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Revised magnetic properties of $CuFeO_2$—a case of mistaken identity

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Abstract

We propose a new model for the understanding of the magnetic properties of $CuFeO_2$, which differs significantly from the generally accepted two-dimensional Ising model. We show that a Heisenberg model with a relatively weak anisotropy gives a much better description of all the magnetic data available for $CuFeO_2$. The model is self-consistent; it allows one to determine for the first time a set of parameters for the exchange interactions and magnetic anisotropy in this frustrated magnetic system. The model is backed up by single-crystal measurements of susceptibility, magnetization and specific heat as a function of magnetic field and temperature.

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

At the beginning of the 1990s, the magnetic properties of $CuFeO_2$ attracted renewed attention both from an experimental [1] and a theoretical [2, 3] point of view due to its frustrated nature. Since this time, this compound has been presumed to be an Ising-like quasi-two-dimensional antiferromagnet on a triangular lattice. Unlike the rest of the ABO_2 family members which have a noncollinear magnetic ground state [4], $CuFeO_2$ orders into a collinear four-sublattice structure at $T_{N2} = 11$ K; the ordering occurs through an intermediate incommensurate phase, which appears at $T_{N1} = 14$ K from a high temperature paramagnetic state [5]. The most interesting effects have been observed when $CuFeO_2$ is placed in a magnetic field, where as many as five spin-flop-like magnetization anomalies have been observed for a field applied along the c-axis (at 80, 130, 220, 260, 420 and 700 kOe), while for $H \perp c$, a phase transition has been found at 240 kOe [6].

Monte Carlo simulation results [6] have suggested that in order for a collinear structure to be stable in a zero field and for the material to undergo several phase transitions in an applied

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field, the second-nearest-neighbour (NN) exchange interaction, J_2, as well as the third-NN exchange interaction, J_3, have to be fairly strong in comparison with the main NN exchange interaction J_1: $J_2/J_1 = 0.5$ and $J_3/J_1 = 0.75$. Although a 2D Ising model with such parameters produces a somewhat similar magnetization curve to the experimental data, there is no compelling physical reason for treating $CuFeO_2$ as an Ising-type magnet. We note that the only magnetic ion in this compound is Fe^{3+}, which in its usual ^6S state with zero orbital momentum is not supposed to possess a significant anisotropy. In addition, the requirement that the exchange interactions J_1 and J_3 take comparable values while the distance between the relevant magnetic moments varies by a factor of two appears unusual. Finally, and perhaps most importantly, our recent inelastic neutron scattering experiments have revealed the presence of a significant dispersion of the magnetic excitations in $CuFeO_2$ both in the basal plane and along the hexagonal axis [7]. Therefore no justification exists for neglecting the interplane interactions or for even suggesting that they are much weaker than the in-plane interactions. As we will show below, the second-NN interaction between the planes may potentially play a much more important role in establishing the magnetic order than the in-plane interactions, J_2 and J_3.

The aim of the present paper is to critically review the available data on the magnetic properties of $CuFeO_2$ and to combine them with our own data obtained on high quality single crystals in order to demonstrate that a 3D Heisenberg model with a modest anisotropy gives a much better description of these properties than the generally accepted 2D Ising model. We take a somewhat unusual approach to the structure of the paper—instead of presenting sequentially the experimental details, our results, a discussion and a comparison with the theory, we describe in turn a particular type of measurement and simultaneously discuss estimates for the relevant magnetic parameters in the light of these results.

We start with an analysis of the magnetization data. The process of magnetization of a powder sample at 8 K in a pulsed field of up to 1000 kOe has been reported by Ajiro *et al* [6]. This study revealed several anomalies in the magnetization curve as described above; it also showed that the saturation magnetization achieved in a field above 700 kOe corresponds to a magnetic moment of nearly 5 μ_B/Fe^{3+} ion. From these results a first estimate of the strength of the antiferromagnetic interaction, J, can be obtained by employing the simple relation $H_{sat} \sim 2JS$, which neglects magnetic anisotropy and also disregards the presence of the different NN interactions. The saturation field of 700 kOe gives $J \sim 19$ K. Note that this is only a very rough estimate, while a more accurate expression $H_{sat} = zJS$ should also include z, the number of neighbouring spins.

In order to see the magnetic anomalies more clearly, Ajiro *et al* [6] repeated the magnetization measurements at 4.2 K for field-oriented samples in fields of up to 390 kOe. These measurements established that the magnetization anomalies for a field applied along the c-axis are at 80, 130, 220, 260 kOe. Later the magnetization measurements in a pulsed field were repeated for a single-crystal sample [8]. These measurements have shown much more clearly the presence of a magnetization plateau between the two transitions at 130 and 220 kOe. A physical interpretation for this plateau has been given in terms of the appearance of a new field-induced five-sublattice structure, where three spins in each unit cell are aligned along the field direction, and the other two are aligned antiparallel to the field [6, 8].

A much clearer picture of the magnetization process, however, was obtained only after measurements were made on single-crystal samples in a steady-state high magnetic field [9–12]. Although the results of these measurements agree with each other in general, there are some minor inconsistencies, which should be resolved in order to arrive at more reliable conclusions. Taking advantage of the high steady-state fields at the Grenoble High Magnetic Field Laboratory, we have made measurements of M versus $H \parallel c$ at various temperatures

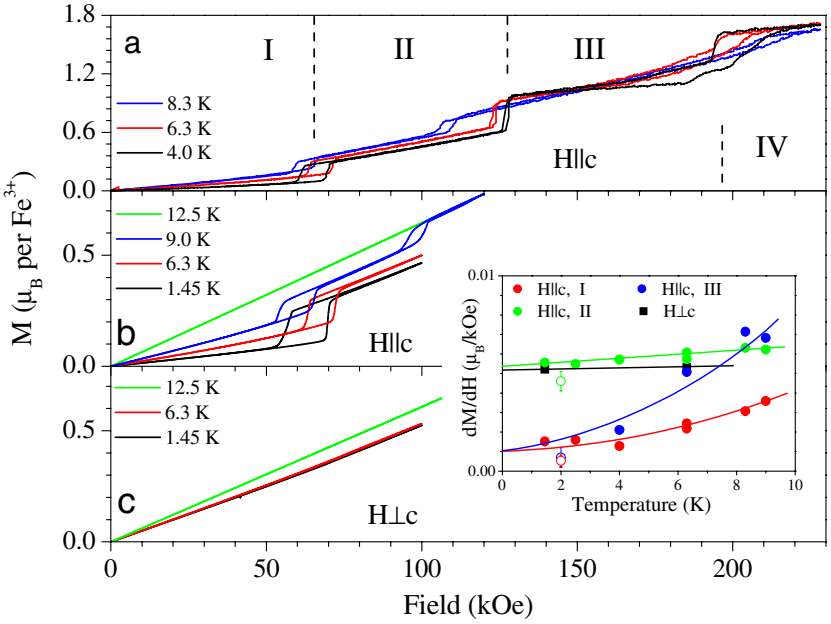

Figure 1. Field dependence of the magnetization of $CuFeO_2$ measured at different temperatures for $H \parallel c$ (panels (a) and (b)) and $H \perp c$ (panel (c)). The inset shows the temperature dependence of the magnetization gradient measured for $H \parallel c$ in field ranges I, II and III and for $H \perp c$ in the range 0–100 kOe. For completeness the data from [13] (open symbols) are also shown.

above 4.2 K in applied fields of up to 230 kOe. These measurements were performed using a standard extraction technique and a resistive magnet; the sample for these measurements was cut from a larger sample used previously for neutron diffraction studies [11]. The same sample was used for more detailed investigations of the temperature dependence of magnetization down to 1.4 K for different directions of an applied field up to 120 kOe using an Oxford Instruments vibrating sample magnetometer (VSM). On both occasions the accuracy of the sample alignment was better than 1°–2°.

The combined results of our magnetization measurements are presented in figure 1. The data in figure 1(a) were obtained using the extraction magnetometer; the data in figures 1(b) and (c) were obtained using the VSM. Clearly defined phase transitions are observed at low temperatures at H_{c1} around 70 kOe and H_{c2} around 130 kOe. A third feature at H_{c3} around 190 kOe is very likely to consist of two phase transitions. The field regions between this transition field are labelled as I, II, III and IV in figure 1. All the transitions are accompanied by a significant hysteresis, which suggests their pronounced first-order nature. The important thing to notice is that at low temperature for $H \parallel c$ the magnetization is almost constant for the field interval I (where $CuFeO_2$ maintains its zero-field two-up–two-down structure) and in the interval III (where the structure is three-up–two-down), while in the field region II the magnetization increases at a significant rate. In order to emphasize the significant difference between the rate of change of the magnetization with applied field in these field regions, the inset shows the temperature dependence of the gradient, $\mathrm{d}M/\mathrm{d}H$, measured for $H \parallel c$ in a field ranges I, II and III and for $H \perp c$ in the range 0–100 kOe. Although the rate of growth is nonzero in any field at higher temperatures, an extrapolation down to $T = 0$ K gives 10^{-6} μ_B/Oe for the regions I and III, while for region II the gradient is five times higher.

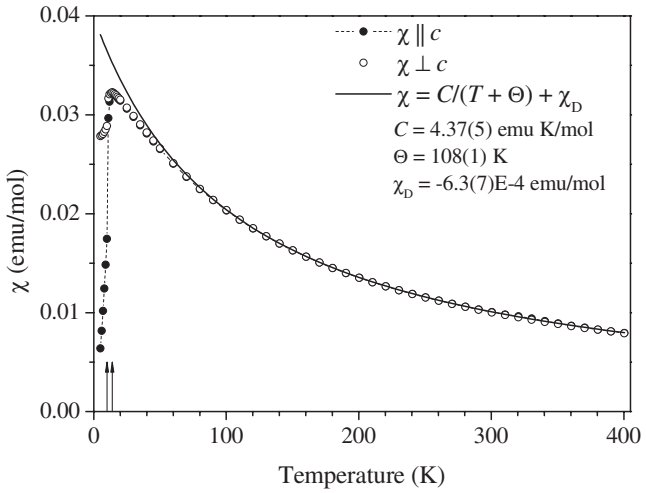

Figure 2. Temperature dependence of the magnetic susceptibility of $CuFeO_2$ measured in a field of 1 kOe for $H \parallel c$ (solid symbols) and $H \perp c$ (open symbols). The solid curve is a fit to a Curie–Weiss dependence with an additional diamagnetic contribution. The arrows indicate the positions of the two successive phase transitions, $T_{N1} = 14$ K and $T_{N2} = 11$ K.

The fact that $\mathrm{d}M/\mathrm{d}H$ is different for different field regions has been noted previously [13]. The explanation suggested is that region II corresponds to an incommensurate five-sublattice-like sinusoidally modulated structure. This suggestion resulted from an analysis of specific heat measurements [10], which, as will be discussed below, now appear questionable, and from the analysis of some extremely small second-harmonic neutron diffraction peaks [12]. Remarkably, $\mathrm{d}M/\mathrm{d}H$ for region II is almost identical to the gradient for $H \perp c$ (see figure 1 inset). If the structure of region II was indeed sinusoidally modulated but still collinear, this fact would simply be a coincidence.

We take the view, however, that this fact is not a coincidence. Instead it suggests that in region II the magnetization process is similar to that for $H \perp c$, which is exactly the case if we presume that the first field-induced phase transition around 70 kOe is spin-flop-like, involving a significant rotation of the spins away from the easy axis to a position nearly perpendicular to it. Adopting an oversimplified two-sublattice Heisenberg antiferromagnetic model with a weak single-ion anisotropy D, one can estimate the gradients for $H \perp c$ and the spin-flop phases as $1/(J + D)$ and $1/(J - D)$ respectively, while the spin-flop transition field is given by $2S\sqrt{JD}$. From here a rough estimate for the anisotropy constant is $D \sim 0.2$ K, which is only 1% of the exchange interaction.

Further evidence for the absence of a significant Ising-like anisotropy in $CuFeO_2$ comes from the single-crystal susceptibility measured over a wide temperature range, 5 K $< T <$ 400 K. The measurements were performed using a Quantum Design SQUID magnetometer. Note that we have used a nearly cubic shaped sample in order to avoid possible complications with the demagnetization factor. Figure 2 shows the temperature dependence of the magnetic susceptibility of $CuFeO_2$ measured in a field of 1 kOe for $H \parallel c$ (solid symbols) and $H \perp c$ (open symbols). As can be seen from the figure, the susceptibility is almost isotropic for $T > T_{N1}$; the difference between $\chi_\parallel$ and $\chi_\perp$ does not exceed 0.5% for $T > 20$ K.

Although there were several reports on the susceptibility of single crystals of $CuFeO_2$ [6, 14–16], the fact that the susceptibility is highly isotropic at $T > T_{N1}$ was either overlooked or not commented upon. This is somewhat surprising, as this fact alone shows

quite clearly that the use of an Ising model for $CuFeO_2$ is not justified. At high temperatures the temperature dependence of the magnetic susceptibility of $CuFeO_2$ is described perfectly well by the Curie–Weiss law (see figure 2) with a small temperature-independent diamagnetic contribution χ_D, arising from a combination of the ion cores and the sample holder. The fit to the experimental data in the temperature interval 100–400 K gives a Weiss constant of 108(1) K in agreement with the previous reports [2], while from the Curie constant one can estimate an effective magnetic moment of 5.92 μ_B in full agreement with the theoretical value for the ^6S state of Fe^{3+} ions. Further analysis of the $\chi(T)$ dependence with a view to possible estimation of the D/J ratio is again complicated by the lack of data on the strength of the different NN exchange interactions. We note, however, that the ESR study reported by Fukuda *et al* [17] has revealed an almost perfectly isotropic g-factor at $T = 70$ K, which rules out the presence of significant anisotropy constant, D, in $CuFeO_2$.

We next consider the heat capacity data available on $CuFeO_2$. Heat capacity data have been reported by several different groups [5, 10–13, 16]. As for the results of the magnetization measurements, the specific heat data reported by the different authors agree with each other in general, while there are some differences requiring further clarification. Most noticeably a first-order phase transition at T_{N2} is marked by a very sharp peak in the specific heat data of Takeda *et al* [5] and Petrenko *et al* [11], but it is barely visible in the data of Mitsuda *et al* [10, 12] and Terada *et al* [13, 16]—the absolute value of the heat capacity at T_{N2} differs by nearly an order of magnitude in these two sets of data.

This difference in the observed specific heat could potentially be explained by the different techniques used for the measurements. Indeed, the standard relaxation technique used in many calorimeters may not necessarily be an ideal method for measuring very sharp anomalies in the specific heat, especially if the transition in question is of first order and therefore involves latent heat. In order to test this suggestion we have remeasured the specific heat of $CuFeO_2$ using a Quantum Design Physical Properties Measurement System and found that our data agree well with the data collected by Takeda *et al* [5] and Petrenko *et al*. We can therefore confirm, as has already been shown in our previous paper [11], that the relaxation technique is capable of producing a very well defined sharp peak in the specific heat of $CuFeO_2$ at T_{N2}. The absence of the peak at T_{N2} in the data of Mitsuda *et al* and Terada *et al* must be caused by some other experimental conditions. In fact, in their very recent publication Terada *et al* [13] stated that they have reviewed their previous data and found that they missed a large sharp peak at T_{N2}.

Having established that the technique used is adequate for the task, we have measured the field dependence of the specific heat of $CuFeO_2$ at different temperatures in a field of up to 90 kOe (see figure 3). The first field-induced phase transition is clearly visible in the specific heat curves and is marked by a pronounced hysteresis. Remarkably, the change in C at H_{c1} is different for low and high temperatures (below and above ~4.5 K)—around the region of the transition C decreases with increasing field at $T < 4$ K and increases with increasing field at $T > 4$ K. This confirms that the temperature dependences of the magnetic excitations in the phases labelled I and II in figure 1 are entirely different, an observation which is consistent with the conjecture that phase II is a noncollinear spin-flop phase.

Figure 3 should be compared with the analogous measurements reported by Mitsuda *et al* [10]. Although their field dependence of the specific heat looks similar, an anomaly observed in C versus H is shifted upwards by approximately 20 kOe. As a result, the magnetic H–T phase diagram produced by these authors (see figure 3 in [10] and figure 1 in [12]) contains an additional region, denoted as 'phase boundary C', which is located just above the H_{c1} and which the authors claim to be, quote, 'a silent feature related to the field dependence of magnetization propagation vector inside the 5-sublattice-like phase' [13]. Our new data presented in figure 3 clearly show, however, that in $CuFeO_2$ the anomaly observed in C versus H

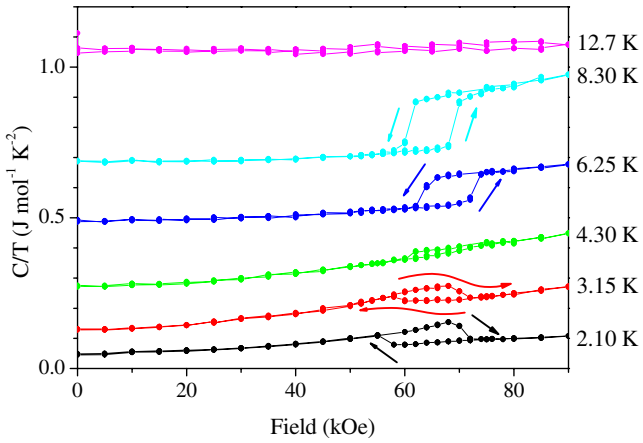

Figure 3. Field dependence of the specific heat divided by temperature, C/T, for $CuFeO_2$ measured for $H \parallel c$ at different temperatures. The arrows indicate the direction of the magnetic field ramping.

coincides well with the jump in magnetization M versus H identifying unambiguously the phase transition field H_{c1}. The presence of 'phase boundary C' [10, 12, 13] cannot therefore be considered as intrinsic to $CuFeO_2$.

The four-sublattice magnetic structure observed at low temperature in $CuFeO_2$ is only one of many available both for the nearly Heisenberg and Ising antiferromagnets on a triangular lattice, which do not satisfy all the NN interactions involved, but provide a set of the degenerate ground states separated by the further neighbour interactions. It is interesting to explore what kind of exchange interactions beyond those of the NN type are responsible for the magnetic structure of $CuFeO_2$. The crystal structure of $CuFeO_2$ belongs to the space group $R\bar{3}m$ with $a = 3.03$ Å and $c = 17.09$ Å in the hexagonal description. Therefore the distances to the first, second and third NN in the basal plane are $a = 3.03$ Å, $\sqrt{3}a \approx 5.25$ Å and $2a = 6.06$ Å respectively, while the distances to the first and second NN between the planes are $\sqrt{c^2/9 + a^2/3} \approx 5.79$ Å and $\sqrt{c^2/9 + 4a^2/3} \approx 6.04$ Å. This simple calculation shows that there is no justification for ignoring the next to nearest neighbour interactions between the hexagonal planes and for considering only the in-plane NN interactions.

Some initial attempts to study further neighbour interactions in $CuFeO_2$ have been made in the past using the perturbed angular correlation measurements [18]. Ultimately the task of establishing the interactions responsible for magnetic properties of $CuFeO_2$ lies with inelastic neutron scattering. However, because of the complicated nature of the observed data [7, 19] further theoretical input is required.

To summarize, we have established that the set of experimental data available on the magnetic properties of $CuFeO_2$ cannot be described by the generally accepted 2D Ising model, as it fails to explain such basic properties of $CuFeO_2$ as the temperature dependence of the susceptibility and the field dependence of the magnetization. A 3D Heisenberg model with a small (about 10% of the exchange) easy-axis-type anisotropy should be developed further (perhaps by including further neighbour interactions) to explain the highly unusual magnetization process in $CuFeO_2$.

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