# Two-dimensional spin correlations and successive magnetic phase transitions in $Nd_2CuO_4$

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$Nd_2CuO_4$ is found to be a quasi-two-dimensional antiferromagnet with $T_N = 255$ K. Successive phase transitions occur due to the $Cu^{2+}$ spin reorientation as well as, at low temperatures, the participation of the $Nd^{3+}$ spins in the three-dimensional long-range order. A sharp peak corresponding to the two-dimensional spin correlations is observed in energy-integrated scans. The magnetic properties at high temperatures are closely similar to those in $La_2CuO_4$.

A new class of high-$T_c$ oxide superconductors typified by $Nd_{2-x}Ce_xCuO_4$ (Refs. 1 and 2) has recently been discovered. These materials are especially interesting because the Hall coefficient appears to be negative in the normal state, suggesting electron rather than hole conduction as in the well-studied oxide superconductors exemplified by $La_{2-x}Sr_xCuO_4$.[3] A second important difference between these two classes is evident in the crystal structures shown in Fig. 1. In $Nd_2CuO_4$ each Cu ion is surrounded by four oxygen atoms located in the $CuO_2$ plane; this contrasts with the $CuO_6$ octahedron structure in $La_{2-x}Sr_xCuO_4$. Further, unlike $La_2CuO_4$, this system contains $Nd^{3+}$ ions which may couple magnetically to the $Cu^{2+}$. Therefore it is essential to elucidate the role of the Nd moments in the overall magnetic properties, particularly their effect on the strongly correlated $CuO_2$ layers.[4] These materials thus provide a test ground for a number of the existing models for the lamellar $CuO_2$ superconductors. Specifically, the underlying mechanism for the superconductivity is almost certainly common to the $Nd_2CuO_4$ and $La_2CuO_4$ materials; thus one may exclude any model which relies on aspects of the material properties which differ in these two systems.

For the past two years we have been studying in detail the static and dynamic spin fluctuations in $La_{2-x}Sr_xCuO_4$.[5] In $La_2CuO_4$ a two-dimensional (2D) quantum spin-fluid (QSF) state exists at high temperatures with spin-fluctuation energies which are enormous.[5,6] The 2D spin correlations persist in the superconducting state,[7] although the characters of both the magnetic structure factor $S(\mathbf{q})$ and the dynamical response function $S(\mathbf{q},\omega)$ are modified drastically by the doped holes. Thus, it is our view that the magnetism and superconductivity are intimately related in the $La_{2-x}Sr_xCuO_4$ superconductors and also that the QSF state generated by the $Cu^{2+}$ spins provides an essential ingredient for the appearance of the novel superconductivity. Based on the experimental information obtained so far[1,2,4] we anticipate the existence of the same QSF state in $Nd_2CuO_4$ as in $La_2CuO_4$. The superconductivity in this new class of materials thus must involve the 2D magnetism in a fundamental way.[8]

We prepared large single crystals of $Nd_2CuO_4$ grown from a nonstoichiometric CuO-rich solution. The

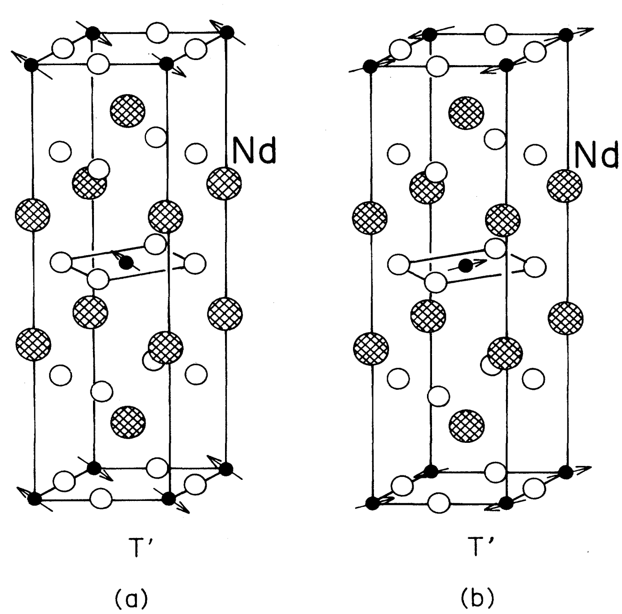


FIG. 1. Crystal structure of $Nd_2CuO_4$ and magnetic structures of the $Cu^{2+}$ spins: (a) $La_2NiO_4$ type, (b) $La_2CuO_4$ type.

 

present flux method is essentially the same as that developed in the work to grow large $La_2CuO_4$ single crystals.[9] The neutron scattering experiments have been carried out utilizing an ingot crystal which includes some flux material due to the difficulty in removing the latter. The size of the crystal is $40\times40\times1.5$ mm$^3$ with the $c$ axis (in a $I/mmm$ representation) (Fig. 1) along the thin direction.

The experiments were carried out on the Tohoku University Neutron Spectrometer Reactor (TUNS) spectrometer at the Japan Research Reactor (JRR2) at the Tokai Establishment of the Japan Atomic Energy Research Institute (JAERI). We employed graphite monochromator, analyzer, and filters. The quasielastic scans were performed with neutrons of energy 30.5 meV ($k=3.83$ Å$^{-1}$). In the triple axis method for either elastic or inelastic scans the neutron energies were chosen to be primarily 13.7 meV ($k=2.57$ Å$^{-1}$). The as-grown crystal was oriented with a $[1\bar{1}0]$ axis vertical so that in the scattering plane peaks with Miller indices ($hhl$) could be accessed. The lattice parameters at 300 K were $a=3.941$ Å and $c=12.16$ Å; these agree with the existing data.[1,2]

We first studied the 3D antiferromagnetic ordering. The 3D Bragg reflections appear at the $(\frac{1}{2}\frac{1}{2}1)$ point but not at the $(\frac{1}{2}\frac{1}{2}0)$ point just below a $T_N$ of about 255 K. This indicates an $La_2NiO_4$-type magnetic structure[10] where the spin direction **S** is parallel to the propagation vector $\tau$ of the [110] axis in the $CuO_2$ plane. The ordered moment could be estimated as $\sim 0.5\mu_B$ per atom, which indicates that only the $Cu^{2+}$ spins participate in the 3D long-range order (LRO) at high temperatures. This moment is essentially identical to that found in the LRO state in $La_2CuO_4$.[11] We find with decreasing temperature two additional phase transitions as shown in Fig. 2. At 80 K a spin reorientation transition occurs from the $La_2NiO_4$-type structure $(\tau \| [\frac{1}{2}\frac{1}{2}0], \mathbf{S} \| [\frac{1}{2}\frac{1}{2}0])$ to the $La_2CuO_4$ structure[11] $(\tau \| [\frac{1}{2}\frac{1}{2}0], \mathbf{S} \| [\frac{1}{2}-\frac{1}{2}0])$ with $Cu^{2+}$ moments oriented perpendicular to the propagation vector as is illustrated in Fig. 1. As discussed in Ref. 12, in tetragonal symmetry for both of these magnetic structures the interplanar ordering may be noncollinear. At 30 K a second transition occurs in which the $Cu^{2+}$ spins again return to the orientation along $[\frac{1}{2}\frac{1}{2}0]$ and at the same time the $Nd^{3+}$ moments begin to participate in the 3D LRO. The upper (80 K) spin reorientation phase transition is difficult to understand in a pure tetragonal crystal structure[12] and specifically a subtle distortion from tetragonality seems to be required. Therefore a further refinement for the determination of the crystal structure for $T<80$ K is needed; a neutron-diffraction study with medium resolution led to inconclusive results. As shown in Fig. 2, upon further cooling below 30 K we find that the peak intensity of the $(\frac{1}{2}\frac{1}{2}1)$ reflection saturates and then decreases; eventually it disappears below 8 K. Concomitantly, the peak intensity of the $(\frac{1}{2}\frac{1}{2}3)$ reflection grows continuously below 30 K on cooling. Since there is no appreciable break in intensity of this reflection at around 8 K where the $(\frac{1}{2}\frac{1}{2}1)$ reflection disappears we conclude that there is no true phase transition at 8 K.

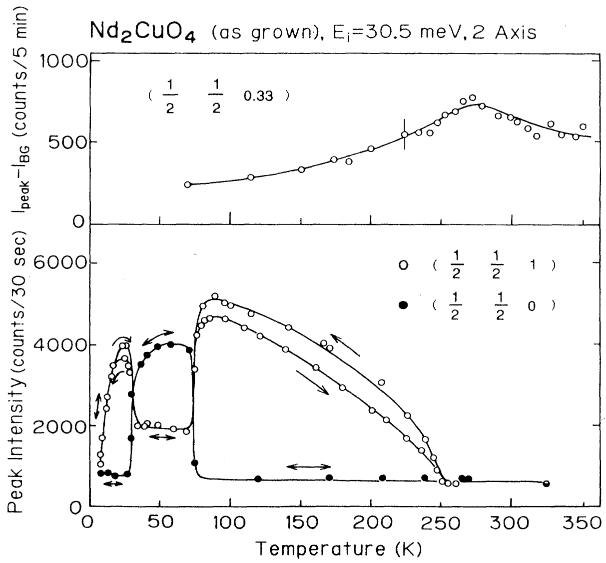


FIG. 2. Temperature evolution of the peak intensities of the 3D antiferromagnetic Bragg reflections and the 2D rod.

We are now in the process of refining the antiferromagnetic structure below 8 K;[13] we speculate that the Nd moments in each $c$ plane couple antiferromagnetically. Specifically, since the magnetic susceptibility at low temperatures does not show any spontaneous magnetization at all, each sublattice consisting of $Nd^{3+}$ or $Cu^{2+}$ moments must satisfy the condition of no net moment. Thus the disappearance of the $(\frac{1}{2}\frac{1}{2}1)$ reflection can be interpreted as reflecting an increase of the staggered moment of the Nd site. There are two singularities in the inverse susceptibility curve corresponding to two phase transitions at around 80 and 30 K, in addition to the Néel temperature of about 255 K. In contrast to $La_2CuO_4$, $Nd_2CuO_4$ exhibits Curie-Weiss behavior in its susceptibility down to at least 30 K; this presumably originates from the paramagnetism of the Nd moments which may couple weakly to the strongly correlated Cu moments.

On structural grounds alone, we anticipated observation of the QSF state at high temperatures in $Nd_2CuO_4$. Indeed, we observe many features similar to those observed previously in the experiments in $La_2CuO_4$.[6] The quasielastic scattering intensity scanned along $(\frac{1}{2}\frac{1}{2}\zeta)$ shows a prominent peak at $\zeta=0.33$, the point at which the outgoing neutron wave vector $\mathbf{k}_f$ is exactly along $\mathbf{c}^*$; that is, $\mathbf{k}_f \| -\mathbf{c}^*$ when the spectrometer is set for elastic scattering at the $(\frac{1}{2}\frac{1}{2}0.33)$ rod position [see Fig. 3(a)]. As described in detail in Ref. 6, this phenomenon provides direct evidence for rapidly fluctuating 2D spin correlations. Specifically, for 2D magnets, when $\mathbf{k}_f$ is parallel to the 2D magnetic rod, an approximate energy integration from $-k_BT$ to the incident energy, $E_i$, is performed with the momentum transfer in the $CuO_2$ plane, $\mathbf{Q}_{2D}$, held constant. Therefore, the instantaneous spin-correlation function

$$\langle S^{\alpha}(-\mathbf{Q}_{2D},0)S^{\alpha}(\mathbf{Q}_{2D},0)\rangle$$

is measured directly by this special two-axis scan. The

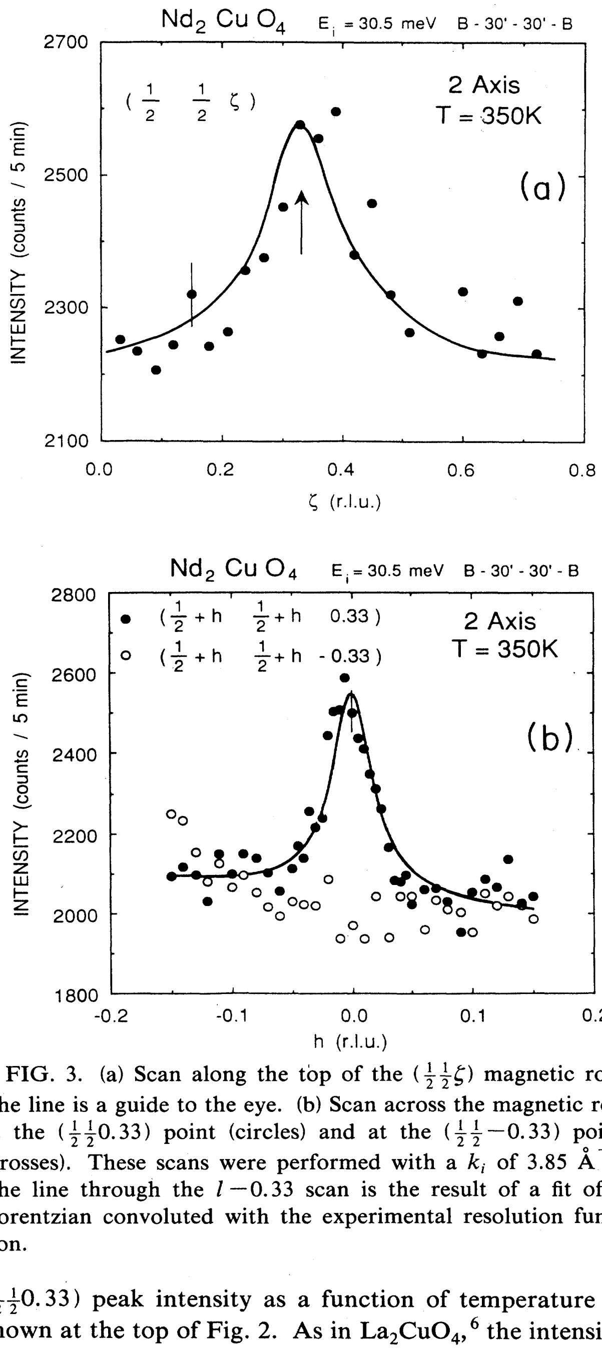


FIG. 3. (a) Scan along the top of the $(\frac{1}{2}\frac{1}{2}\zeta)$ magnetic rod. The line is a guide to the eye. (b) Scan across the magnetic rod at the $(\frac{1}{2}\frac{1}{2}0.33)$ point (circles) and at the $(\frac{1}{2}\frac{1}{2}-0.33)$ point (crosses). These scans were performed with a $k_i$ of 3.85 Å$^{-1}$. The line through the $l-0.33$ scan is the result of a fit of a Lorentzian convoluted with the experimental resolution function.

$(\frac{1}{2}\frac{1}{2}0.33)$ peak intensity as a function of temperature is shown at the top of Fig. 2. As in $La_2CuO_4$,[6] the intensity rises slowly as $T_N$ is approached and then drops gradually with the onset of 3D LRO. This fact together with data to be discussed suggests that the transition to 3D LRO is driven by the interplanar interaction.

As shown in Fig. 3, a rather sharp peak is observed in the focusing scan across the 2D rod at $(\frac{1}{2}\frac{1}{2}0.33)$; in contrast, no magnetic signal is observed in the scan across the rod at $(\frac{1}{2}\frac{1}{2}-0.33)$. This difference demonstrates that the scattering function is governed by fast 2D spin fluctuations just as in the QSF state of $La_2CuO_4$. In order to confirm the inelasticity, we have measured directly the elastic component using three-axis scans; we find that the elastic component is barely visible as in the original $La_2CuO_4$ results.[6] In addition, a single peak centered around the 2D rod position is observed in constant energy scans with energies up to 6 meV suggesting a large energy scale for the spin fluctuations. The result is consistent with the two-magnon Raman experiment[14] that shows behavior similar to that in $La_2CuO_4$.

Finally we investigated the effect of heat treatment on the antiferromagnetism, since the conductivity was found to depend on the heat treatment as in the $La_2CuO_4$ case. We prepared two other single crystals which were cut from the same ingot. One was annealed in flowing Ar gas at 950 °C for 15 h and the other was in an oxygen gas flow at 600 °C for 200 h. We have obtained almost identical results for each crystal with no significant effect of the heat treatment on the antiferromagnetic transition. This result is very different from the $La_2CuO_4$ case where the 3D transition temperature drops by about 100 degrees in oxygenated crystals.[15] This is consistent with the $\mu$SR experiments[4] which show that the magnetism in $Nd_{2-x}Ce_xCuO_4$ is much less sensitive to the doping than that in $La_{2-x}Sr_xCuO_4$. Further research is required to determine if this reflects a fundamental difference in the way electrons and holes disturb the local magnetic structure.

In summary, we find that the magnetism in $Nd_2CuO_4$ is quite similar to that in $La_2CuO_4$. Therefore the present measurements suggest a common mechanism for the appearance of the superconductivity in $Nd_{2-x}Ce_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ with the magnetism playing an essential role. Clearly, it is now important to document the effect of Ce doping on the QSF state in $Nd_{2-x}Ce_xCuO_4$. Although it is not a central focus of the research on the relation between the magnetism and the superconductivity, the magnetic phase transitions observed here also include very interesting concepts frequently discussed in modern magnetism such as frustration, competing anisotropies, and exchange interactions.

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