Noncollinear magnetic structures in antiferromagnetic La_2CuO_4

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A symmetry analysis has yield the slightly noncollinear antiferromagnetic structure of $La_2CuO_4(D_{2h}^{18})$. A first-order transition can occur to a slightly ferromagnetic phase in a magnetic field. This transition is accompanied by a change in the initial antiferromagnetic structure. The results are compared with experimental data (R. J. Birgeneau *et al.*, Preprint, 1988; T. Thio *et al.*, Preprint, 1988).

The compound La_2CuO_4 is the parent of a series of metal-oxide compounds with high superconducting transition temperatures. Several neutron-diffraction studies[1–4] have revealed that at low temperatures (below 250 K) La_2CuO_4 goes into a collinear antiferromagnetic state with the structure shown in Fig. 1. It was recently suggested by Birgeneau *et al.*[4] and Thio *et al.*[5] that the antiferromagnetic structure is not collinear. Those investigators reported the experimental observation of a jump in the magne-

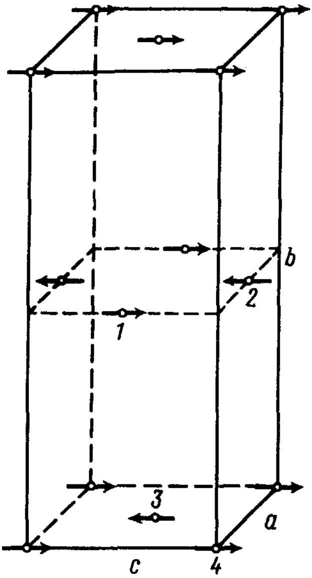

FIG. 1. Magnetic structure of La_2CuO_4 $(H=0)$ according to neutron-diffraction experiments.[1-3]

tization which they attributed to a transition to a state with a weak ferromagnetism. In the present letter we report the use of Ozyaloshinskii's thermodynamic theory[6] to determine noncollinear antiferromagnetic structures which La_2CuO_4 may acquire through a second-order phase transition out of its paramagnetic state. We also discuss the possible transition to a slightly ferromagnetic state in a magnetic field.

It can be seen from Fig. 1 that the unit cell contains four magnetic copper ions. The possible-collinear magnetic structures are conveniently represented by the following three antiferromagnetism vectors $\mathbf{L}_i$ and the ferromagnetism vector $\mathbf{M}$:

$$\begin{aligned} &\mathbf{L}_1=\mathbf{S}_1-\mathbf{S}_2-\mathbf{S}_3+\mathbf{S}_4 \qquad &&\mathbf{L}_3=\mathbf{S}_1+\mathbf{S}_2-\mathbf{S}_3-\mathbf{S}_4\\ &\mathbf{L}_2=\mathbf{S}_1-\mathbf{S}_2+\mathbf{S}_3-\mathbf{S}_4 &&\mathbf{M}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4\,. \end{aligned} \tag{1}$$

The crystallographic symmetry of La_2CuO_4 is described by space group D_{2h}^{18} (C_{mca}) Since the magnetic ordering involves a change in the type of unit cell (from base-centered to primitive), an expanded symmetry group (which contains a centered translation in addition to "point" transformations) must be considered in the derivation of the irreducible representations which are responsible for a magnetic phase transition. In this manner we found 16 different one-dimensional irreducible representations, but only the following pairs of components of the vectors $\mathbf{L}_i$ and $\mathbf{M}$ transform under identical representations:

$$\mathbf{L}_{1Y} \text{ and } \mathbf{L}_{3Z}\,;\ \mathbf{L}_{1Z} \text{ and } \mathbf{L}_{3Y};\ \mathbf{L}_{2Z} \text{ and } M_Y;\ \mathbf{L}_{2Y} \text{ and } \mathbf{M}_Z. \tag{2}$$

Correspondingly, their products are invariant and appear in an expansion of the thermodynamic potential, which can be written as follows:

$$\Phi = \Phi_0 + \frac{A_1}{2}\mathbf{L}_1^2 + \frac{A_2}{2}\mathbf{L}_2^2$$
$$+ \frac{A_3}{2}\mathbf{L}_3^2 + \frac{C_1}{4}\mathbf{L}_1^4 + \frac{C_2}{4}\mathbf{L}_2^4 + \frac{C_3}{4}\mathbf{L}_3^4 - \frac{a_1}{2}\mathbf{L}_{1Z}^2 - \frac{\partial_2}{2}\mathbf{L}_{2Z}^2$$
$$+ \beta_1 L_{1Z} L_{3Y} + \beta_2 L_{1Y} L_{3Z} + \frac{B}{2}\mathbf{M}^2 + d_1 L_{2Z} M_Y + d_2 L_{2Y} M_Z - \mathbf{MH}\,. \quad (3)$$

As usual, $A_i = \lambda_i (T - T_{Ni})$ and B determine the exchange interaction. A phase transition occurs to that antiferromagnetic state for which T_{Ni} has the maximum value. The state L_{1Z} is realized according to the neutron-diffraction data; we should correspondingly assume that T_{N1} is maximal. The terms which describe the anisotropy have also been chosen in light of the experimental data (the spins are mostly directed along the Z axis[3]) Working from the specific quasi-two-dimensional structure of La_2CuO_4, for which the exchange interaction between $(\mathbf{S}_1, \mathbf{S}_2)$ and $(\mathbf{S}_3, \mathbf{S}_4)$layers is very weak, the temperature T_{N1} should differ only slightly from T_{N2}, i.e., we should have $T_{N1} - T_{N2} \ll T_{N1}, T_{N2}$. We can accordingly assume $\lambda_1 = \lambda_2 = \lambda_3$ and $C_1 = C_2 = C_3$. Under these assumptions, a minimization of potential (3) with $\mathbf{H} = 0$ leads to the solution

$$L_{1Z}^2 = \left(\frac{\lambda}{C}\right)(T_{N1} - T) \text{ and } L_{3Y} = \frac{\beta_1}{A_3} L_{1Z}\,, \quad (4)$$

Accordingly, if the basic antiferromagnetic structure is determined by the component L_{1Z} in accordance with the experimental data, then we will see a "weak antiferromag-

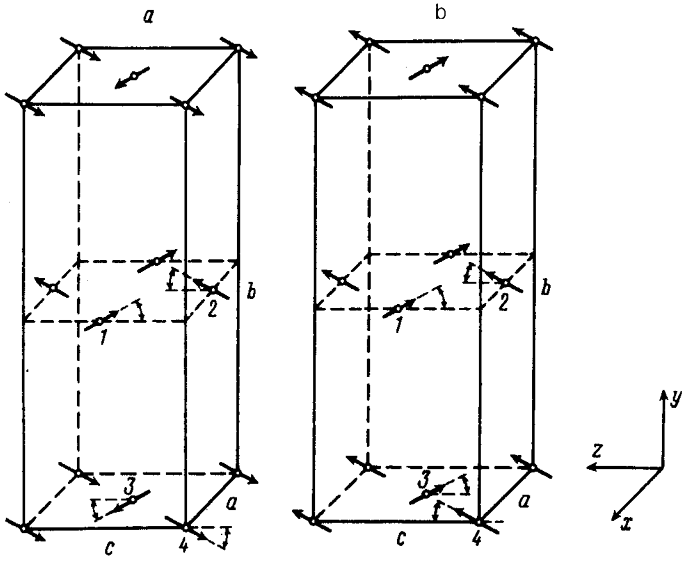

FIG. 2. Magnetic structure of La_2CuO_4 according to a symmetry analysis. a—$H = 0$; b—$H > H_c$.

netism" of the L_{3Y} type. This type corresponds to an excursion of the spins from the (XY) planes along the Y axis, in such a way that if the spins deviate upward in one plane they will deviate in the opposite direction in the nearest-neighbor planes (Fig. 2a) According to (4) the deviation angle is β_1/A_3 The presence of a noncolinear antiferromagnetism is confirmed by the observation of a gap in the spin-wave spectrum. From the experimental data on the IR spectra, inelastic neutron scattering, and the two-magnon optical scattering,[5] we find the deviation angle to be 0.17°.

If we apply a magnetic field along the Y axis, a magnetization

$$M_Y = H_Y/B \tag{5}$$

arises. As the magnetic field is increased, there exists a certain critical field at which the degradation in terms of exchange energy associated with the transition from state $\mathbf{L}_1$ to state $\mathbf{L}_2$ see (2)], of magnitude $(L_0^2/2)\lambda(T_{N1} - T_{N2})$, is compensated for by the improvement in terms of magnetic energy, given by $d_1 L_0 H/B$. In our approximation we have $L_1(T) \approx L_2(T)$. We will denote this quantity by $L_0(T)$. Comparing the values of the thermodynamic potentials for the two antiferromagnetic structures, we find the following expression for the critical field H_c of the (first-order) transition from antiferromagnetic structure L_{1Z} (with an admixture of L_{3Y}; Fig. 2a) to a state with a slight ferromagnetism (Fig. 2b):

$$H_c = L_0(T)(T_{N1} - T_{N2})\lambda B/2d_1\ . \tag{6}$$

A linear relationship between H_c and $L_0(T)$ agrees with the experimental result.[5] At $H > H_c$ the magnetization is given by the following expression, instead of (5):

$$M_Y = \frac{1}{B}(d_1 L_0 + H_Y). \tag{7}$$

During a transition to a slightly ferromagnetic state in a field, there should accordingly be a jump in the magnetization, with a magnitude proportional to $L_0(T)$ according to (7) From the experimental data of Ref. 5 we find the value $H_D = d_1 L_0 = 80$ kOe at $T = 0$. According to (5) and (7) the slopes of the $M(H)$ dependence at $H < H_c$ and $H > H_c$ are the same, in agreement with the data of Refs. 4 and 5. It should be noted that in the case of an $\mathbf{L}_1$ ordering (without an $\mathbf{L}_2$ admixture) the magnetic structure is an "antiferromagnetic" alternation of ferromagnetically ordered (YZ) planes. During the appearance of the $\mathbf{L}_2$ phase, we will have an alternation of ferromagnetically ordered (XY) planes.

Analysis of experimental data[7] on the nuclear quadrupole resonance at ^{139}La in the antiferromagnetic phase of La_2CuO_4 provides further evidence in favor of a magnetic structure which is more complex than that determined exclusively by the vector $\mathbf{L}_1$. According to Ref. 7, a local magnetic field with a nonvanishing component along the Y axis appears at the ^{139}La nuclei. The noncollinear antiferromagnetic structure proposed in the present letter leads specifically to the appearance of a field H_Y which alternates in direction at the La sites; the field H_Y has the same sign as the skew of the magnetic moments in the layer of Cu atoms closest to the given La atom.

The predictions of the thermodynamic theory thus agree qualitatively with the experimental data.[4,5] There are two important discrepancies between our results and the theoretical premises of Ref. 5: 1. The skew angles in the noncollinear antiferromagnetic phase ($L_{1Z}L_{3Y}$) and the slightly ferromagnetic phase ($L_{2Z}M_Y$) must by no means be the same. 2. A field-induced transition to a slightly ferromagnetic phase should be accompanied by a change in the exchange structure (Fig. 2b). The antiferromagnetic structure of each of the layers ($\mathbf{S}_1$, $\mathbf{S}_2$) and ($\mathbf{S}_3$, $\mathbf{S}_4$) will remain the same in the process. The relative arrangements of the spins in neighboring layers, however, will reverse. In principle, the change in the energy here could be on the order of the exchange energy. However, in view of the stratified nature of this structure, one might suggest that the exchange interaction between layers would be substantially weaker than the basic "in-layer" exchange interaction. Reconciliation with experimental data requires that the value of the quantity $(T_{N1} - T_{N2})/T_{N1}$ be much less than 1. A similar transition has been observed in $CoSO_4$ (D_{2h}^{16}) by N.H. Kreines.[4] We should stress that a change in the magnetic structure during this transition in La_2CuO_4 can be monitored easily by neutron diffraction in a field. Furthermore, above the Neel point T_{N1} the external magnetic field should induce an antiferromagnetic L_2 order in La_2CuO_4, and this event will give rise to an anisotropic susceptibility χ above T_{N1} and an anomalous growth of χ_Y (Refs. 8 and 9).

In the nonsuperconducting state of $YBa_2Cu_3O_6$, the neutron-scattering data[10] reveal an antiferromagnetic structure similar to that observed in La_2CuO_4. By virtue of the higher point symmetry of the compound[11] $YBa_2Cu_3O_6$ (D_{2h}^1), however, noncollinear structures like those discussed above should not arise in this case.

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