Magnetic properties of the spherelike clusters

The extrapolated susceptibility measurements of Wang *et al.*[4] from above 2 K suggested a possible ferromagnetic

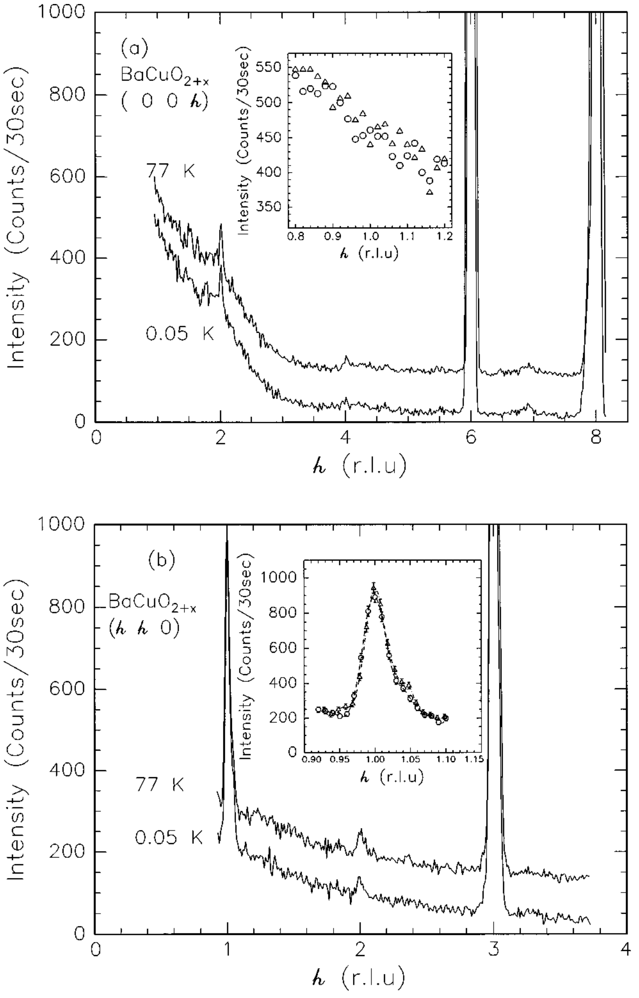

FIG. 3. (a) Diffraction pattern of single crystal $BaCuO_{2+x}$ along the $(h\,h\,0)$ and (b) along the $(0\,0\,h)$ directions at $T=0.05$ and at 77 K. No extra reflections indicating a magnetic ordering associated with the spherelike clusters are observed. The inset in (a) shows the scattering at 77 and at 0.05 K of the (0 0 1) reflection precluding simple antiferromagnetic or ferrimagnetic ordering of the spherelike clusters. The inset in (b) shows the (1 1 0) reflection intensity at $T=77$ K (circles) and at $T=0.05$ K (triangles). The difference of the integrated intensities at the two temperatures indicates that the spherelike cluster magnetic system does not undergo a spontaneous ferromagnetic transition down to at least 0.05 K.

(FM) phase transition below 1 K. The simplest antiferromagnetic structure for the spherelike clusters is such that the moment of the sphere at the body center of the cube is antiparallel to that at the origin. Such an arrangement would have resulted in an extra Bragg reflection at the nominal (0 0 1) position. Neutron-scattering measurements along $(0\,0\,h)$, $(h\,h\,0)$, and along $(h\,h\,h)$ showed no evidence of antiferromagnetic arrangement associated with the spheres down to 0.05 K. Figures 3(a) and 3(b) show diffraction patterns along the $(h\,h\,0)$ and the $(0\,0\,h)$ direction with no new reflections. In particular the inset in Fig. 3(a) shows two scans performed at 77 and 0.05 K at zero magnetic field of the (0 0 1) reflection demonstrating that the sphere system is not simply antiferromagnetic or ferrimagnetic. No extra reflections that could not be indexed as nuclear Bragg reflections or antiferromagnetic reflections associated with the or-

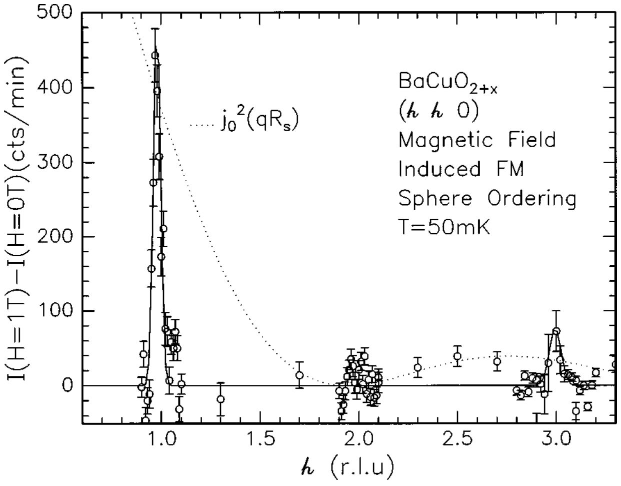

FIG. 4. Difference between intensities of scans along the $(h\,h\,0)$ direction with applied magnetic field of 1 T and at zero magnetic field at $T=0.05$ K. The intensity gain at the nuclear positions is due to the induced long-range ferromagnetic order of the spherelike moments. The absence of intensity gain at the (2 2 0) position is due to the vanishingly small value of the magnetic form factor of the sphere (shown as dotted line) at that momentum transfer, as discussed in the text.

dering of the ringlike clusters, mentioned above, were observed. In addition, the difference between the integrated intensities of the scans in Figs. 3(a) and 3(b) show no evidence for spontaneous FM order down to $T=0.05$ K. Although we can rule out simple magnetic structures or incommensurate ones along the principal directions of the crystal, our study does not cover all of reciprocal space, so that more complex noncollinear magnetic structures associated with the spherelike clusters cannot be excluded. Based on the uncertainties of observed Bragg reflection intensities, we estimate that an average ferromagnetic moment associated with the spherelike clusters is $0\ \pm 0.15\mu_B$ per Cu^{2+} at 0.05 K.

Application of magnetic field along the $(1\,\bar{1}\,0)$ direction caused certain Bragg reflections to gain intensity, in particular the (1 1 0) reflection. Figure 4 shows the difference between the intensity of scans along the $(h\,h\,0)$ direction under applied magnetic field of 1 T and zero magnetic field at 0.05 K. Assuming that the ordering is associated with the Cu_{18} spheres which are located at the origin of the unit cell and at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ the allowed ferromagnetic reflections are those with $h+k+l=$even coinciding with the nuclear reflections. The widths of the peaks in Fig. 4 are resolution limited. The absence of gain in the intensity of the (2 2 0) reflection (see Fig. 4) is due to the fact that the magnetic form factor of the sphere $[\sin(QR_S)/QR_S]$, assuming a radius $R_S\approx 3.43$ Å, vanishes near the momentum transfer (Q) of this reflection. The magnetic structure factor for the Cu_{18} sphere is given by

$$F_S=2N_S p_0 \mu f(\mathbf{Q})[\sin(QR_S)/QR_S], \tag{3}$$

where $N_S=18$ is the number of Cu atoms per sphere cluster, the factor 2 reflects the 2 spheres per unit cell, μ is the ordered moment per Cu^{2+} in a sphere, and the other parameters are as in Eq. (1). The dotted line in Fig. 4 shows the squared form factor of the sphere cluster which vanishes at the (2 2 0) reflection $(QR_S=\pi)$. Calculations of the magnetic structure factor, F_S, using the exact positions of spins on the spheres yield values that are very close to those obtained using the spherical form factor. The ratio of the ferromagnetic component of the intensity under applied external magnetic field to that at zero field $[I(H)-I(0)]/I(0)$ for any reflection is given by

$$\frac{I(H)-I(0)}{I(0)}=\frac{F_S^2}{F_{\rm nucl}^2} \tag{4}$$

where $F_{\rm nucl}$ is the nuclear structure factor of the Bragg reflection on which the FM peak is superimposed. Using Eqs. (3) and (4) we calculate an average magnetic moment of $0.55\pm 0.1\mu_B$ per Cu^{2+} in a Cu_{18} sphere at 1 T and at $T=0.05$ K. This is lower than the expected $\approx 1\mu_B$ for a Cu^{2+} as has been extracted by Wang *et al.*[3,4] One possibility for this lower value is that the simple collinear model used [Eq. (3)] is wrong. As mentioned above, our experimental data does not exclude more complex, presumably noncollinear and incommensurate arrangement of the magnetic spheres in the absence of external magnetic field. An alternative possibility for the discrepancy may be related to the uncertainty in the value used for the nuclear structure factor for the (1 1 0) Bragg reflection, $F_{\rm nucl}$, which is required for the calculation of the magnetic moment [Eq. (4)]. In our calculation for the magnetic moment we used a value for $F_{\rm nucl}$ that was extracted from the structural parameters obtained from powder-diffraction analysis of similar samples $(x\approx 0)$ as listed in Table I. These structural parameters were also used to calculate Bragg reflection intensities for the single crystal and were in fairly good agreement with all nuclear reflections of the single crystal. We noticed that other structural models for $BaCuO_{2+x}$ with $x\approx 0$ (Refs. 2,14–16) yielded $F_{\rm nucl}$ values that were either larger or smaller than the value used in this study. With these values the induced FM moment was calculated to be in the range of 0.3 up to $1.1\mu_B$ per Cu spin in the sphere.[17] However, the overall fit of these models to other nuclear reflections was poorer than the one listed in Table I.

Another way to extract the magnetic moment is by measuring and modeling the induced FM intensity versus applied magnetic field, $I_{\rm mag}$. Figure 5 shows an isotherm of the intensity of the (1 1 0) reflection versus magnetic field at 4.2 K. The solid curve is the intensity calculated assuming

$$I_{\rm mag}=C(B_J(x))^2+B, \tag{5}$$

where $x\equiv gJ\mu_B/k_BT$, $J=9$, and C is a scaling factor, B is a background term, and B_J is the Brillouin function[11]

$$B_J=\frac{2J+1}{2J}\text{ctnh}\left(\frac{(2J+1)x}{2J}\right)-\frac{1}{2J}\text{ctnh}\left(\frac{x}{2J}\right). \tag{6}$$

The good fit of the data by Eq. (6) confirms that the sphere system although internally ferromagnetic with $J=9$ is in the paramagnetic state.

We hypothesize that the absence of spontaneous long-range FM order down to $T=0.05$ K is due to frustration as discussed below. Possible magnetic interactions that might lead to long-range order of the spheres are of the dipole-

TABLE I. Structural parameters for $BaCuO_{2+x}$ ($x \approx 0$) at $T = 294$ K obtained from powder-diffraction data and best fit the Bragg reflection intensities of the single crystal used in this study. The model structure has I_{m3m} symmetry ($a = 18.26$ Å) with the following generating atomic positions.

Atom	x	y	z	Occupancy
Ba	0.0	0.31	0.151	1
Ba	0.0	0.3646	0.3646	1
Ba	0.176	0.176	0.176	1
Ba	0.0	0.0	0.0	0.33
Cu	0.25	0.1493	0.3507	1
Cu	0.0	0.1267	0.1267	1
Cu	0.2067	0.00	0.0	1
Cu	0.43	0.0	0.0	0.75
O	0.0736	0.0736	0.187	1
O	0.145	0.145	0.3455	1
O	0.266	0.266	0.0842	1
O	0.3366	0.000	0.000	1
O	0.0	0.0854	0.449	0.375
O	0.0281	0.2267	0.433	0.375
O	0.24	0.0	0.5	0.67

dipole and superexchange types. The dipole-dipole interaction between two antiparallel spins on the spheres, $E \approx \mu_s^2/d_{ss}^3$ is on the order of 0.05 K, whereas the dipolar interaction of a sphere with its nearest-neighbor ring is estimated at 0.136 K. Effective superexchange interaction of nearest-neighbor sphere-sphere clusters is expected to be much weaker than that of the sphere-ring clusters, because of the larger distances, and more intervening nonmagnetic ions involved. Thus, the most dominant coupling between nearest-neighbor spheres is via an intervening ring. Regardless of the type of interaction (ferromagnetic or antiferromagnetic) with the ring, the net effect on nearest-neighbor spherelike clusters is to align their spins in a FM arrangement. However, because of the antiferromagnetic arrangement of the ring spins this arrangement is frustrated as is shown in Fig. 6. Also, locally each sphere interacts with eight rings, and the interaction cancels out due to the antiferromagnetic arrangement of the rings. Freezing the spin on the sphere in a certain direction leads to frustration, and the system seems to choose the disordered (paramagnetic) or a more complex magnetic state consistent with the present study.

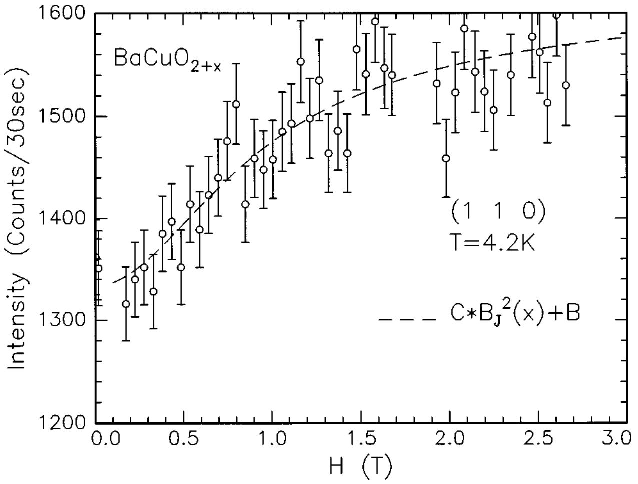

FIG. 5. Peak intensity of the (1 1 0) reflection versus applied magnetic field at $T = 4.2$ K. The solid line is calculated using the Brillouin function where $J = 9$, and two adjustable parameters.

In conclusion, our magnetic studies confirmed the existence of spherical magnetic entities in $BaCuO_{2+x}$ and confirmed the antiferromagnetic structure of $BaCuO_{2+x}$ below $T_N \approx 12$ K proposed by Wang *et al.*[3,4] No indication of a spontaneous ferromagnetic (or simple antiferromagnetic) ordering of the spherelike magnetic Cu_{18} clusters is observed down to 50 mK, contrary to the suggestions inferred from magnetic-susceptibility measurements performed down to 2 K by Wang *et al.*[3,4] However, diffraction scans under applied magnetic field, at temperatures of 0.05 to 4.2 K, show an increase in intensity for a set of reflections [in particular, the cubic (1 1 0) reflection], indicating a field-induced FM moment of the spherelike clusters. The FM diffraction pattern under applied magnetic field along the ($h\,h\,0$) direction is consistent with the form factor of the Cu_{18} sphere with $J = 9$.

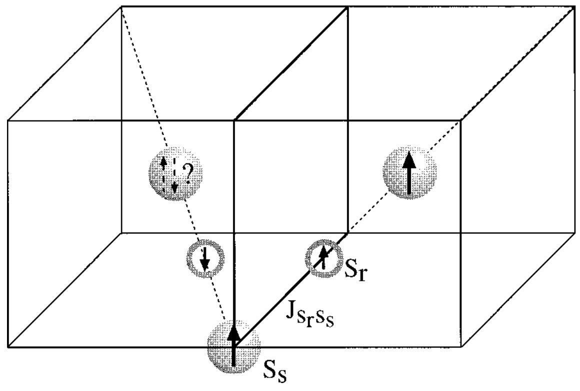

FIG. 6. Schematic illustration of two adjacent unit cells showing that the magnetic coupling between two nearest-neighbor sphere spins mediated by the ring spins leads to frustration due to the antiferromagnetic arrangements of the ring spins.

We suggest that the disorder (paramagnetic) or more complex magnetic structure of the spherelike clusters is due to frustration caused by the AF order of the Cu_6 rings.

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[17] All models described in Refs. 2 and 14–16 predict the existence of the ringlike and spherelike clusters but differ mainly with regard to the oxygen content outside the clusters. Aranda and Attfield (Ref. 15) claim that $BaCuO_{2+x}$ is a complex oxocarbonate with the carbonate groups (CO_3) lying between clusters.