Noncollinear magnetic structure in the low-temperature tetragonal phase of La_2CoO_4

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A magnetic structure which is noncollinear in the *xy* plane should be observed in the low-temperature phase of the compound La_2CoO_4.

The magnetic properties of the La_2CuO_4 system and of related compounds have recently attracted much interest in connection with the problem of high-T_c superconductivity (see, for example, Ref. 1 and the bibliography there). In particular, attempts have been made to learn more about the magnetism of Cu ions with a spin $S = 1/2$ in a structure of the La_2CuO_4 type by studying magnetic transitions in the isomorphous compound[2] La_2CoO_4, in which the Co ions have a spin $S = 3/2$, and also in the compound[3] La_2NiO_4, in which the Ni ions have a spin $S = 1$.

In this letter we will show that the low-temperature magnetic phase of the compound La_2CoO_4 should be a fundamentally noncollinear antiferromagnet if the crystal structure is characterized by the space group $P4_2/ncm$ (according to the data of Ref. 2). The noncollinearity which arises is completely different from that in the compound[4,5] La_2CuO_4.

From the crystal-symmetry standpoint, this system undergoes the following changes.[2] First, the high-temperature tetragonal phase ($I4/mmm$) becomes an orthorhombic phase ($Cmca$) at $T_1 \cong 500$ K as a result of the softening of one of the doubly degenerate rotational TO modes at the boundary of the Brillouin zone. As in La_2CuO_4, oxygen octahedral surrounding the ion of the $3d$ transition metal undergo a rotation. Since the magnetic moments of the Co ions are directed along the rotation axis of the octahedral (the x axis) in this case, the magnetic structure which arises is a strictly collinear, four-sublattice antiferromagnet of precisely the same type as in the La_2NiO_4 system.[3]

The compound La_2CoO_4 is distinguished by a second structural phase transition at $T_2 \simeq 135$ K (a first-order transition according to Ref. 2) from the orthorhombic

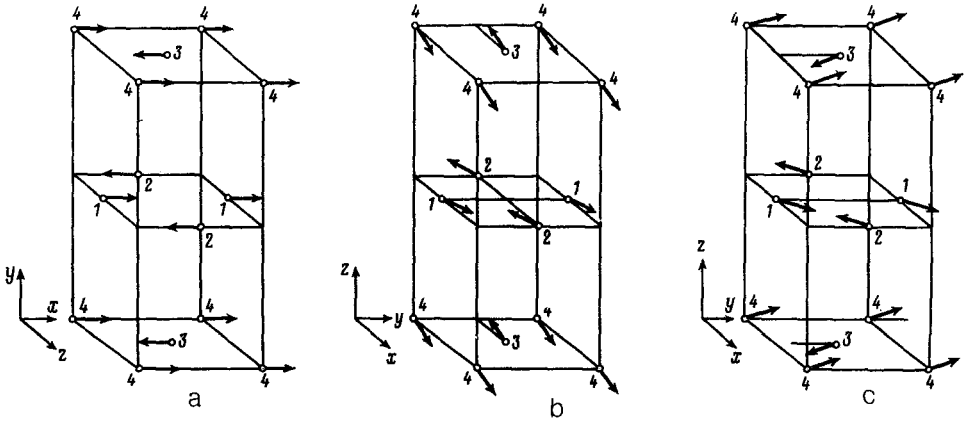

FIG. 1. a—Collinear antiferromagnetism (of the La_2NiO_4 type) above the temperature of the first-order structural phase transition (the establishment of *Cmca*); b—noncollinear ordering in the tetragonal phase with an L_{1x} fundamental mode (the establishment of $P4_2/ncm$); c—noncollinear ordering in a tetragonal phase with an L_{1y} fundamental mode (the establishment of $P4_2/ncm$).

phase to a tetragonal phase. The corresponding change in symmetry is linked with additional rotations of the oxygen octahedral around vertical fourfold axes (as a consequence of the softening of yet another rotational mode of an octahedron). The symmetry group *Cmca* changes to $P4_2/ncm$.

As we will see below, the first-order phase transition which we mentioned above necessarily leads to a special magnetic structure. We will take Dzyaloshinskiĭ's approach[6] to describe the magnetic properties of the new tetragonal phase. For this purpose we expand the magnetic part of the free-energy functional, making the assumption that the averaging over the elastic degrees of freedom accompanying the transition has already been carried out. This case corresponds to the situation which would prevail if a purely magnetic phase transition had occurred in our system, which has a symmetry group $P4_2/ncm$. We assign labels to the Co ions as explained in Fig. 1a. We introduce corresponding magnetic moments m_1, m_2, m_3, and m_4; and we determine the antiferromagnetism vectors L_1, L_2, and L_3 and also the ferromagnetism vector M from

$$L_1 = m_1 - m_2 - m_3 + m_4, \quad L_2 = m_1 - m_2 + m_3 - m_4,$$

$$L_3 = m_1 + m_2 - m_3 - m_4, \quad M = m_1 + m_2 + m_3 + m_4. \tag{1}$$

We single out the following linear combinations of the vectors $\vec{L}_i$ and $\vec{M}$ which we have introduced:

$$L_{1x} + L_{2y};\ L_{1x} - L_{2y};\ L_{1y} + L_{2x};\ L_{1y} - L_{2x};\ L_{3x};\ M_z\ .$$

These particular linear combinations form the bases of one-dimensional representations of the group D^*_{4h}. The pairs L_{1z}, L_{2z}; L_{3x}, L_{3y}; and M_x, M_y form the bases of the equivalent two-dimensional representations of the point group of the crystal. We

can then construct corresponding invariant combinations and derive the magnetic part of the functional, G_M:

$$G_M = \frac{A_1}{2}(L_{1x}^2 + L_{2y}^2) + \frac{A_2}{2}(L_{1y}^2 + L_{2x}^2) + \frac{A_3}{2}(L_{3x}^2 + L_{3y}^2)$$

$$+\frac{A_4}{2}(M_x^2 + M_y^2) + \frac{A_5}{2}(L_{1z}^2 + L_{2z}^2) + \frac{A_6}{2}L_{3z}^2 + \frac{A_7}{2}M_z^2$$

$$+\beta_1 L_{1x}L_{2y} + \beta_2 L_{1y}L_{2x} + d_1(L_{1x}L_{3x} - L_{2x}L_{3y}) + d_2(L_{1x}M_y - L_{2x}M_x)$$

$$+g_1(L_{1x} - L_{2y})L_{3x} + g_2(L_{1y} + L_{2x})M_x + d_3(L_{3x}M_y + L_{3y}M_x) - \vec{M}\cdot\vec{H}. \qquad (2)$$

In this case we have used the coordinate designations which are customary for systems of tetragonal symmetry (in contrast with the *Cmca* group, for which the long axis of the unit cell runs along the y direction, we have used z to represent this axis). According to the experimental data of Ref. 2, the magnetic state in the low-temperature phase is described by either the x or y projection of the vector $\vec{L}_1$.

A first consequence of expression (2) is that the magnetic order in a system described by the space group $P4_2/ncm$ must be noncollinear in principle. If the magnetic mode L_{1x} is the fundamental mode, an L_{2y} "admixture" is necessarily superimposed on it. In other words, the moments in one horizontal layer rotate clockwise, those in the neighboring layer rotate counterclockwise, etc. We recall that the noncollinearity of the magnetic structure in the compound La_2CuO_4 was caused by an excursion of the moments from the horizontal plane and by the appearance of a slight vertical antiferromagnetic component.

It is also obvious that the mixed terms in expression (2) indicate that specific effects could be observed. In particular, if a magnetic field is imposed along the z axis the system will or will not undergo a spin–flip transition, depending on the nature of the magnetic ordering. If the initial structure is described by a vector L_{1x}, a transition is possible; incidentally, this transition would confirm that it is the vector L_{1x}, rather than L_{1y}, which is responsible for the magnetic order in the system. The behavior of the system in a vertical magnetic field thus provides the information we need to decide what the nature of the structure is, and it erases a certain amount of ambiguity in the results of Ref. 2.

The behavior of the system in strong horizontal fields is no less interesting. In this case a spin–flip transition in a field parallel to the x axis would occur without a change in the nature of the basic ordering (the vector $\vec{L}_1$), while the transition to a state characterized by the vector $\vec{L}_{2x}$ would occur in a field of greater magnitude, directed along the y axis. In general, one would expect a characteristic change in the conductivity upon the spin–flip transition, as in the La_2CuO_4 system.[1] The behavior of the system in response to doping might turn out to be completely nontrivial. By altering the concentration of La ions, one might be able to vary the interval along the temperature scale in which the $P4_2/ncm$ phase exists and to observe the effects noted above.

In summary, the actual magnetic structure should be more complex (Fig. 1, b

and c) than would follow from an interpretation of the neutron diffraction data of Ref. 2.

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[4]T. Thio *et al.*, Phys. Rev. B **38**, 905 (1988).
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[6]A. S. Borovik-Romanov, *Lectures on Low-Temperature Magnetism*, Novosibirsk, 1976, p. 49.

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