Origin of the weak ferromagnetism in Gd_2CuO_4

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The magnetic properties of Gd_2CuO_4 have been investigated by magnetization, electron paramagnetic resonance (EPR) and neutron-diffraction measurements in the temperature range 1.5–50 K to determine the magnetic phase diagram and to search for the origin of the weak ferromagnetism which has been observed in this compound. Gd_2CuO_4 is found to have a rather complex magnetic phase diagram consisting of at least four distinct magnetic phases. The nature of the weak ferromagnetism is discussed and a possible origin of both the weak ferromagnetism and the phase transitions is proposed.

I. INTRODUCTION

The magnetic properties of the series of electron-doped high-T_c superconducting materials with general formula $R_{2-x}Ce_xCuO_4$ have been under intense investigation since their discovery. According to Ref. 1, the members of this family can be divided into two groups depending on whether or not they exhibit weak ferromagnetism (WF). The compound Gd_2CuO_4 occupies a unique place in this family for two reasons: First, although it is as easily doped with Ce or Th as the other members of the family, it does not, as they do, become superconducting.[2] Second, it was in Gd_2CuO_4 that ferromagnetic ordering of the rare-earth planes was observed in CuO_2-layer compounds.[3] It has also been found[4–7] that below the copper ordering temperature [T_N(Cu)=285 K] Gd_2CuO_4 exhibits weak ferromagnetic behavior, although this phenomenon is forbidden in the space group $I4/mmm$ to which the structure given by Ref. 1 belongs.

The magnetic properties of Gd_2CuO_4 have been the subject of a large number of publications.[1–8] Three anomalies have been found in the temperature dependence of its magnetic susceptibility: at 6.5, 20, and 270 K.[1,4–7] The reasons for the lower and higher anomalies have been clarified by neutron-diffraction experiments on ^{158}Gd-enriched Gd_2CuO_4 single crystals: At T_N(Cu) the Cu magnetic moments order to a La_2NiO_4-like antiferromagnetic (AF) structure with the propagation vector $\kappa=(\frac{1}{2},\frac{1}{2},0)$ and the spin direction of Cu ions parallel to [110]. At T_N(Gd)=6.4 K the gadolinium ions order antiferromagnetically with the propagation vector $\kappa=(0,0,0)$. The two centrosymmetrically related Gd atoms in the primitive unit cell are oppositely oriented.[3] Thus the rare-earth subsystem in Gd_2CuO_4 below T_N(Gd) consists of ferromagnetic Gd planes, parallel to the CuO_2 planes, with alternate planes oppositely oriented. Figure 1 shows the arrangement of moments in this low-temperature structure (AFM2). Antiferromagnetic resonance and magnetic measurements made below T_N(Gd) indicate that Gd_2CuO_4 is an *easy plane* antiferromagnet. They also show that there is a continuous spin reorientation at $H=8.8$ kOe ($T=1.8$ K) and a spin-flip transition at $H=110$ kOe ($T=1.5$ K).

The origin of the intermediate anomaly, at 20 K, in the magnetic susceptibilty of Gd_2CuO_4 is not so clear. The fact that such intermediate anomalies only occur in those compounds of the R_2CuO_4 family which exhibit weak ferromagnetism suggests strongly that the two effects are linked. In the absence of microscopic information, it is not easy to interpret this unusual behavior, and the present experiments were undertaken to provide additional data in this temperature range. With these data, using symmetry arguments, it has been possible to suggest a possible explanation for the existence of WF in Gd_2CuO_4 which is consistent with other experimental observations.

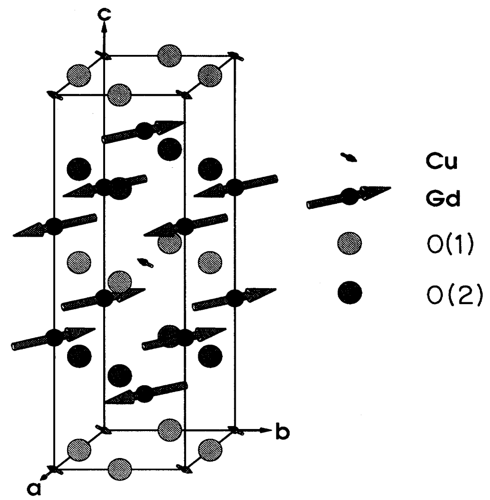

FIG. 1. Schematic drawing of the magnetic structure of Gd_2CuO_4 in the AFM2 phase ($T < 6.4$ K).

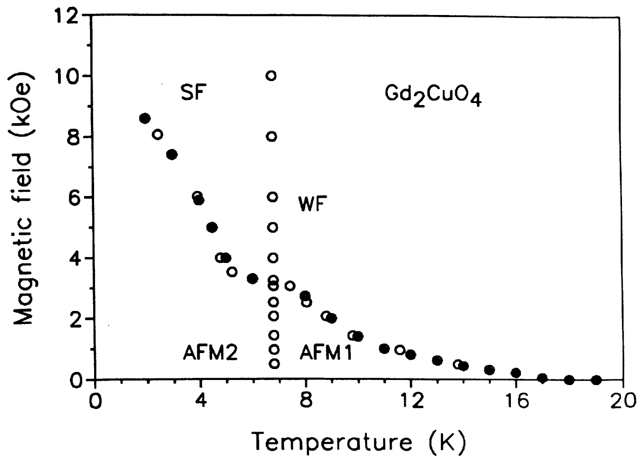

FIG. 2. The H-T phase diagram of Gd_2CuO_4 for magnetic field $H \| a$. The open circles correspond to phase boundaries determined from the temperature dependence of the magnetization at fixed magnetic field and solid circles to boundaries deduced from the field dependence of the magnetization at fixed temperature.

II. EXPERIMENTAL RESULTS

In this paper we report the results of an experimental study of the magnetic properties of Gd_2CuO_4 at low temperatures. The electron paramagnetic resonance (EPR) and magnetization have been measured in relatively weak magnetic fields of up to 10 kOe, and neutron-diffraction measurements have been made in zero field in the temperature range 1.5–50 K. The magnetic measurements were made using a conventional vibrating-sample magnetometer. The magnetization of the sample was measured both as a function of magnetic field at constant temperature and as a function of temperature at constant magnetic field. EPR experiments in the X band were done with a Bruker ESR 300 spectrometer, using a gas-flow cryostat (Oxford ESR9) and a Varian rectangular dual cavity (TE104). The neutron experiments were carried out on the 2AX diffractometer at the Saphir reactor (PSI Würenlingen) with the sample in an ILL-type helium-vapor-cooled cryostat.

Figure 2 shows the H-T phase diagram of Gd_2CuO_4 in magnetic fields of up to 10 kOe constructed from all available measurements. There appear to be at least four different magnetic phases in this region of H and T. The existence of the three phases—weak ferromagnetic (WF) phase, spin-flop (SF) phase, and the second antiferromagnetic phase (AFM2) and the phase boundaries between them—could be inferred from our earlier data.[3] The phase boundary which is almost parallel to the H axis, at $T_N(\mathrm{Gd}) = 6.4$ K, shows that $T_N(\mathrm{Gd})$ is almost independent of magnetic field at low fields. Above 50 kOe, $T_N(\mathrm{Gd})$ displays strong field dependence up to 110 kOe at which field it has dropped to 1.5 K.[3] This boundary corresponds to the second-order spin-flip transition.

The transition to the SF phes can take place only when the Gd subsystem is ordered and, as we explain in Ref. 3, can be attributed to a continuous spin reorientation between the antiferromagnetic and spin-flop phases. In the AFM2 phase at $H = 0$, the spins lie in the $\langle 110 \rangle$ directions; then as the field ($H \| \mathbf{a}$) increases, the spins rotate to become almost perpendicular to H in the SF phase. Magnetic measurements, and especially the field dependence of magnetization at fixed temperature, have proved very useful in elucidating the nature of the magnetic anomalies in Gd_2CuO_4. Some typical plots of the magnetization vs magnetic field at fixed temperatures around $T \approx 20$ K are shown in Fig. 3. The two important features observed

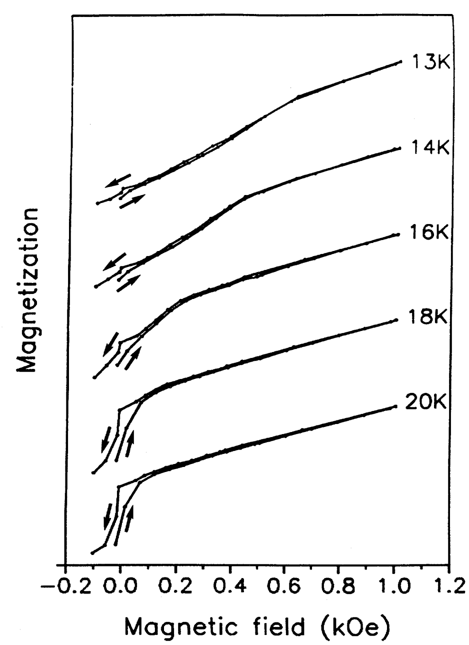

FIG. 3. Magnetization of Gd_2CuO_4 as a function of magnetic field applied parallel [100] at different temperatures. The arrows indicate measurements for increasing and decreasing fields.

which indicate the presence of a phase transition are (1) the small but significant hysteresis at $H=0$ in $m(H)$, which is present at all temperatures above $T_c \approx 20$ K (up to 270 K) and which gradually disappears below T_c; (2) the form of the $m(H)$ curves in the temperature range $T_N(\mathrm{Gd}) < T < T_c$, which have two almost linear parts with different slopes which meet an H_c. The value of H_c depends strongly on the temperature.[4] These results show clearly that the WF phase only exists in Gd_2CuO_4 in zero field for $T > T_c$, although below T_c it can be induced by a magnetic field applied in the **a-b** plane. It can be concluded that at $T_c \approx 20$ K, in zero field, a WF-AF phase transition occurs. An important characteristic of the WF phase is the value of the internal field H_i, which induces the weak ferromagnetic moment in the **a-b** plane. This can be determined by extrapolating the upper part $(H > H_c)$ of the $m(H)$ curve to $m=0$. Different extrapolation procedures give values of H_i between 600 and 700 Oe, compatible with previous measurements.[1,4–7] It should be noted that H_i is independent of temperature in the range $T_N(\mathrm{Gd}) < T \ll T_N(\mathrm{Cu})$. Thus H_i is an effective field due to exchange interactions between the ordered copper moments and the rare-earth sites, as was proposed previously.[4] The lower part of the $m(H)$ curve $(H < H_c)$, when extrapolated to $H=0$, passes through the origin, which confirms that a pure antiferromagnetic phase is stable when $H < H_c$.

Further evidence for the existence of the phase transition near 20 K was obtained in the EPR measurements. At temperatures below T_c, a strong anomaly in $d\chi/dH$ vs H occurs in weak magnetic fields[1] as shown in Fig. 4. This anomalous signal is found only when the radio frequency field h is in the **a-b** plane perpendicular to H. The inset in Fig. 4 shows the low-field part of the EPR spectra which demonstrates the noisy nature of the signal. These fluctuations are an important feature of the anomaly because they suggest the existence of some degree of disorder in the crystal and magnetic structures of Gd_2CuO_4.

In the neutron-diffraction experiments, the integrated intensities of the 002, $\frac{1}{2}\frac{1}{2}1$, and $\frac{1}{2}\frac{1}{2}3$ reflections were measured in the temperature range 1.5–50 K. The intensity of the 002 reflection was used to monitor the spontaneous ordering of the Gd sublattices below $T_N(\mathrm{Gd})$. It showed no significant variation between 7 and 40 K, indicating that in this temperature range it contains no appreciable magnetic contribution. The intensity of the $\frac{1}{2}\frac{1}{2}1$ reflection is plotted as a function of temperature between 1.5 and 50 K in Fig. 5. Above 50 K its intensity has been found to fall continuously and to disappear at $T_N(\mathrm{Cu})$.[8] The broad minimum in the intensity between 40 and 8 K also suggests the presence of some kind of transition around $T=20$ K. The most unexpected feature of the data is the sudden and almost complete disappearance of the $\frac{1}{2}\frac{1}{2}1$ reflection at $T \sim T_N(\mathrm{Gd})$. Below $T_N(\mathrm{Gd})$ the $\frac{1}{2}\frac{1}{2}1$ intensity rises again in much the same way as the 002 reflection.

The $\frac{1}{2}\frac{1}{2}3$ reflection was found to be very weak and was difficult to measure because of $\lambda/2$ contamination from 116 which is a strong nuclear reflection. However, by using a neutron wavelength of 0.84 Å and a 0.5-mm erbium filter, it was possible to almost completely eliminate $\lambda/2$ and to show that the $\frac{1}{2}\frac{1}{2}3$ intensity remains close to zero in the whole temperature range. The scattering amplitude in this reflection due to the induced moment on the Gd sublattices must therefore be of opposite sign and almost equal in magnitude to that of the Cu sublattice. This implies that the susceptibility of the Gd sublattices is almost independent of temperature and that $\mu_{\mathrm{Gd}} = \chi\mu_{\mathrm{Cu}}$, with $\chi = 0.9 \pm 0.3$. At the temperature (7 K) at which the $\frac{1}{2}\frac{1}{2}1$ reflection disappeared, a search was made for magnetic scattering at other positions in the Brillouin zone. The directions scanned were $(\frac{1}{4}\frac{1}{4}0)$ to $(\frac{3}{4}\frac{3}{4}0)$, $(\frac{1}{4}\frac{1}{4}1)$ to $(\frac{3}{4}\frac{3}{4}1)$, and $(\frac{1}{2}\frac{1}{2}0)$ to $(\frac{1}{2}\frac{1}{2}1)$. No significant magnetic scattering was observed in any of these scans, and it was concluded that three-dimensional

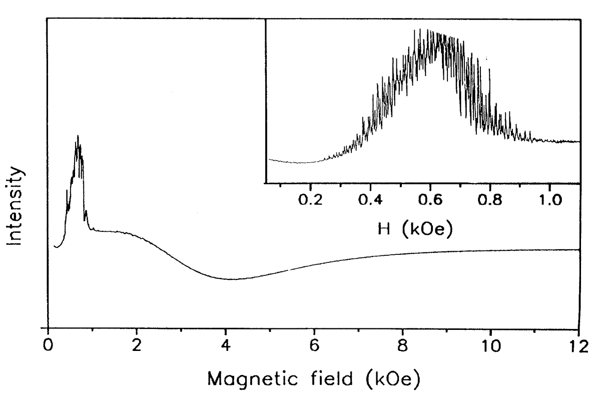

FIG. 4. EPR spectrum of Gd_2CuO_4 with the constant and radio frequency fields applied in the **a-b** plane $(h \perp H)$ at $v=9.39$ GHz and $T=12$ K. The inset shows the low-field part of the spectrum.

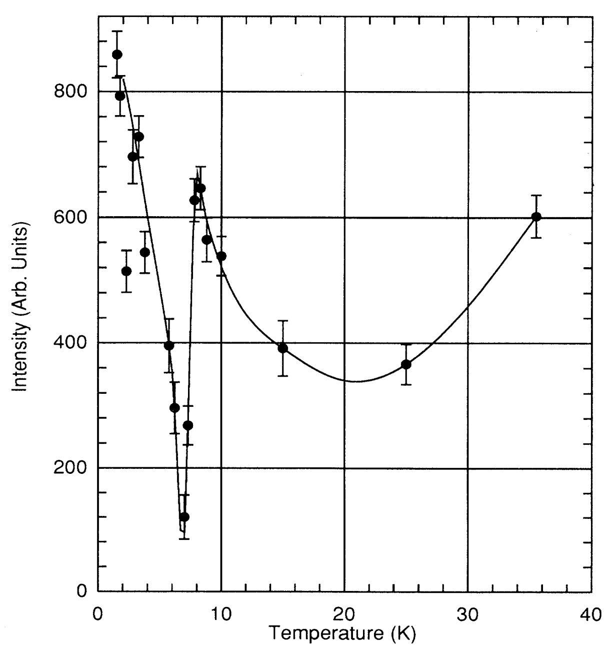

FIG. 5. Temperature dependence of the intensity of neutron scattering in the $\frac{1}{2}\frac{1}{2}1$ reflection of Gd_2CuO_4.

magnetic order is lost temporarily at a temperature just above T_N(Gd).

III. DISCUSSION

The experimental results reported above and the earlier studies[1–4] lead to the following conclusions.

(1) In the temperature region $T_c < T < T_N$(Cu), the copper spins have long-range antiferromagnetic order with a significant weak ferromagnetic component parallel to the basal plane. The bulk of the measured weak ferromagnetic moment arises from polarization of the paramagnetic Gd sublattice by exchange interaction with the ordered Cu subsystem.

(2) At $T = T_c$ a phase transition to a purely antiferromagnetic (AFM1) state with "hidden" weak ferromagnetism takes place. The weak ferromagnetic (WF) phase can easily be reinduced by relatively weak magnetic fields applied perpendicular to the c axis in the temperature region $T_N(\mathrm{Gd}) < T < T_c$.

(3) Such behavior suggests that a WF moment exists independently in each CuO_2 plane and that the phase transition at T_c is associated with the appearance of substantial antiferromagnetic correlation between the WF moments of adjacent CuO_2 planes. The weak ferromagnetism results from a strong intraplanar spin-spin interaction. The role of the relatively weak interplanar interaction is to produce some correlation between the orientation of the weak ferromagnetic moments in neighboring CuO_2 planes.

Since the crystal structure proposed for Gd_2CuO_4 (Ref. 1) is incompatible with existence of weak ferromagnetism, it is necessary to postulate the existence of some weak spontaneous distortion of the ideal crystal structure which will allow it. [The distortions indispensable for weak ferromagnetism cannot result from lattice "adjustment" under magnetic order (as in the case of magnetostriction) and must exist even at $T > T_N$(Cu).] On the basis of symmetry arguments alone, there are many ways in which the crystal lattice might be distorted in order to allow weak ferromagnetism. The number of such ways can be sharply reduced if proposition (3) above is valid. Symmetry analysis carried out for an isolated CuO_2 plane leads to only four irreducible distortions of the two-dimensional CuO_2 layer that allow weak ferromagnetism; these are shown in Fig. 6. The distortions arise from displacements of the oxygen atoms, perpendicular to [cases (1) and (2)] or along [cases (3) and (4)] the Cu-O chains, without any change in the copper positions. All the distorted two-dimensional structures retain the planar point symmetry $4mm$, but the axial directions are rotated by $\pi/4$ and the area of the unit cell is doubled as shown in Fig. 6. The symmetry of the resulting three-dimensional distorted lattice may belong to either tetragonal or orthorhombic classes depending on the correlation between the signs of the oxygen displacements in neighboring CuO_2 layers.

The character of the weak ferromagnetism within each CuO_2 layer depends strongly on the type of in-plane distortion. The symmetry analysis gives the following forms for the additional terms in the intraplanar exchange energy due to the four different types of oxygen displacement illustrated in Fig. 6:

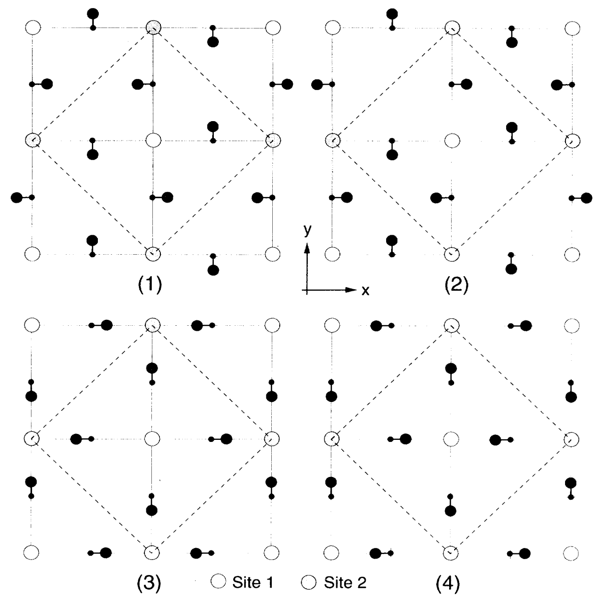

FIG. 6. Possible displacements of the oxygen atoms in the CuO_2 planes of Gd_2CuO_4 that could lead to weak ferromagnetism. The dashed outline shows the unit cell of the modified planar lattice.

$$\text{case (1):}\quad D_1(L_xM_y - L_yM_x) = 2D_1(S_{1x}S_{2y} - S_{1y}S_{2x}) \; ; \tag{1}$$

$$\text{case (2):}\quad D_2(L_xM_y + L_yM_x) = 2D_2(S_{1x}S_{1y} - S_{2y}S_{2x}) \; ; \tag{2}$$

$$\text{case (3):}\quad D_3(L_xM_x + L_yM_y) = D_3(S_{1x}^2 + S_{1y}^2 - S_{2x}^2 - S_{2y}^2) \; ; \tag{3}$$

$$\text{case (4):}\quad D_4(L_xM_x - L_yM_y) = D_4(S_{1x}^2 - S_{1y}^2 - S_{2x}^2 + S_{2y}^2) \; . \tag{4}$$

Here $\mathbf{S}_1$ and $\mathbf{S}_2$ denote the sublattice magnetizations of Cu; $\mathbf{L} = \mathbf{S}_1 - \mathbf{S}_2$ and $\mathbf{M} = \mathbf{S}_1 + \mathbf{S}_2$ are the antiferromagnetic and ferromagnetic vectors, respectively. Each of the parameters D_1, D_2, D_3, and D_4 is linear in the relevant oxygen displacement, and each of them is zero in the case of an undistorted lattice.

The weak ferromagnetic moment for the anisotropic Dzyaloshinski-Moriya exchange interaction has the form

$$\mathbf{M} \propto \frac{[\mathbf{D} \times \mathbf{L}]}{J} \, ,$$

where J is the isotropic exchange interaction between nearest neighbors in the CuO_2 plane and the vector $\mathbf{D}$ is parallel to c. $\mathbf{M}$ is therefore always perpendicular to $\mathbf{L}$. X-ray studies[9,10] show that the displacement of oxygen atoms must be perpendicular to the Cu-O chains, i.e., of type (1) or (2). In case (1) the magnitude of the anisotropic exchange D is proportional to $\cos^2\phi+\sin^2\phi$, where ϕ is the angle that **L** makes with the x axis in the **a**-**b** plane. For case (2) it depends on $\cos^2\phi-\sin^2\phi$. Thus, for (1), the modulus of the weak ferromagnetic moment in each CuO_2 plane is independent of ϕ, whereas in case (2) it would have a very strong ϕ dependence. The observation that the magnitude of the weak ferromagnetic moment is virtually independent of the direction of the applied field in the **a**-**b** plane implies a type (1) distortion. This conclusion is consistent with the observation in Mössbauer experiments, of an orthorhombic electric field at the Gd sites, which also implies a type (1) distortion.[11] It is noteworthy that among the four structures which allow weak ferromagnetism only for (1) is there a real antisymmetric exchange interaction of the Dzyaloshinski-Moriya type between nearest neighbors in the CuO_2 plane.

It should be stressed that a necessary condition for the existence of weak ferromagnetism in the CuO_2 layers is that the oxygen displacements shown in Fig. 6 [case (1)] are coherent over relatively long distances. This is because the sign of **M** is determined by the sign of the Dzyaloshinski parameter $\mathbf{D}_1$, which, in turn, is determined by the direction of the oxygen displacements. If the oxygen displacements were not strongly correlated within a CuO_2 plane, it would not be possible to magnetize the copper sublattice, even using a relatively strong external magnetic field, because of the strong intraplanar antiferromagnetic exchange interaction. In fact, a rather weak magnetic field of a few hundred Oe is able to induce almost complete alignment of all the weak ferromagnetic fragments of the magnetic structure.

Since no evidence for coherent displacement of the oxygen atoms in the long-range structure of Gd_2CuO_4 was obtained from x-ray measurements, it must be assumed that there is no appreciable correlation between the signs of the displacements in neighboring CuO_2 planes along the **c** direction. Long-range correlation between oxygen displacements within the CuO_2 planes will give rise to rods parallel to **c** in reciprocal space passing through the points $(h/2k/2l)$ with $h+k$ even. Corresponding diffuse intensity should be found in x-ray- and neutron-scattering patterns. It may be significant that a small anomalously broad temperature-independent peak was observed at the $(\frac{1}{2}\frac{1}{2}0)$ position in neutron-scattering experiments[8] which could have had such an origin.

Such *two-dimensional weak ferromagnetism,* if it exists, must affect all the magnetic properties of Gd_2CuO_4, and the consequences will now be elaborated. It should be recalled that the net magnetization **m** is the sum of contributions $\mathbf{m}_{Cu}$ and $\mathbf{m}_{Gd}$ from the Cu and Gd sublattices, respectively. Since $\mathbf{m}_{Gd} \gg \mathbf{m}_{Cu}$, the Cu contribution to the total magnetization is negligible. Nevertheless, it is the exchange interaction within the Cu sublattice that gives rise to long-range magnetic order of Cu and this in turn magnetizes the Gd sublattices. The effective exchange field at each Gd ion has two contributions: One, due to the nearest CuO_2 plane, is proportional to **M**, and the other, due to the next-nearest CuO_2 plane, is proportional to **L**. It is this latter field which induces the antiferromagnetic magnetization of Gd which contributes scattering to the $\frac{1}{2}\frac{1}{2}1$ and $\frac{1}{2}\frac{1}{2}3$ magnetic reflections. As long as an applied magnetic field does not exceed a few hundred Oe, the former, the ferromagnetic exchange field of each CuO_2 plane, determines the magnetization of the Gd planes adjacent to it. This situation persists down to $T\sim 10$ K at which temperature the Gd-Gd exchange becomes comparable to kT. Further cooling then results in competition between the Cu-Gd and Gd-Gd exchange interactions until eventually spontaneous ordering of Gd the sublattices takes place at T_N(Gd).

In the temperature range T_N(Cu) to ~ 20 K, the overall magnetic structure of Gd_2CuO_4 is built up of weakly interacting *sandwich layers* stacked along **c**. Each such layer consists of a CuO_2 plane sandwiched between two Gd planes and possesses a spontaneous weak ferromagnetic moment. Because of the weakness of the interlayer coupling and the low anisotropy in the basal plane, a relatively weak magnetic field can easily change the orientation of the magnetic moments in the individual layers. As a result, the bulk magnetic properties of Gd_2CuO_4 under an external magnetic field are very similar to those of a classical weak ferromagnet. Nevertheless, if the in-plane magnetic field tends to zero, the correlation between the signs of the weak ferromagnetic moments in neighboring layers will vanish. Three-dimensional macroscopic weak ferromagnetic domains of opposite magnetization will not exist even in zero field: Their counterparts are two-dimensional weak ferromagnetic domains in the sandwich layers. The above reasoning shows why the magnetic properties of Gd_2CuO_4 at $T>20$ K resemble those of a weak ferromagnet even though there is no long-range correlation between the signs of the oxygen displacements in adjacent CuO_2 planes.

Using the model outlined above, a possible explanation of the nature of the further transformations of the magnetic structure which occur when the temperature falls below about 50 K can be given. It seems probable that the driving mechanism for these structural changes is the antiferromagnetic interaction between neighboring Gd layers. Because of the large magnitude of the Gd moment, this interaction becomes the dominant one at low temperature. At temperatures between T_N(Cu) and about 50 K, the exchange between neighboring CuO_2 planes leads to three-dimensional antiferromagnetic ordering of the La_2NiO_4 type and a structure in which the relative orientations of the vectors **L** in neighboring CuO_2 planes are strongly correlated. If, as has been postulated, the signs of the Dzyaloshinski parameter $\mathbf{D}_1$ in different CuO_2 planes are randomly distributed, the two exchange interactions mentioned above are mutually frustrating. In this temperature range, the arrangement of the antiferromagnetic vectors **L** in different CuO_2 planes is ordered and the random nature of the structural distortion in these planes imposes a frustrated random arrangement on the WF vectors **M**. There are two distinct antiferromagnetic Gd-Gd interactions which are important: that between the Gd planes in adjacent sandwich layers and that between the two Gd planes in the same sandwich layer. Satisfying the former forces the **M** vectors in adjacent layers to be antiparallel and thus transfers the effects of randomness in the structural distortion to the antiferromagnetic vectors **L**. Satisfying the latter, on the other hand, destroys the WF moment **M** of the layers themselves. The behavior of the magnetization, and the results of the neutron-diffraction experiments shown in Fig. 5, can be explained if the effects of interlayer Gd-Gd exchange start to be manifest at a higher temperature than those of the intralayer exchange. Below 50 K the appearance of some correlation between the **M** vectors in adjacent sandwich layers leads to partial disorder of the **L** vectors and a consequent reduction in the intensity of the $\frac{1}{2}\frac{1}{2}1$ magnetic reflection. However, when the temperature falls to around T_c, intralayer Gd-Gd antiferromagnetic correlation starts to be important and to reduce the magnitude of the **M** vectors of the layers themselves. This effect not only lowers and finally eliminates the WF moment, but also reduces the exchange field, leading to disorder of the **L** vectors, which explains the recovery of intensity in $\frac{1}{2}\frac{1}{2}1$. The disappearance of the $\frac{1}{2}\frac{1}{2}1$ reflection just above T_N(Gd) indicates a temporary breakdown of three-dimensional order of the copper sublattice during the total reorganization of the magnetic structure required to satisfy the strong antiferromagnetic correlations in both the Cu and Gd sublattices. The critical behavior associated with this transition should be rather unusual and needs to be investigated.

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