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Antisymmetric exchange interactions and weak ferromagnetism in Bi_2CuO_4

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Detailed measurements of the temperature and magnetic field dependences of the magnetization of hydrothermally grown Bi_2CuO_4 single crystals have been performed. It is concluded from an analysis of the experimental data that Bi_2CuO_4 is a weak ferromagnet with a net magnetization in the basal plane. The application of a magnetic field in the basal plane induces a phase transition from a weak ferromagnetic to an antiferromagnetic structure.

I. INTRODUCTION

The magnetic and structural properties of Bi_2CuO_4 have been widely studied in recent years, both because of their possible relationship to high-T_c superconductivity and as an interesting example of three-dimensional (3D) $S=\frac{1}{2}$ Heisenberg antiferromagnet. Initially, Bi_2CuO_4 was inferred to be a one-dimensional antiferromagnet,[1] however, later neutron investigations[2-7] revealed without any doubt a three-dimensional antiferromagnetic ordering as a ground state. Some discrepancies also existed in the description of the structure of Bi_2CuO_4. Two different space groups have been proposed for the crystal structure of Bi_2CuO_4 (see Ref. 6 for discussion and references): $I4$ and $P4/ncc$. Neutron and x-ray-diffraction studies have confirmed unambiguously the $P4/ncc$ symmetry of the Bi_2CuO_4 compound. It has been established[6] that Bi_2CuO_4 is a 3D antiferromagnet in which the Cu^{2+} magnetic moments are oriented in the basal tetragonal plane and has a Néel temperature in the range 42–50 K. The magnetic moment of Cu^{2+} ions is about $(0.7-0.85)\mu_B$ at low temperature.[6-8] Because of the low crystal symmetry, exchange interactions are strongly anisotropic.[8] Moreover, some anisotropy, described by a four-site exchange interaction term, is observed in the tetragonal plane.

Recently Bi_2CuO_4 single crystals have been grown by a hydrothermal technique.[9] Their structure and lattice constants are similar to those observed in Ref. 6 although some orthorhombic distortion cannot be excluded. Zero-field nuclear spin-echo experiments[9] performed on the hydrothermally grown Bi_2CuO_4 single crystals have revealed the presence of a spontaneous magnetic moment. In order to obtain a deeper insight into the magnetic properties and to confirm the presence of a ferromagnetic component of magnetization in Bi_2CuO_4 grown by a hydrothermal technique we have carried out magnetization measurements on the same single crystals as those used previously in Ref. 9.

II. EXPERIMENT

Details of the crystal growth have been published in Ref. 9. The single crystals are platelet shapes, with typical dimensions of $0.5\times0.5\times0.1$ mm. The measured lattice constants, $a=8.4674(30)$ Å, $b=8.4796(32)$ Å, and $c=5.8038(20)$ Å, although suggesting orthorhombic symmetry, at the same time do not exclude (within experimental uncertainty) the tetragonal symmetry of Bi_2CuO_4. Unfortunately, we have not been able to determine the space group of our crystals.

The magnetic susceptibility and magnetization measurements were performed using a quantum design SQUID magnetometer with magnetic fields up to 5 T and with temperatures in the range from 4.2 K up to room temperature. The magnetic susceptibility measured in a magnetic field $H=1$ kOe applied perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) to the c axis is shown in Fig. 1. Figure 2 shows the same data plotted as $\chi_\perp^{-1}$ and $\chi_\parallel^{-1}$ as a function

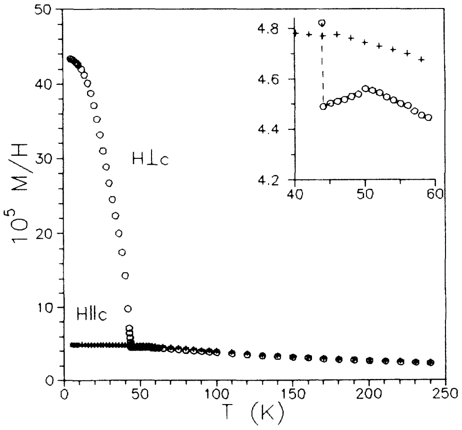

FIG. 1. Magnetic susceptibility of Bi_2CuO_4 single crystal as a function of temperature measured in magnetic field of 1 kOe applied parallel and perpendicular to the c axis. (The inset shows an expanded view near T_N.)

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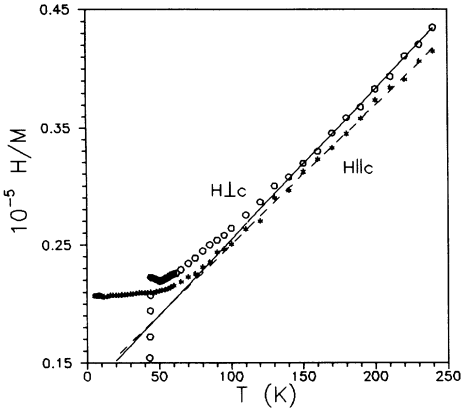

FIG. 2. Inverse magnetic susceptibility of Bi_2CuO_4 single crystal as a function of temperature ($H = 1$ kOe).

of temperature. In the paramagnetic region the susceptibility follows the Curie-Weiss law $\chi = C/(T+\Theta)$ with $\mu_{\rm eff}^{\parallel} = 2.06\mu_B$, $\Theta_{\parallel} = 108$ K, $g_{\parallel} = 2.4$ and $\mu_{\rm eff}^{\perp} = 1.98\mu_B$, $\Theta_{\perp} = 98$ K, $g_{\perp} = 2.28$. These values are to be compared to those obtained by Yamada *et al.*[6]: $g_{\parallel} = 2.16$, $g_{\perp} = 2.07$, and $\Theta = 96$ K for both directions.

Below 100 K some deviation from the Curie-Weiss law is observed, particularly a sudden small jump in magnetization $M_{\perp}$ at $T \approx 50$ K. Below 50 K a strong anisotropy of magnetization is also observed, for the configurations $H \perp c$ and $H \parallel c$, due to appearance of long-range antiferromagnetic ordering.

To investigate the magnetic ordering in more detail, we have determined the field dependence of the magnetization at different temperatures below 50 K. The results of measurements with the magnetic field parallel and perpendicular to the c axis are shown in Figs. 3 and 4.

Because of the form of studied crystals the influence of different demagnetizing factors in both field configurations should be taken into account. However, it is worth stressing that due to small values of magnetization, the demagnetizing fields only insignificantly modify the effective magnetic fields, even in the case of $H \perp c$ (for $H > 200$ Oe).

In the case of $H \parallel c$ the dependence, $M_{\parallel}(H)$ is linear for all temperatures and passes through the origin within experimental uncertainty. For $H \perp c$, the $M_{\perp}(H)$ curve acquires a distinctly different character at relatively low fields. This nonlinear magnetization is probably due to magnetic domain structure expected for weak ferromagnets.

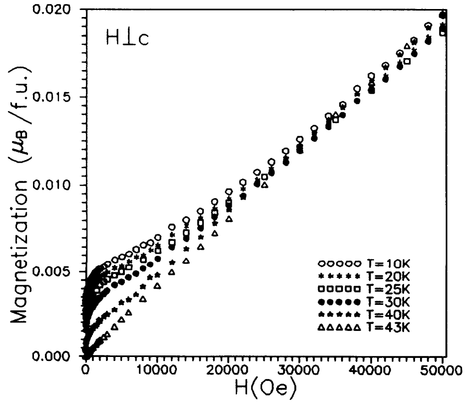

FIG. 3. Magnetization of Bi_2CuO_4 versus magnetic field applied perpendicular to the c axis.

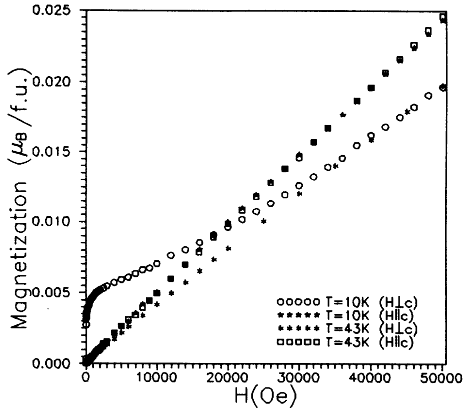

FIG. 4. Magnetization of Bi_2CuO_4 versus field applied parallel and perpendicular to the c axis.

The existence of a weak ferromagnetic moment in (001) plane is confirmed by careful inspection of $M_{\perp}(H)$ curves at higher fields. In this region $M_{\perp}$ becomes proportional to the applied field and the extrapolation to the $H = 0$ results in the ferromagnetic component $M_{\rm WF}$ with a magnitude which is strongly dependent on temperature: $M_{\perp}(T,H) = M_{\rm WF}(T,0) + \chi_{\perp}H$. The observed temperature dependence of the weak ferromagnetic moment $M_{\rm WF}(T,0)$ is shown in the inset of Fig. 5. For weak ferromagnetic materials one should expect, in frames of spin-wave theory,[10] the following temperature dependence: $M_{\rm WF}(T) = M_{\rm WF}(0)[1 - DT^2]$. The experimental data presented in Fig. 5 are in excellent agreement with the theoretical prediction.

It should be mentioned that for $T = 10$ K the slope of the magnetization curve, $M_{\perp}(H)$, increases at the field of about 20 kOe. A similar effect but at lower fields is observed for $M_{\perp}(H)$ curves measured in higher temperatures. It appears that the magnetic field induces a phase transition from the weak ferromagnetic structure to pure antiferromagnetic one (with a negligibly small ferromagnetic component). Figure 4 shows that for fields $H > 30$

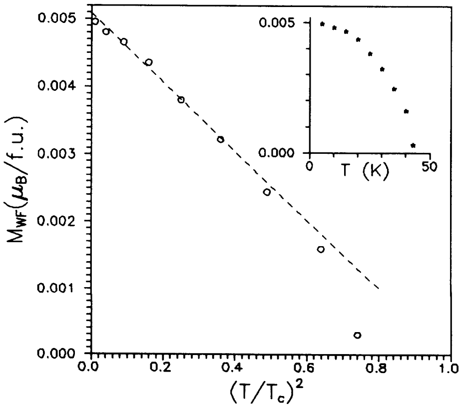

FIG. 5. Weak ferromagnetic moment of Bi_2CuO_4 as a function of $(T/T_N)^2$. [In the inset the relation $M_{\rm WF}(T)$ is also shown.]

kOe the slopes dM/dH of magnetization curves $M_\perp(H)$ measured at 10 and 43 K are practically the same. Because in lower fields, after saturation of weak ferromagnetism, there exists also a field range with nearly constant dM/dH it is possible to fit the linear $M(H)$ relations to both lower and higher field ranges. The field value, in which an intersection of both lines takes place, is considered as the critical field $H_{\rm cr}$ of the field-induced transition. As an example, an estimation of the critical field for $T=10$ K is shown in Fig. 6. It is seen that the observed transition is not sharp. One of possible reasons of transition broadening could be a disorientation of the a axis (the sample consisted of several single crystals oriented only along c axis, with the a axis arbitrarily distributed). Although, the values of $H_{\rm cr}$, obtained in these conditions, are determined with significant errors (of several kOe), they characterize the existing field-induced transition.

III. DISCUSSION

The temperature and field dependences of the magnetization below and above Néel temperature T_N may be analyzed in terms of the Landau theory of second-order phase transitions (see Ref. 11 for a discussion of thermodynamical properties of weak ferromagnets in terms of the Landau theory). For weak-ferromagnetic crystals with structure described by $P4/ncc$ space group and for copper ions located on sites of $4c$ (of point symmetry 4),[4] the free energy of the considered magnetic system may be expanded in terms of the sublattice magnetization or, equivalently by $\mathbf{m}=\mathbf{M}_1+\mathbf{M}_2$ and $\mathbf{l}=\mathbf{M}_1-\mathbf{M}_2$, as follows:

$$F=\tfrac{1}{2}(Al^2+Bm^2+al_z^2+bm_z^2)+\gamma(m_xl_y-m_yl_x)+\tfrac{1}{4}Cl^4-\mathbf{mH}\,, \tag{1}$$

where a and b are the second-order anisotropy constants, while γ describes the strength of the antisymmetric Dzyaloshinsky-Moriya exchange interactions.

Note that the first two terms in (1) describe the isotropic symmetric exchange while the experimentally observed[8] strong anisotropic exchange is included in the effective anisotropy constants a and b.

It can be shown that $(A-\gamma^2/B)=0$ at T_N, therefore for temperatures close to T_N we may write

$$A-\gamma^2/B=\alpha(T-T_N)\,, \tag{2}$$

and consequently

$$m_z=H_z/(B+b)\,, \tag{3}$$

$$m_x=\frac{\gamma}{B}l(T,H=0)+\frac{H_x}{B}\left[1+\frac{\gamma^2}{2\alpha B(T-T_N)}\right] \quad \text{for } T<T_N\,, \tag{4}$$

$$m_x=\frac{H_x}{B}\left[1+\frac{\gamma^2}{\alpha B(T-T_N)}\right] \quad \text{for } T>T_N\,. \tag{5}$$

It results from Eqs. (3) and (4) that the Dzyaloshinski-Moriya interaction induces a weak ferromagnetic moment in basal plane. Moreover, the same interaction is responsible for a peak at $T=T_N$ observed experimentally for the perpendicular susceptibility. Such peak is not predicted for $\chi_\parallel$ in accordance with experimental data.

Taking into account Eqs. (3)–(5) and the experimental data, it is easy to find exchange and anisotropy parameters determining the energy of the system through expression (1). We applied here the following procedure. From the data taken at high field and low temperature we have estimated $\chi_\perp=3.3\times10^{-5}$ and consequently $B=\chi_\perp^{-1}=3\times10^4$; from the value of weak ferromagnetic moment extrapolated to $T=0$,

$$M_{\rm WF}(0)=\gamma/Bl(0)=5.07\times10^{-3}\mu_B/\text{f.u.}$$

and assuming $l(0)=1.7\mu_B/\text{f.u.}$, as found in Ref. 6, we obtained $\gamma/B=3\times10^{-3}$ and consequently $\gamma\approx100$. Having determined the values of γ and B we are able to calculate the canting angle, ψ, between magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$. Since $tg\psi=\gamma/B$, then we have $\psi\approx0.17°$. From the divergent contribution to the initial slope of magnetization near T_N we have roughly estimated $\alpha\approx60\ \mathrm{K}^{-1}$.

In spite of the fact that the presented conventional theoretical model describes properly the experimental data, it is clear that this model does not predict any field-induced phase transition for a magnetic field applied in a basal plane. To describe the experimentally observed phase transition from weak ferromagnetic structure to the antiferromagnetic one it is necessary to replace the generally used expression for the Dzyaloshinsky-Moriya interaction

$$\gamma(m_xl_y-m_yl_x)$$

by the following one (allowed by symmetry of the system):

$$\Gamma(m_xl_y+m_yl_x)(l_x^2-l_y^2)\,. \tag{6}$$

It is easy to show that for such an interaction the following two magnetic structures are expected to exist for magnetization in the basal plane:

$$\text{(I)}\quad \varphi=0\,,\quad m_x=\frac{\Gamma l_y^3(0)}{B}\,,$$

$$\text{(II)}\quad \varphi=45\,,\quad m_x\approx0\,,$$

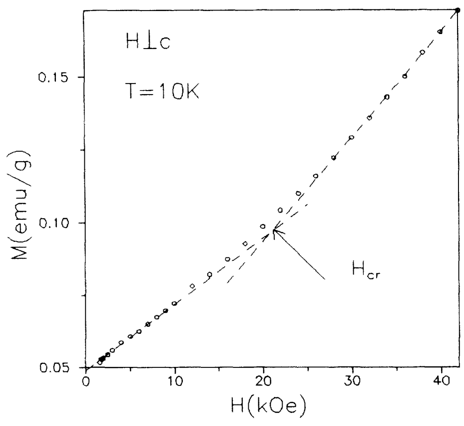

FIG. 6. The critical field estimation for $T=10$ K ($H\perp c$).

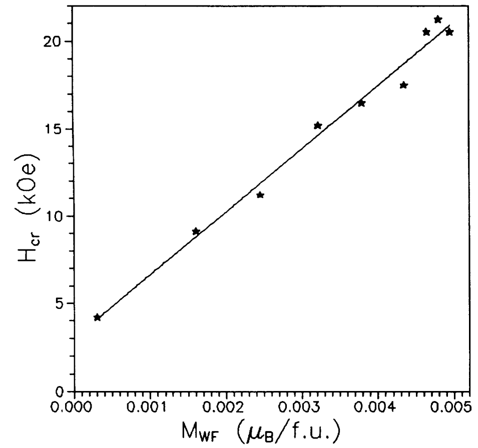

FIG. 7. Critical field H_{cr} as a function of the weak ferromagnetic moment M_{WF}.

where φ is the angle between l and the x axis.

It should be noted that the proposed form (6) of the antisymmetric exchange interaction has no particular effect on the functional dependences given by Eqs. (3)–(5) [except that γ should be replaced by $\Gamma l^2(0)$]. Configuration I (weak ferromagnetic) has lower energy than configuration II at magnetic field $H \leq |\Gamma| l_x^3(0)$ up to $H_{cr} \approx |\Gamma| l^3(0)$ (assuming $\Gamma < 0$). For $H \geq |\Gamma| l^3(0)$ the magnetic field-induced phase transition for antiferromagnetic structure ($m = 0$) is expected to appear. This transition depends on temperature and it is shifted to lower fields when temperature is increased.

Since $m_x(H=0)=\Gamma l^3(0)/B$, the critical field H_{cr} can be given in the following form:

$$H_{cr}=m_x(0)B \quad \text{or} \quad H_{cr}=m_x\chi_\perp^{-1} \; . \tag{7}$$

Figure 7 shows the experimental dependence of critical field H_{cr} as a function of the weak ferromagnetic moment M_{WF}. One can see in Fig. 7 that the relation $H_{cr}(M_{WF})$ is nearly linear. The value of $B = 4 \times 10^4$ determined as a slope of $H_{cr}(M_{WF})$ agrees quite well with the value $B = 3 \times 10^4$ estimated previously from Eqs. (3) and (4).

IV. CONCLUSION

A detailed study of the temperature and field dependence of the magnetization performed on hydrothermally grown Bi_2CuO_4 single crystals has shown the presence of weak ferromagnetic moment in the basal plane. It has been suggested that weak ferromagnetism in Bi_2CuO_4 arises due to the fourth-order antisymmetric (anisotropic) exchange interactions. Moreover, the presence of this term is responsible for the magnetic field-induced spin reorientation in the basal plane from a weak ferromagnetic structure to a pure antiferromagnetic one.

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