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Antiferromagnetic Ordering and Paramagnetic Behavior of Ferromagnetic Cu_6 and Cu_{18} Clusters in $BaCuO_{2+x}$

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Magnetization and neutron diffraction measurements on polycrystalline $BaCuO_{2+x}$ revealed a combination of magnetic behaviors. The Cu_6 ring clusters and Cu_{18} sphere clusters in this compound had ferromagnetic ground states with large spins 3 and 9, respectively. The Cu_6 rings ordered antiferromagnetically below the Néel temperature T_N = 15 ± 0.5 kelvin, whereas the Cu_{18} spheres remained paramagnetic down to 2 kelvin. The ordered moment below T_N was 0.89(5) Bohr magnetons per Cu in the Cu_6 rings, demonstrating that quantum fluctuation effects are small in these atomic clusters. The Cu_{18} clusters are predicted to exhibit ferromagnetic intercluster order below about 1 kelvin.

The strong antiferromagnetic (AF) coupling between the Cu spins in the CuO_2 planes of the undoped parent compounds of the high transition temperature cuprate superconductors (*1*) results from an indirect 180° bond angle Cu^{2+}–O^{2-}–Cu^{2+} superexchange interaction ($J \sim 1000$ K). Aharony *et al.* (*2*) have argued that an intervening O^{1-} ion produced by a localized doped hole on the O^{2-} ion results instead in an indirect ferromagnetic (FM) interaction between the adjacent Cu spins, which in turn was predicted to strongly modify the magnetic properties of the parent cuprate. It is thus important to further clarify the conditions under which FM versus AF Cu-Cu interactions occur in copper oxides. An alternative cause of the FM interactions has been predicted to be a change in the Cu–O–Cu bond angle from 180° to 90° (*3*); however, the intermediate angle at which the crossover from AF to FM coupling occurs is unknown.

Here, we summarize a study of the magnetic properties of the compound $BaCuO_{2+x}$. Despite its simple chemical formula, this compound has a large body-centered-cubic (bcc) unit cell (space group $Im3m$, a = 18.25 Å) with 90 formula units per unit cell (*4*, *5*). The cell contains six lone CuO_4 units, eight Cu_6O_{12} ring clusters, and two $Cu_{18}O_{24}$ sphere clusters formed from edge-shared CuO_4 units (Fig. 1). The Cu_6O_{12} ring clusters are formed by six edge-shared CuO_4 squares. The Cu–O–Cu bond angle in a six-membered and eight-membered ring is 75.5° and 81.6°, respectively. Magnetic susceptibility [$\chi(T)$] measurements (*5*–*7*) of the compound showed Curie-Weiss–like behavior with a clear deviation from linearity below a temperature (T) of about 100 K. Electron spin resonance (ESR) measurements of the same compound (*5*, *8*) indicated a phase transition at ~15 K. Preliminary neutron scattering measurements (*9*) on polycrystalline samples showed a phase transition at 13 K, consistent with the ESR studies. Unpolarized and polarized neutron diffraction measurements combined with magnetization measurements revealed that $BaCuO_{2+x}$ exhibits a combination of magnetic behaviors. The Cu_6 and Cu_{18} clusters have FM ground states with large spins S_r = 3 and S_s = 9, respectively. The Cu_6 rings exhibit long range AF intercluster order below T_N = 15 K, with no apparent magnetic coupling to the lone Cu ions or the Cu_{18} clusters. In contrast, these latter two species remain paramagnetic down to 2 K and interact antiferromagnetically with an effective coupling strength J = 1.1 meV. Extrapolation of the magnetic susceptibility $\chi(T)$ data below 2 K predicts that the Cu_{18} clusters should exhibit FM intercluster order below ~1 K. Our results are relevant to many cuprate superconductors which show buckling of the CuO_2 planes and significant deviations of the Cu–O–Cu bond angle from 180°, and to engineering new cuprates with novel properties.

A 1:1 molar mixture of $BaCO_3$ (99.99%) and CuO (99.99%) was thoroughly ground and heated to 800°C for 24 hours. The sample was then repeatedly reground and fired at 925°C for 24 hours. The sample was finally reheated to 900°C for 10 hours and cooled to room temperature (T) at a rate of 10°C per hour under He gas. Magnetization (M) data were obtained with a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

The inverse of the molar magnetic susceptibility, $\chi = M/H$, for $BaCuO_{2+x}$ is plotted versus T from 2 to 400 K (Fig. 2) for applied magnetic fields H = 500 G and H = 10 kG. The data in Fig. 2A above ~300 K approach the linear Curie-Weiss law $\chi^{-1} = (T - \theta)/C$. The molar Curie constant is $C = N_A g^2 S(S + 1)\mu^2_B/3k_B$, where N_A is Avogadro's number, g and S = 1/2 are, respectively, the gyromag-

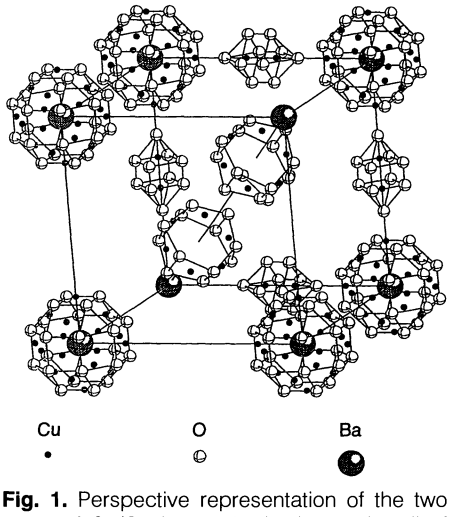

Fig. 1. Perspective representation of the two types of Cu/O clusters in the bcc unit cell of $BaCuO_{2+x}$. The $Cu_{18}O_{24}$ sphere-like clusters are located at the (000) and at the (1/2 1/2 1/2) (not shown); the Cu_6O_{12} ring-like clusters are located at the (1/4 1/4 1/4) and the remaining seven equivalent positions with their axis of highest symmetry along the corresponding body diagonal (only two rings are shown). The lone spins are located along principal directions adjacent to the spheres (partially occupied). Both clusters consist of closed one-dimensional strips of CuO_4 oxygen edge-sharing squares.

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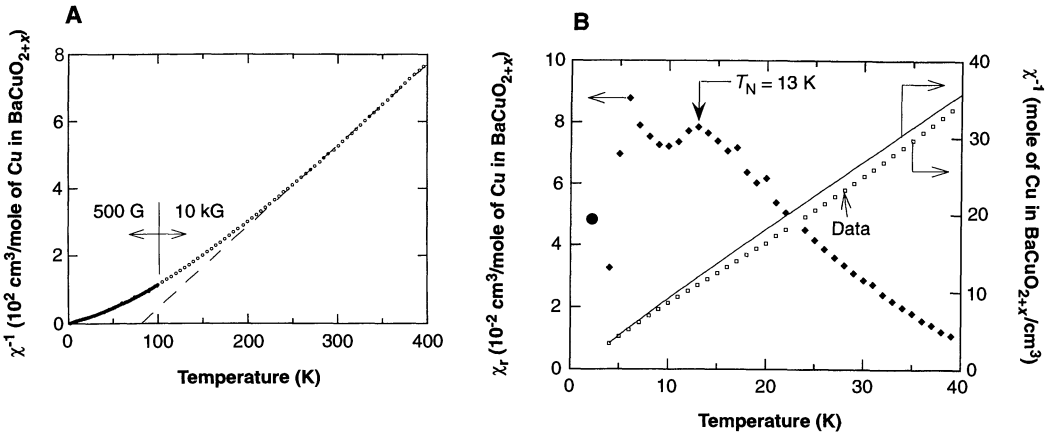

Fig. 2. (**A**) Inverse magnetic susceptibility χ^{-1} versus temperature T for $BaCuO_{2+x}$. The dashed line is a linear fit to the data above 300 K. (**B**) Expanded plot of (A) below 40 K. The solid curve is the predicted behavior of the AF-coupled lone Cu ions and Cu_{18} sphere clusters, whereas the filled squares are the derived data for the Cu_6 rings, and the filled circle is $\chi_r(2K)$ derived from the data shown in Fig. 3.

netic factor and spin of the Cu^{2+} ion, μ_B is the Bohr magneton, and k_B is Boltzmann's constant. Fits to the χ^{-1} data between ~300 and 400 K obtained in H = 500 G (not shown) and 10 kG yield C ~ 0.39 cm^3 K per mole of Cu, $g = 2.10 \pm 0.05$, and θ = 81 K, as shown by the dashed line in Fig. 2A (*10*). The large positive Weiss temperature, θ, shows that the dominant interactions in the compound are FM.

However, in contrast to the prediction of molecular field theory, long-range FM ordering was not observed at (or below) $T = \theta$; rather, χ^{-1} exhibited positive curvature with decreasing T and then exhibited linear Curie-Weiss behavior again between 2 and 6 K (Fig. 2B), with C = 1.13 cm^3 K per mole of Cu and θ = 0.4 K. The large positive (FM) θ at high T and the large increase of C with decreasing T indicates that the Cu clusters in $BaCuO_{2+x}$ have a maximal spin FM ground state (confirmed below), with lower spin excited states. This corresponds to short-range zero-dimensional FM order for the ground state. The shape of $\chi^{-1}(T)$ in Fig. 2A is very similar to that of a $(Cr^{+3})_4$ cluster with an FM spin 6 ground state and spin 5 to 0 excited states (*11*). In such cases, the high-T limit of θ (≈80 to 90 K in the present case) is on the order of the energy splitting of the ground and highest excited states. The value of C for T = 2 to 6 K is close to the value (1.1 cm^3 K per mole of Cu) calculated for isolated Cu_{18} clusters with g = 2.1 and S_s = 9. This indicates that the Cu_6 rings do not contribute to the observed Curie-Weiss susceptibility below 6 K.

To clarify the magnetic character of $BaCuO_{2+x}$ at low T, we obtained $M(H)$ isotherms with fields $H \leq 55$ kG. The data at 2 K are shown in Fig. 3. With increasing H, $M(H)$ nearly saturated by about $H \sim 20$ kG; at higher fields, M increased approximately linearly with H, written as $M(2K,H) = M_0(2K) + \chi_0(2K)H$. From a comparison of the shapes of Brillouin functions for $g \sim 2$ and various spin values with the data, the saturation was found to arise from a large spin $S \sim 10$. The only candidate in the structure that could have approximately this spin value is the Cu_{18} sphere cluster, which we therefore conclude remains paramagnetic to 2 K with a FM ground state with spin S_s = 9. On the other hand, the saturation moment $M_0(2\ K) \sim 31\ \mu_B$ per unit cell is about one-sixth less than the value 37 μ_B per unit cell expected for the two Cu_{18} sphere clusters in the unit cell, assuming g = 2.10 (above) and the relation $M_0 = 2gS_s\mu_B$ per unit cell. This comparison suggests that the Cu_6 rings do not contribute to M_0, consistent with the above Curie constant at 2 to 6 K, and that the three lone Cu spins S_1 = 1/2 adjacent to each sphere cluster are antiferromagnetically coupled to the sphere cluster spin S_s.

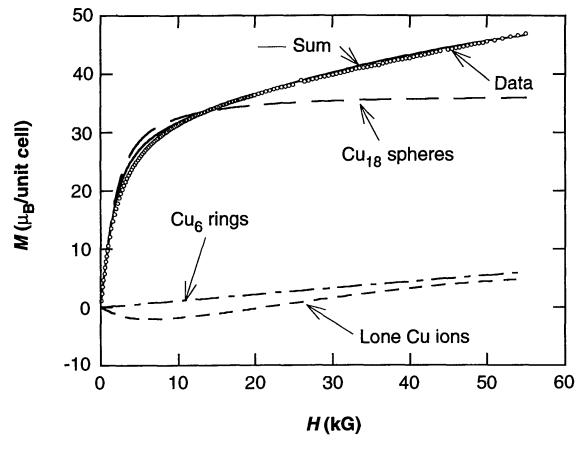

Fig. 3. Magnetization (M) versus magnetic field (H) for $BaCuO_{2+x}$ at 2 K. The solid curve labeled Sum is a theoretical fit to the data (Eq. 1), and the contributions to the sum from the lone Cu ions, the Cu_6 ring clusters, and the Cu_{18} sphere clusters are as indicated.

The T dependence of χ_0 obtained from $M(H)$ isotherms showed a peak at a temperature T_N ~ 12 to 15 K (not shown), suggesting the onset of long-range AF order below T_N (see also below). Because only the Cu_6 ring clusters, postulated above to have a maximal FM ground state spin S_r = 3, have not yet been accounted for above, they are apparently the entities that exhibit the postulated long-range AF order below T_N. In the absence of a spin-flip or spin-flop transition below T_N, the magnetization M_r of a Cu_6 ring is expected to be linear in H at all T within our (T,H) parameter range; that is, $M_r = \chi_r H$. Thus, at T = 2 K and for $H \geq 20$ kG, the Cu_{18} sphere clusters are saturated and the AF-ordered Cu_6 clusters together with the Cu lone spins (see below) are responsible for the nearly linear increase of M with H in Fig. 3.

From the above discussion, the magnetization $M(H,T)$ of a unit cell of $BaCuO_{2+x}$ is the sum of contributions from the six lone Cu ions, two Cu_{18} spheres, and eight Cu_6 rings:

$$M(H,T) = 6M_1(H,T) + 2M_s(H,T) + 8\chi_r(T)H \quad (1)$$

The AF coupling between M_s and M_1 is taken into account by molecular field theory. A good fit of Eq. 1 to the data in Fig. 3 was obtained with g = 2.0, J = 1.1 meV, and $\chi_r(2K) = 1.45 \times 10^{-2}$ μ_B/kG per Cu_6 ring = 8.1×10^{-2} cm^3/(mole of Cu_6 rings), where J is the effective AF coupling energy between the lone spin and a Cu_{18} cluster. The fit is the solid curve in Fig. 3, where the separate contributions of the Cu_6 rings, the Cu_{18} clusters, and the lone Cu ions are also shown.

In the low-field limit one obtains

$$3\chi_1(T) + \chi_s(T) = \frac{(C_s + 3C_1)T - 6\lambda C_s C_1}{T^2 - 3\lambda^2 C_s C_1} \quad (2)$$

where C_s and C_1 are, respectively, the Curie constants for a Cu_{18} sphere cluster ($S_s = 9$) and a lone Cu ion ($S_1 = 1/2$). With $g = 2.1$ and $\lambda = 10$, subtraction of $3\chi_1(T) + \chi_s(T)$ in the units appropriate to Fig. 2 from the observed $\chi(T)$ yields, according to Eq. 1, the Cu_6 ring susceptibility $\chi_r(T)$, shown in Fig. 2 along with the calculated $[3\chi_1(T) + \chi_s(T)]^{-1}$. As independently deduced above, $\chi_r(T)$ shows a maximum at $T_N \sim 13$ K in Fig. 2B, indicative of long-range AF ordering of the Cu_6 ring cluster magnetic moments below T_N. The observed χ^{-1} data and the predicted $[3\chi_1(T) + \chi_s(T)]^{-1}$ below ~6 K in Fig. 2B suggest that the Cu_{18} sphere clusters will undergo long-range FM intercluster order below ~1 K.

Neutron diffraction measurements were carried out on the HB-4 powder diffractometer, on the HB-1A triple axis spectrometer, and on the HB-1 spin polarized triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The 10-g pellet-like polycrystalline sample was wrapped in a thin aluminum foil and loaded into an aluminum can under a He atmosphere and was then mounted in various cryostats for different measurements.

The reflections allowed by the bcc crystal structure of $BaCuO_{2+x}$ are of the type $h + k + l$ = even. At temperatures below 15 K additional reflections at the (111) and at the (221) positions were observed. The 2θ scans of the (111) reflection above and below 15 K are shown in Fig. 4A. The integrated intensity of the (111) reflection is temperature-dependent and a phase transition occurs at $T_N = 15.0 \pm 0.5$ K (Fig. 4, inset). Scans around the (100) and (201) reflections, with better statistics, did not reveal any appreciable intensity at $T = 4.2$ K, and high-order magnetic reflections were not identified because of the extensive overlap and dominance of nuclear reflections. High resolution neutron powder diffraction measurements were performed above and below T_N, which confirmed that no structural distortion occurs over the temperature range 4 to 16 K, suggesting that the (111) reflection is associated with an AF long-range order. Polarized neutron measurements on the same sample confirmed that the (111) reflection is magnetic in origin (*12*).

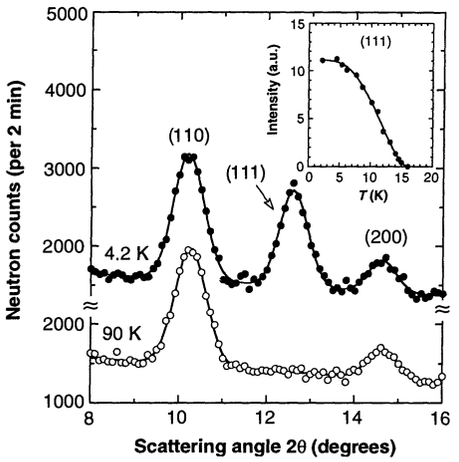

Fig. 4. Unpolarized neutron scattering intensity versus scattering angle 2θ of $BaCuO_{2+x}$, $\lambda = 2.35$ Å, at 4.2 K and at 90 K. The inset shows the temperature dependence of the integrated intensity of the (111) reflection. The solid curve is a guide to the eye; a.u., arbitrary units.

To model the magnetic structure, we assumed that the observed magnetic reflections are primarily associated with the Cu_6 ring clusters. This is based on the general observation that AF models incorporating the Cu_{18} spheres always predict prominent (100) and (201) reflections in contrast to the experimental observations. The proposed model is such that the spins internal to each ring are ferromagnetically aligned, and the nearest neighbor Cu_6 ring spins antiferromagnetically aligned [for a cubic structure, powder diffraction measurements are insufficient for the determination of the actual direction of the moment (*13*)]. The magnetic structure factor can be written generally as

$$F = p_0 \mu f(\mathbf{Q}) \sum_{i=1}^{8} F_i \sigma_i \exp(i\mathbf{r}_i^0 \cdot \mathbf{Q}) \qquad (3)$$

where $p_0 = 0.27 \times 10^{-12}$ cm, μ and $f(\mathbf{Q})$ are, respectively, the magnetic moment and the magnetic form factor of an individual Cu^{2+} ion on the ring, and $\sigma_i = \pm 1$. 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 j spin 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 $\epsilon \sim 0.1008$. The plus or minus sign in the parentheses are chosen so that each $\mathbf{r}_{i,j}$ is orthogonal to the axis of highest symmetry of a ring. The structure factor in Eq. 3 of the (hkl) reflection is then given by

$$F = 2p_0 \mu f(\mathbf{Q}) i \sin\left[\frac{\pi}{2}(h + k + l)\right] \times [F_1 - F_2 \exp(i\pi h) - F_3 \exp(i\pi k) - F_4 \exp(i\pi l)] \qquad (4)$$

Because of the $\sin[\pi/2(h + k + l)]$ factor, only (odd, odd, odd) and (even, even, odd) types of reflections are allowed. For the former case we get $F = 16p_0\mu f(\mathbf{Q})\{\cos[2\pi h\epsilon]\cos[2\pi k\epsilon] + \cos[2\pi k\epsilon]\cos[2\pi l\epsilon] + \cos[2\pi l\epsilon]\cos[2\pi h\epsilon]\}$, so that when $\epsilon = 0$, F reaches the maximum value of $48p_0\mu f(\mathbf{Q})$. For the latter case, $F = 16p_0\mu f(\mathbf{Q})\sin[2\pi h\epsilon]\sin[2\pi k\epsilon]$, where h,k are even indices. With this model, the observation of the (111) and (221) reflections and the absence of the (100) and (201) reflections can be reproduced. Assuming that $f(\mathbf{Q})$ is the form factor of a localized Cu^{2+} ion (*14*), an ordered magnetic moment $\mu = (0.89 \pm 0.05)\mu_B$ for each Cu in the Cu_6 ring is found. The proximity of the observed ordered moment to that predicted ($1.1\ \mu_B$) for a free spin Cu^{2+} with $g = 2.2$ reinforces our belief that the sole contributors to the ordered magnetic moment are the Cu_6 ring clusters. A similar value for the ordered moment [$\mu = 0.96(4)\ \mu_B$] was found in the infinite FM chain-like cluster in Li_2CuO_2 (*15*), where the Cu–O–Cu bond angle is 94°. Ferromagnetism in the cuprate $La_4Ba_2Cu_2O_{10}$ has also been reported (*16*).

In conclusion, the magnetic properties of $BaCuO_{2+x}$, which has a complex structure with 90 formula units per unit cell, can be understood in terms of the properties of the constituent lone Cu spins and Cu_6 and Cu_{18} clusters. Each type of cluster is found to have a ferromagnetic ground state demonstrating that the 75.5° and 81.6° Cu–O–Cu superexchange interactions between adjacent Cu spins in each cluster are ferromagnetic. It is surprising that the Cu_6 rings exhibit long-range AF order below $T_N = 15$ K, whereas the Cu_{18} spheres remain paramagnetic to 2 K. We speculate that high magnetic fields will lead to novel magnetic properties of the Cu_{18} clusters at temperatures below T_N.

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