Anisotropic magnetization characteristic of Cu_3O_4 planes in $Ba_2Cu_3O_4Cl_2$

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Anisotropic magnetization measurements of single-crystal $Ba_2Cu_3O_4Cl_2$ with $(Cu_A)_2(Cu_B)O_4$ planes, where the subscripts A and B denote the sites of Cu atoms, revealed characteristic features of this material: (1) below $T=332$ K, antiferromagnetically ordered Cu_A spins have a weak-ferromagnetic moment due to the Dzialoshinsky-Moriya interaction; (2) around $T=80$ K, a maximum appears in the temperature dependence of the magnetization, probably due to paramagnetic Cu_B spins interacting antiferromagnetically in the two-dimensional Cu_B network; and (3) below $T=32$ K, the field-dependent magnetization shows the flip or the rotation of antiferromagnetically ordered Cu_A spins, which indicates the presence of the easy axis of the magnetization for Cu_A spins below this temperature. [S0163-1829(97)51702-4]

Cuprates, including high-T_c superconductors, have a rich variety of crystal structures and physical properties. Among them, $Ba_2Cu_3O_4Cl_2$ is one of the most interesting materials. $Ba_2Cu_3O_4Cl_2$ is an insulator with a layered structure composed of Cu_3O_4 planes (the inset of Fig. 1) and blocking layers[1]. This structure is similar to those of the high-T_c superconductors. The symmetry of the crystal structure is tetragonal (space group: $I4/mmm$) at room temperature.[1] For Cu atoms in the Cu_3O_4 plane, there are two sites, i.e., Cu_A and Cu_B sites; the Cu_3O_4 plane is composed of a Cu_AO_2 square lattice and extra Cu_B atoms located at the centers of every other squares like a checker board. Neighboring Cu atoms interact magnetically by superexchange interactions through O between them; a Cu_A-O-Cu_A 180° interaction is antiferromagnetic, and a Cu_A-O-Cu_B 90° one is ferromagnetic or antiferromagnetic. Consequently, adjacent Cu_A atoms interact ferromagnetically via Cu_B, which would cause a magnetic frustration. Under this situation, the magnetic ground state of this material has been of great interest. Noro *et al.* reported that the temperature dependences of magnetization and electron spin resonance show two magnetic anomalies in this material.[2] Experiments on zero-field μSR,[3] antiferromagnetic electron-spin resonance,[4] and neutron scattering[5] have revealed that Cu_A and Cu_B spins order antiferromagnetically at $T\sim330$ K and ~30 K, respectively. Our recent measurements on temperature- and magnetic-field-dependent anisotropic magnetization $M(T,H)$ of a large single-crystal $Ba_2Cu_3O_4Cl_2$ support this scenario with the two magnetic transitions and, in addition, show aspects of ordered and free spins for both Cu sites.

Polycrystalline $Ba_2Cu_3O_4Cl_2$ samples were prepared by the usual solid-state reaction.[2] They were checked by x-ray diffraction and revealed to be pure. Single crystals of $Ba_2Cu_3O_4Cl_2$ were grown by the traveling-solvent floating-zone method with an image furnace. We did not use solvent at the beginning of the growth, since $Ba_2Cu_3O_4Cl_2$ melts almost congruently and the molten zone with a proper composition is obtained after a few cm of growth. The growth was performed at an oxygen pressure of 0.3 MPa, which enables a stable growth. Powder x-ray-diffraction patterns show that the grown crystals contain no impurity phases except a little amount of CuO, which is in excess in the molten zone. The effect of the impurity phase on the magnetization measurements was negligible. Backscattering Laue photographs show that the degree of the misalignment of the crystallographic axes is within $\sim1°$. The anisotropic magnetization of the crystal was measured by a SQUID magnetometer. The measurements were performed after the sample was put in zero field at temperatures higher than $T=350$ K, since hysteresis in the magnetization is sometimes observed below $T\sim330$ K. The x-ray (Cu K_α line) diffraction measurement of the polycrystalline samples was performed using a He closed-cycle cryostat in a temperature range from $T=370$ K down to 10 K.

Temperature-dependent magnetization $M(T)$ curves under a magnetic field H of 2 kOe parallel to the crystallographic axes [100], [110] and [001] are shown in Fig. 1. Hereafter, we will represent a H direction for M as a subscript on M, such as $M_{[100]}$ and M_{plane} for $H\|[100]$ and $H\|$plane, respectively. For both $H\|[100]$ and $H\|$ [110], i.e.,

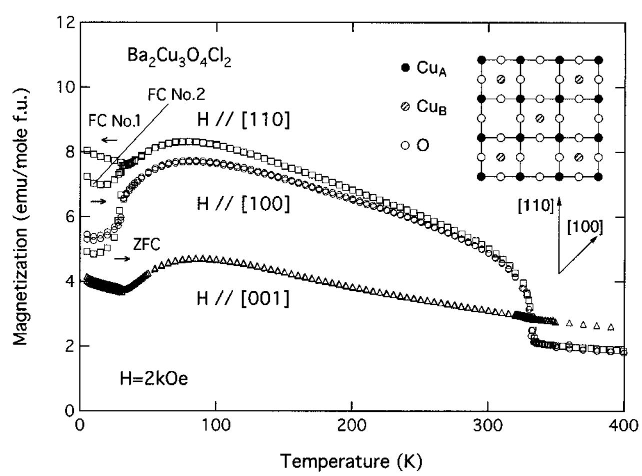

FIG. 1. The temperature dependence of the magnetization for $H\|[100]$, [110], and [001]. The data for FC No. 1 were taken when the sample was cooled in a field of 2000 kOe. Those for FC No. 2 and ZFC were taken after the sample was cooled in fields of 200 Oe and 0 Oe, respectively. Inset: the schematic representation of Cu_3O_4 plane in $Ba_2Cu_3O_4Cl_2$.

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$H\|$plane, abrupt changes in $M(T)$ curves occur at $T=332$ K and 32 K. An increase of M_{plane} just below $T=332$ K resembles that due to a ferromagnetic transition. The increase of M_{plane} is so small for a ferromagnetic moment that weak ferromagnetism would appear below this temperature. A sudden decrease or a change of the slope in the $M_{[100]}(T)$ and $M_{[110]}(T)$ curves is observed just below $T=32$ K. Only for $H\|[110]$, hysteresis in the temperature dependence of the magnetization appears below $T=32$ K, which will be discussed in detail later. On the other hand, changes in $M_{[001]}(T)$ at both anomaly temperatures are not as drastic as those in $M_{plane}(T)$. At $T=332$ K, there is an almost negligible increase. Since the degree of the slight increase is sensitive to the angle between the directions of H and c axis, there would be no intrinsic increase. At $T=32$ K, the slope of $M(T)$ changes. The two anomaly temperatures, $T=332$ K and 32 K, agree well with those where the antiferromagnetic transitions of Cu_A and Cu_B spins occur, as reported in Refs. 3−5. Some of the aspects described below also support the picture of the transitions at these anomaly temperatures. Hence, we call these anomalies as transitions hereafter. We also notice that there exist maxima around $T=80$ K in the $M(T)$ curves for the three H directions.

The measured magnetization can be decomposed into three terms attributed to the magnetism of Cu spins, the diamagnetism of core electrons and the Van Vleck magnetism. The latter two terms are independent of temperature. The value of the diamagnetic susceptibility of core electrons, χ_{core}, is estimated to be -2.4×10^{-4} emu/mole f.u.[6] Since the Van Vleck susceptibility χ_{VV} for $Ba_2Cu_3O_4Cl_2$ is unknown, we used the value of $[2\chi_{VV}(H\|\text{plane})+\chi_{VV}(H\perp\text{plane})]/3$ for Sc_2CuO_4, 2.3×10^{-5} emu/Cu mole,[7] as that for $Ba_2Cu_3O_4Cl_2$, assuming that χ_{VV} for $Ba_2Cu_3O_4Cl_2$ is isotropic. The sum of χ_{core} and χ_{VV} is -1.7×10^{-4} emu/mole f.u. Under a magnetic field of 2 kOe, $(\chi_{core}+\chi_{VV})H$ is -0.34 emu/mole f.u., which is an order smaller than the value of the measured magnetization; the magnetization of $Ba_2Cu_3O_4Cl_2$ is determined mainly by the magnetism of the Cu spins.

The crystal structure of $Ba_2Cu_3O_4Cl_2$ was investigated by temperature-dependent x-ray-diffraction measurements. The diffraction pattern indicates a tetragonal unit cell with lattice constants of $a_0=5.5234\pm0.0019$ Å and $c_0=13.8517\pm0.0063$ Å at $T=290$ K, which is in agreement with the previous report.[1] No changes in the crystal structure are observed in the whole temperature range measured. The temperature dependence of lattice constants is shown in Fig. 2. Above $T=50$ K, the lattice constant c_0 decreases monotonically with decreasing temperature, while the lattice constant a_0 is almost independent of temperature. The temperature dependence of the lattice constants is extremely anisotropic compared with those of high-T_c superconductors.[8] The slopes in the temperature dependence of a_o and c_o change below $T=50$ K, which may indicate a relation between the magnetic transition at $T=32$ K and the lattice properties.

Above $T=332$ K, where M is proportional to H for any field directions (see Fig. 3), the Cu_A and Cu_B spins are paramagnetic. We simply fitted the $M(T)$ curves above $T=332$ K by the Curie-Weiss rule $M(T)/H-(\chi_{core}+\chi_{VV})=C/(T-\Theta)$. Using the estimated values of χ_{core} and χ_{VV}, we obtained $C=0.85$ emu K/mole f.u. and $\Theta=-375$ K for H$\|$plane, and $C=1.22$ emu K/mole f.u. and $\Theta=-430$ K for H$\|$c. These values of C coincide well with the calculated value $C=Ng^2J(J+1)\mu_B{}^2/3k_B=1.13$ emu K/mole f.u., where we assumed g to be 2 and J to be 1/2. The values of $-\Theta$ are almost the same as that of the Néel temperature for Cu_A spins. The obtained values of the parameters are reasonable, if we neglect magnetic interactions other than that between Cu_A spins.

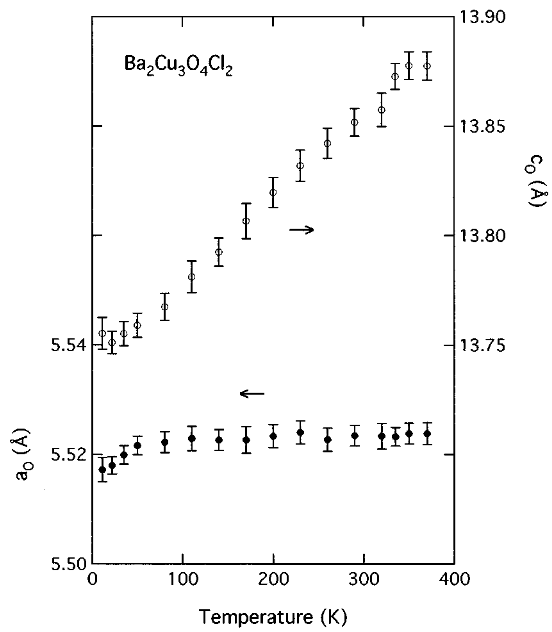

FIG. 2. The temperature dependence of lattice constants a_0 and c_0.

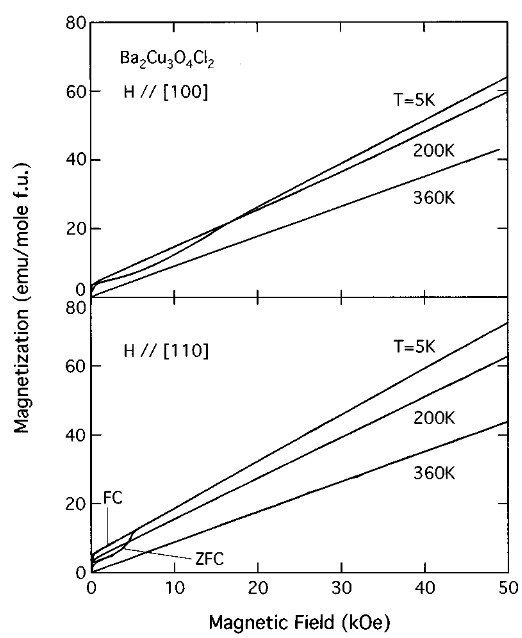

FIG. 3. The magnetic-field dependence of the magnetization $M(H)$ for $H\|[100]$ and $[110]$. The FC data for $H\|[110]$ are taken for a sample cooled in a magnetic field of $H=2$ kOe parallel to $[110]$.

In order to investigate the possibility of the weak ferromagnetism below $T=332$ K in detail, we measured a magnetic-field-dependent magnetization $M(H)$ at several temperatures. Representative results for $H\|[100]$ and $H\|[110]$ are shown in Fig. 3. For $H\|[001]$, $M(H)$ is proportional to H up to 50 kOe at any temperatures; the data for $M_{[001]}$ are not shown in the figure. For $H\|$plane and $T<332$ K, $M(H)$ is linear in H with an offset, although a deviation from the linearity is observed at low fields below $T=32$ K. This deviation will be discussed later and we will concentrate on the linear parts for a while. The linearity of the $M(H)$ curve is better for $H\|[110]$ than that for $H\|[100]$. The value of ferromagnetic moment is small, as shown by the offset of the $M(H)$ curve, and the $M(H)$ curves show no trace of saturation up to $H=50$ kOe, so that weak ferromagnetism exists below $T=332$ K in this material. Almost no anisotropy in the size of the weak-ferromagnetic moment for $H\|$plane indicates that this weak ferromagnetism is due to the Dzialoshinsky-Moriya (DM) interaction.[9] The Hamiltonian of this interaction is represented as $\mathcal{H}_{D-M}=\mathbf{D}\cdot[\mathbf{S}_1\times\mathbf{S}_2]$, where $\mathbf{D}$ is determined by the symmetry of the positions of atoms surrounding magnetically coupled Cu atoms. Considering the symmetry for every combinations of adjacent Cu atoms on an assumption that $S=1/2$ for both Cu_A and Cu_B spins, we conclude that $\mathbf{D}$ is finite only for the nearest Cu_A atoms; consequently, it is understood that this weak ferromagnetism is caused by an antiferromagnetic ordering of Cu_A spins below $T=332$ K. In the case considered above, $\mathbf{D}$ is parallel to the c axis; the weak-ferromagnetic moment can rotate freely in the plane perpendicular to the c axis, in accordance with our experimental results. No weak-ferromagnetic moment for $H\|c$ axis is also consistent with the DM interaction with $\mathbf{D}\|c$.

The H-linear $M(H)$ curve suggests that we could decompose the magnetization into two components, i.e., weak-ferromagnetic M_O and H-linear χH. The coefficient χ of the latter is the sum of paramagnetic susceptibility and antiferromagnetic perpendicular susceptibility. This decomposition is very important to understand whether the characteristic features shown in Fig. 1, such as the maxima in $M(T)$ curves, originate from M_O or χ. For $H\|$plane, we obtained M_O and χ by fitting the measured magnetization $M_{[110]}(H)$ at $H=8$, 9, and 10 kOe, where $M(H)$ is linear in H, to the formula $M=M_O+\chi H$ at each temperature using the method of least squares. If we use the data of $M_{[100]}$, there appears an ambiguity in the analysis due to the worse linearity, although the discussion in the following does not change seriously. For $H\|c$ axis, only the H-linear component exists; $M_O=0$ and $\chi=M/H$. The obtained results are shown in Fig. 4. For $H\|$plane, M_O is almost zero above $T=332$ K. Owing to the weak ferromagnetism, $M_O(T)$ shows an abrupt increase just below this temperature and gradually increases with lowering temperature. There is no anomaly in the $M_O(T)$ curve at the lower transition temperature, $T=32$ K. Assuming that the size of the staggered moment of Cu_A is the same as that for La_2CuO_4 and $0.6\mu_B$,[10] we can estimate the canting angle from the antiparallel direction to be ~0.05 degrees.

For both $H\|$plane and $H\|c$ axis, $\chi(T)$'s show similar behaviors with maxima around $T=80$ K. Below $T=32$ K, χ is

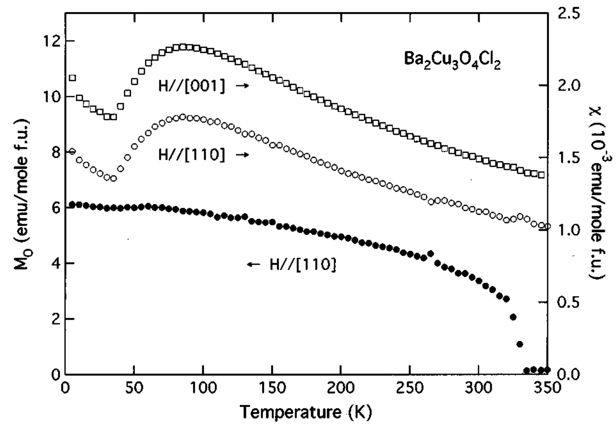

FIG. 4. The temperature dependence of M_O and χ (see the text for the definition of these parameters).

the sum of the perpendicular susceptibilities of the antiferromagnetically ordered Cu_A and Cu_B spins. For 32 K $<T<332$ K, χ is the sum of the perpendicular susceptibility of the antiferromagnetically ordered Cu_A spins and the susceptibility of the paramagnetic Cu_B spins. The perpendicular susceptibility is usually almost T independent and the paramagnetic one can be T dependent; it is plausible that the maximum at $T\sim80$ K is a characteristic feature of the paramagnetic Cu_B spins. A maximum appears in the temperature dependence of magnetic susceptibility for the low-dimensional magnet with an antiferromagnetic interaction. The maximum in $\chi(T)$ of $Ba_2Cu_3O_4Cl_2$ could be explained by the Cu_B spins interacting antiferromagnetically in the two-dimensional Cu_B network. For the $S=1/2$ antiferromagnetic Heisenberg model on a square lattice, superexchange coupling constant J is $\sim k_BT_{max}/2$, where T_{max} is the temperature where the maximum in the susceptibility appears.[11] Assuming that this model is applicable to Cu_B spins, we can estimate J_{Cu_B} to be ~40 K, which is more than a magnitude smaller than those for the high-T_c superconductors and probably for the Cu_A spins in $Ba_2Cu_3O_4Cl_2$.

For $H\|$plane and $T<32$ K, as mentioned above, the deviation from the linearity in $M(H)$ appears at low fields. The $M_{[100]}(H)$ curve is concave at low fields and shows crossover to a H-linear line at high fields. This curve is independent of the magnetic field on cooling. The $M_{[110]}(H)$ curve shows a more abrupt change around $H=4.7$ kOe for a zero-field-cooled sample, while it is linear without the deviation for that cooled in a field of $H\gtrsim200$ Oe. These two $M_{[110]}(H)$ curves are identical for $H\gtrsim5$ kOe. These $M_{[110]}(H)$ curves are reproducible for any field sweeps below $T=32$ K; they depend only on the field on cooling. When the cooling field is decreased from ~200 to 0 Oe, the $M_{[110]}(H)$ curve changes gradually from the FC to the ZFC curves shown in Fig. 3. The dependence of the $M_{[110]}(H)$ curves on the cooling field is consistent with the hysteresis in the $M_{[110]}(T)$ curve shown in Fig. 1.

The ZFC $M_{[110]}(H)$ curves in low field ($H\lesssim3$ kOe) and high field ($H\gtrsim5$ kOe) regions are represented as $M_{O,LF}+\chi_{LF}H$ and $M_{O,HF}+\chi_{HF}H$, respectively, where $M_{O,HF}\sim1.9M_{O,LF}$ and $\chi_{HF}\sim1.4\chi_{LF}$. The relation $M_{O,LF}\sim(1/2)M_{O,HF}$ indicates that the half of the weak-ferromagnetic moments originating from Cu_A spins orient to

[110] direction and the other half to $[1\bar{1}0]$. This relation of M_O also indicates that the moment cannot rotate freely at low fields. The deviation from the linearity in the ZFC $M_{[110]}(H)$ curve, as well as that in the ZFC $M_{[100]}(H)$ curve, can be explained by an assumption that the easy axes of magnetization for Cu_A spins, [110] and $[1\bar{1}0]$, appear below $T=32$ K. The spin directions of Cu_A would be [110] and $[1\bar{1}0]$ with the same probabilities. When H is applied along [110], spins with direction [110] would flip at a certain field; the direction of all spins aligns with $[1\bar{1}0]$. When H is applied along [100], the direction of spins would rotate to [010] direction gradually with increasing H.

For the field-cooled condition, the same assumption can be applicable. Under a field parallel to [110], the weak-ferromagnetic moment aligns with the field direction; the magnetization is H linear. Under that parallel to [100], the moments become oriented parallel to [110] and $[1\bar{1}0]$ with the same probabilities in the cooling procedure; the situation for the field-cooled sample is the same as that for the zero-field-cooled one and thus $M_{[100]}(H)$ curve is independent of the cooling field.

A problem we encounter here is why the $M_{[110]}(H)$ curves are determined only by a field on cooling. It is difficult to explain the problem by a pure magnetic origin. In the case of such origin, the situation would be the same as that for a ferromagnet with magnetic domains and, once H larger than 5 kOe is applied, the $M_{[110]}(H)$ curve would converge on a single curve. The cooling-field dependence of the $M_{[110]}(H)$ curve might be caused by a coupling between the easy axis of the magnetization for the Cu_A spins and a lattice distortion below $T=32$ K; the orientations of the crystallographic axes of the distorted lattice might be determined by the direction of the Cu_A spins in the cooling procedure and any field sweeps below $T=32$ K might not change the orientations of the crystallographic axes. However, we found no clear evidence for such coupling in our x-ray-diffraction data of polycrystalline samples (Fig. 2). Investigations by techniques more sensitive to lattice properties, such as x-ray diffraction of single crystal and optical measurements, are necessary to clarify the possibility of this coupling.

In summary, the temperature- and magnetic-field-dependent magnetization $M(T,H)$ revealed a rich variety of magnetic properties of $Ba_2Cu_3O_4Cl_2$. The temperatures where anomalies in $M(T,H)$ appear, $T=332$ K and 32 K, agree well with those of the antiferromagnetic transitions of the Cu_A and Cu_B spins, respectively, which are confirmed by other experiments.[4–6] Below $T=332$ K, the antiferromagnetically ordered Cu_A spins have a weak-ferromagnetic moment due to the Dzialoshinsky-Moriya interaction. Above $T=32$ K, the weak-ferromagnetic moment rotates freely in the (001) plane, while, below $T=32$ K, the Cu_A spins have an easy axis of the magnetization, along [110], which causes the flip and the rotation of the ordered Cu_A spins. The degree of the increase of the magnetization due to the spin flip, appearing in the $M_{[110]}(H)$ curve below $T=32$ K, only depends on a field on cooling. The origin of this cooling-field dependence should be explained by further experiments. An analysis with a formula $M(H,T)=M_O(T)+\chi(T)H$ shows that maxima in the $M(T)$ curves originate from the behavior of $\chi(T)$. The maxima could be explained by the Cu_B spins with a two-dimensional network of antiferromagnetic interactions. The superexchange interaction constant J_{Cu_B} can be estimated to be ~ 40 K.

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