Magnetic behavior of Nd in Nd_2CuO_4 above 1.5 K

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A neutron-scattering investigation of the static and low-energy ($\hbar\omega \leqslant 2$ meV) magnetic signals in undoped single-crystalline Nd_2CuO_4 is presented from 1.5 K to room temperature, with supporting measurements on Pr_2CuO_4 and La_2CuO_4 single crystals. The experiment reveals the existence of two distinct contributions associated with the Nd magnetic moments. The first is two-dimensionally correlated in the a-b plane, appears around the Cu three-dimensional (3D) Néel ordering temperature T_N, and vanishes between 20 and 70 K. The second, present already above T_N, is quasielastic and characteristic of a paramagnetic state. We interpret the coexistence of these two Nd contributions within the framework of a paramagnetic sublattice experiencing a magnetic field due to the 3D ordering of the Cu sublattice. This may explain why 3D long-range order associated with the Nd moments is only detected below 37 K by resonant x-ray scattering at the Nd absorption edge. Futhermore, critical scattering is observed at every Cu spin transition: the antiferromagnetic transition at T_N and the two Cu spin reorientation transitions observed around 72.5 and 30 K. [S0163-1829(98)03501-2]

I. INTRODUCTION

The family of $(RE_{2-x}Ce_x)CuO_4$ compounds (RE denotes rare earth) undergoes a superconducting phase transition with a $T_c^{\max} \sim 24$ K for $x \sim 0.15$. These materials were initially considered to be electron doped,[1] but recent measurements revealed a more subtle situation;[2,3] nevertheless the main character of the charge carriers is considered to be negative. The undoped parent RE_2CuO_4 compounds display complex magnetic properties due to the interplay between the ordered Cu moments and the RE. This is especially clear in the case of Nd_2CuO_4, where one of the consequences of this interplay between Cu and Nd moments is the sequence of Cu spin reorientation transitions observed[4–8] around 72.5 and 30 K. These two transitions correspond to an interchange between the typical La_2CuO_4 and La_2NiO_4 magnetic phases.[4–8] The influence of the Nd moments is also visible in the Cu spin dynamics.[9] Lately, the interest in $(Nd_{2-x}Ce_x)CuO_4$ has been renewed because of the coexistence of Nd magnetic ordering with superconductivity[10] and the possible heavy fermion character observed[11] for $x \geqslant 0.15$. Recently, several inelastic neutron-scattering investigations have been devoted to measuring the low-energy modes in Nd_2CuO_4 (below 1 meV) associated with Nd at low temperature ($T \leqslant 1.5$ K).[12–14]

We present an investigation of the static and dynamic low-energy magnetic contributions in Nd_2CuO_4 from 1.5 K to room temperature and a comparison with Pr_2CuO_4 and La_2CuO_4. This comparison allows one to distinguish between Cu and RE magnetic contributions since, firstly, in Nd_2CuO_4 the Nd sublattice orders,[15,16] while in Pr_2CuO_4 the Pr sublattice, although it carries a moment, does not order,[15–17] and secondly, in La_2CuO_4 the La ions carry no magnetic moment. In all three systems, the Cu moments order antiferromagnetically (AF) below T_N ($T_N = 243$ K for Nd_2CuO_4, $T_N = 247$ K for Pr_2CuO_4, and $T_N = 320$ K for La_2CuO_4) and give rise to magnetic Bragg peaks denoted, in the nuclear cell, by $Q = (q_h/2, q_k/2, q_l)$, q_h and q_k being odd integers and q_l being an integer.[18] Below T_N, the RE (=Nd, Pr) moments experience an effective magnetic field derived from the Cu sublattice, which should influence the RE magnetism. The work presented here reveals the existence of two distinct signals both associated with the Nd moments: one being static and corresponding to an induced two-dimensional (2D) ordering and the other one being quasielastic and paramagnetic (at least above 40 K). Our observation is consistent with a lack of order in the Nd sublattice above 40 K even while under the influence of the internal magnetic field associated with the 3D ordering of the Cu moments. Furthermore, it may explain why 3D long-range order (LRO) was observed only below 37 K in recent resonant x-ray scattering performed at the Nd absorption edge.[19] This is a new result since the Nd moments have previously been considered to exhibit 3D LRO on account of the Cu sublattice as soon as one passes below T_N.[7,20] It shows that the two sublattices (Cu and Nd) are only weakly interacting at high temperature, as already suggested in Ref. 4, and it sheds some light on the complex magnetic phase diagram observed for Nd_2CuO_4. Finally, we observed critical scattering associated with the Cu sublattice at each Cu spin reorientation, implying a significant second-order character of these transitions.

II. EXPERIMENT AND RESULTS

Nd_2CuO_4, Pr_2CuO_4, and La_2CuO_4 single crystals were grown in air by spontaneous crystallization from melts with

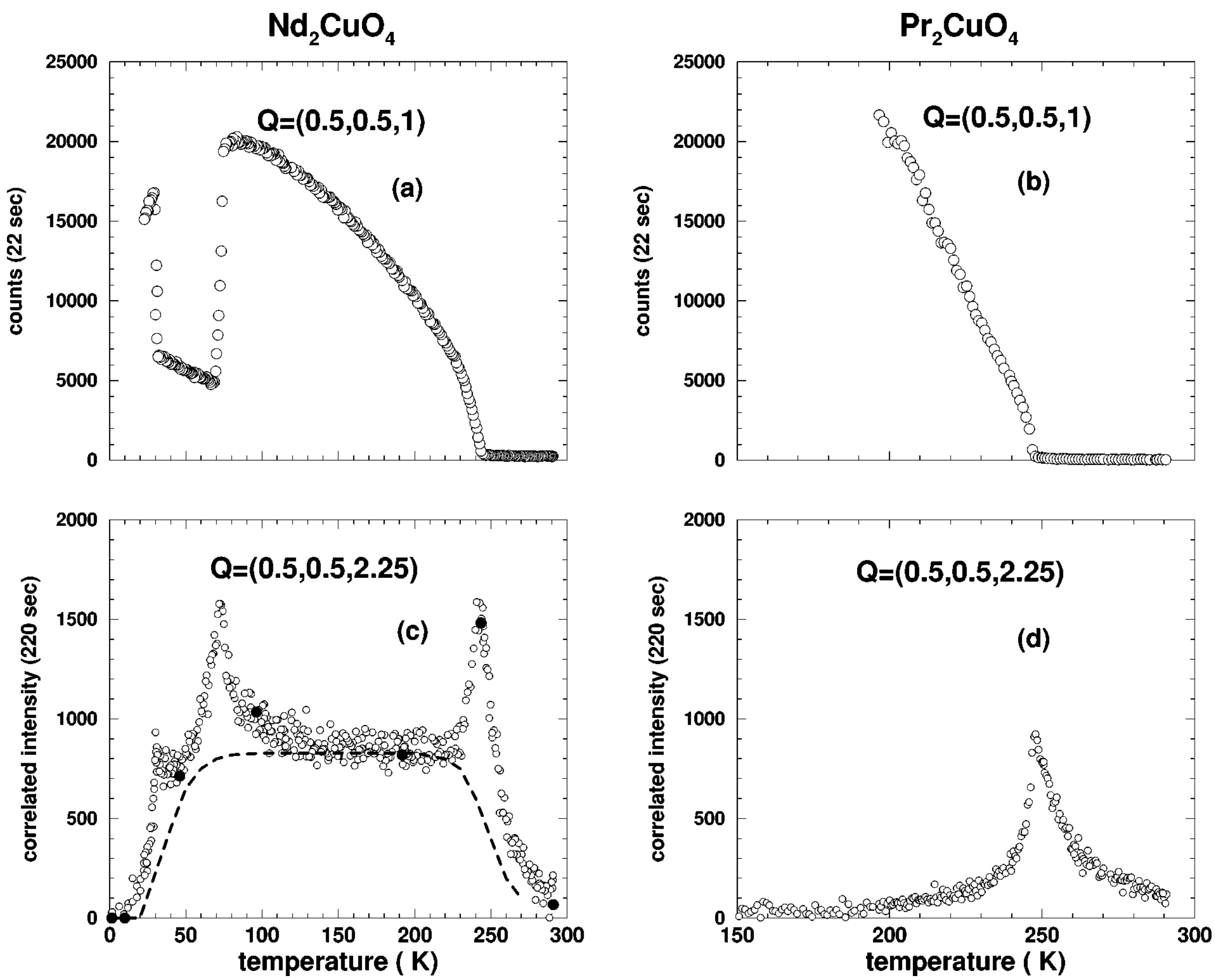

FIG. 1. The upper graphs [(a) and (b)] display the (0.5, 0.5, 1) magnetic Bragg intensity vs temperature for Nd_2CuO_4 (left) and Pr_2CuO_4 (right). The lower graphs [(c) and (d)] show the (0.5, 0.5, 2.25) magnetic intensity corrected for the ''background'' deduced as described in the text. Filled symbols correspond to the peak intensity of the scans along the $(q_h q_h 0)$ direction. The dotted line illustrates the approximate temperature dependence of the induced 2D Nd ordered signal.

excess CuO. The total volume of each sample is about $0.5\ \mathrm{cm}^3$. The RE_2CuO_4 (RE=Nd, Pr) single crystals are platelets with a small mosaic spread. No subsequent heat treatments were performed.

The neutron-scattering experiments were performed at the Orphée reactor (Saclay) on a cold source triple-axis spectrometer. We worked essentially at fixed initial neutron wave vector $k_i = 1.55\ \text{Å}^{-1}$ with an energy resolution of 0.18 meV [full width at half maximum (FWHM)] at zero energy transfer. Several scans were performed with enhanced resolution. A Be filter was placed in the incident beam to eliminate higher-order contamination. Nd_2CuO_4 and Pr_2CuO_4 samples were mounted in a ^{4}He cryostat. For La_2CuO_4, a small furnace was used. Both monochromator and analyzer were made of pyrolytic graphite (PG002). The analyzer was curved in the horizontal direction. The scattering plane was chosen to measure the (q_h, q_h, q_l) reflections.

The first goal of this experiment was to look for magnetic scattering away from the magnetic Bragg reflections. Because of the very strong in-plane Cu-O-Cu superexchange interaction, one could expect magnetic diffuse intensity concentrated along rods centered at the in-plane AF positions and oriented along the tetragonal axis (c^* direction). Thus we followed, from 1.5 K to room temperature, the intensity at $Q = (0.5,0.5,2.25)$ and $\hbar\omega = 0$ in Nd_2CuO_4 and Pr_2CuO_4 (see Fig. 1). The choice of $q_l = 2.25$ is a compromise between good resolution and minimal absorption, which is non-negligible in the case of Nd. At some temperatures, a constant energy scan was performed along the diagonal (110), revealing the existence of a well-defined peak in the a-b plane centered at $q_h = q_k = 1/2$ (see Fig. 2); from these scans we could deduce the background level (including the incoherent scattering) and the correlated intensity. In parallel, the magnetic Bragg intensity at $Q = (0.5,0.5,1)$ was measured to determine the Cu spin transition temperatures. These data are displayed in Fig. 1.

We repeated the measurement on a La_2CuO_4 crystal around $T_N = 320$ K. As for the two RE_2CuO_4 compounds, we performed Q scans across the magnetic rod at various temperatures. The corrected data are displayed in Fig. 3 and compared with Pr_2CuO_4. The correlated intensity at $Q = (0.5,0.5,2.25)$ displays the same temperature dependence with a comparable amplitude in Pr_2CuO_4 and La_2CuO_4.

At $Q = (0.5,0.5,2.25)$, a signal is observed above 20 K for Nd_2CuO_4, which peaks at each Cu spin reorientation (around 30 and 72.5 K) and around T_N. This signal is Q resolution limited in the a-b plane (see Fig. 2). Above T_N, this contri-

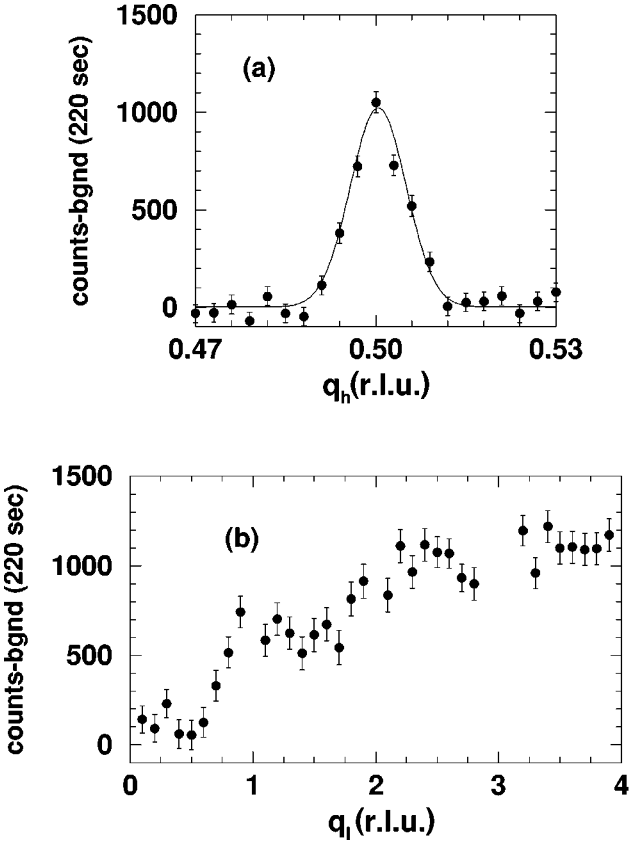

FIG. 2. Q scans along (a) the $(q_h q_h 0)$ and (b) the $(00q_l)$ directions across $Q=(0.5,0.5,2.25)$ for Nd_2CuO_4 at $T=99$ K. Both scans are corrected for a ''background'' (bgnd) deduced from the ''off-rod'' signal $Q=(0.475,0.475,q_l)$. These two scans show that the intensity observed at $Q=(0.5,0.5,2.25)$ (see Fig. 1) is Q resolution limited in the a-b plane [graph (a)] and essentially uncorrelated along the c axis [graph (b)].

bution is strongly reduced for all systems. For Nd_2CuO_4, scans performed along the c^* axis reveal the existence of an essentially uncorrelated intensity along the $(0.5,0.5,q_l)$ rod. This intensity strongly decreases at $q_l \sim 0$ (see Fig. 2), and

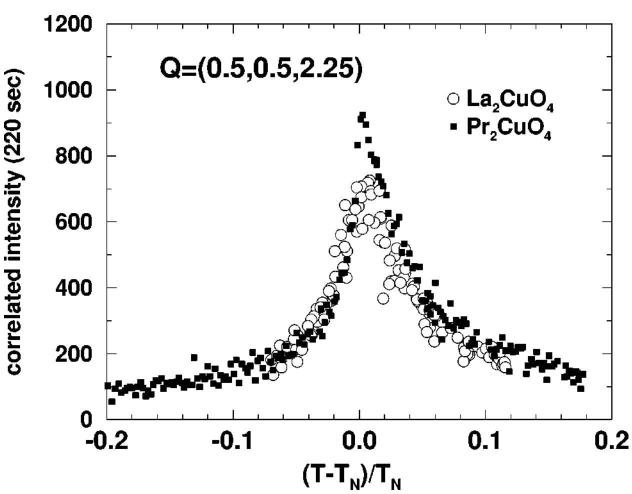

FIG. 3. $Q=(0.5,0.5,2.25)$ contribution vs temperature for both La_2CuO_4 ($T_N=320$ K) and Pr_2CuO_4 ($T_N=247$ K). The background has been deduced from scans along $(q_h q_h 0)$ performed across $Q=(0.5,0.5,2.25)$ at different temperatures.

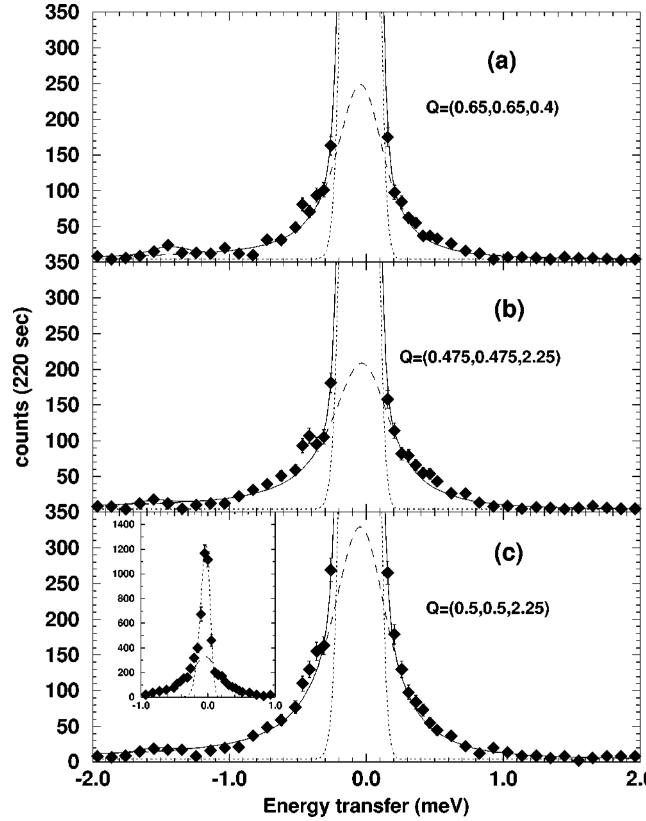

FIG. 4. Energy scans at $T=59$ K for different Q values: top: $Q=(0.65,0.65,0.4)$, middle: $Q=(0.475,0.475,2.25)$, and bottom: $Q=(0.5,0.5,2.25)$. The lines correspond to the different contributions fitted to the scan. The dotted line is the resolution-limited component due to incoherent scattering for plots (a) and (b), whereas for plot (c) it also contains the Nd two-dimensionally correlated signal (see the inset where the incoherent contribution has been subtracted). The dashed line is a Lorentzian fit of the quasielastic signal (present at any wave vector). A spurious peak is present around -1.53 meV in all scans (most likely due to $2k_f$ second-order contamination via the 21 meV crystal field level).

shows the same trend at any temperature where the signal exists independently of the Cu spin orientation (La_2NiO_4 or La_2CuO_4 phases). The decrease of intensity at $q_l \sim 0$ resembles the typical effect of the geometrical factor in magnetic neutron scattering, but we do not know enough about the 2D arrangement of the Nd moments to confirm this.

To probe the nature of the $Q=(0.5,0.5,q_l)$ rod contribution in Nd_2CuO_4, we performed at several temperatures energy scans from -2 meV to 2 meV ''on-rod'' at $Q=(0.5,0.5,2.25)$, ''off-rod'' at $Q=(0.475,0.475,2.25)$, and finally at a general point $Q=(0.65,0.65,0.4)$ (see Fig. 4). These scans reveal that, in addition to the energy-resolution-limited signal peaked along $Q=(0.5,0.5,q_l)$, there exists a quasielastic signal present at any wave vector. Since this quasielastic signal is not peaked along $Q=(0.5,0.5,q_l)$, it was actually part of the ''background'' measured previously ''off-rod'' to deduce the correlated intensity, and consequently does not appear in Fig. 1. Finally, scans along the c^* direction $Q=(0.1,0.1,q_l)$ done at an energy transfer $\hbar\omega=0.25$ meV reveal a sizable modulation below 10 K with a period of about 3.4 r.l.u. (reciprocal lattice units) (see Fig. 5) corresponding to the spacing z between the two Nd layers separated by the CuO_2 layer ($z \sim 0.296$, in relative lattice units). At an energy transfer of 0.25 meV, the measured intensity is only coming from the quasielastic component since one is far enough away from the elastic incoherent peak. Also, this energy transfer corresponds roughly to the position of the lowest Nd excitation seen below 2 K.[14] The period of this modulation (3.4 r.l.) shows that the quasielastic contribution present in all of Q space is directly related to the Nd moments. Furthermore, the modulated intensity can be described by a simple $\sin^2(\pi z q_l)$ law compatible with antiferromagnetic dynamic correlation along the c^* direction between Nd moments inside the bilayer at 0.25 meV, although the static correlation between these moments appears to be ferromagnetic from elastic diffraction.[7,20]

With increasing temperature, the amplitude of the quasielastic component decreases while its width increases linearly in temperature and their product is essentially constant. Using a Lorentzian line shape, one finds a half width at half maximum (HWHM) of ~ 0.5 meV at 200 K and a HWHM of ~ 0.2 meV at 60 K. Below 40 K, the energy line shape changes and seems better described by an overdamped inelastic line. To be complete, one has to say that the fitted intensity is always significantly higher on the $Q = (0.5,0.5,q_l)$ rod (Fig. 4), implying that there might exist weak correlations in the paramagnetic subsystem. Note also that the Cu spin fluctuations[9] enter in the energy window of our measurement *only* on-rod and above 100 K, and therefore do not interfere with the present experiment.

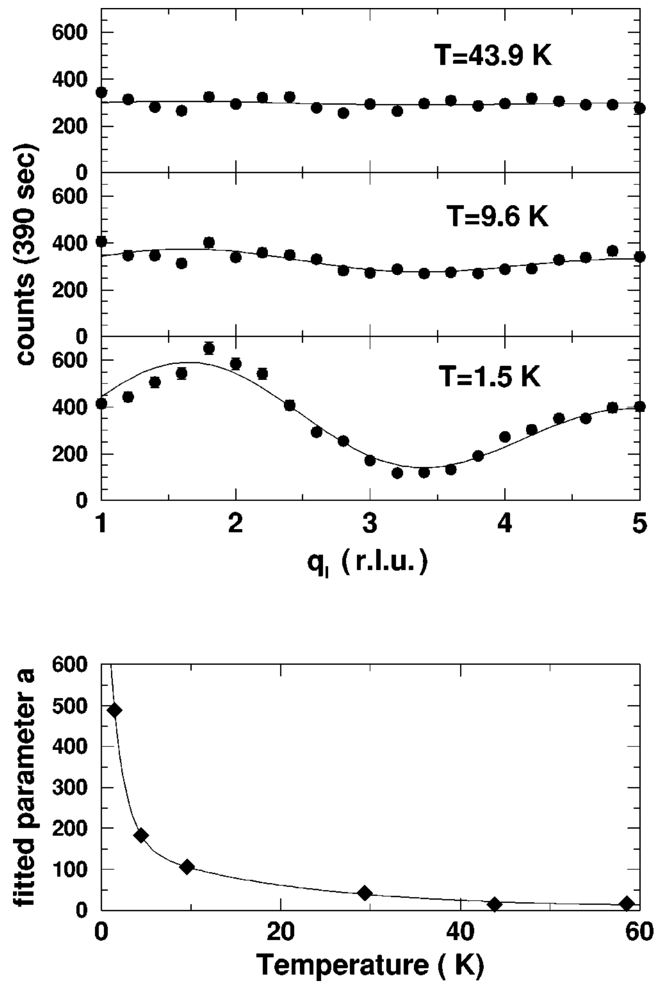

FIG. 5. Top: $Q = (0.1,0.1,q_l)$ scans vs q_l performed at various temperatures for Nd_2CuO_4 at a fixed energy transfer of $\hbar\omega = 0.25$ meV. A modulation appears clearly below 10 K corresponding to the distance between the two Nd layers separated by the CuO_2 along the c axis. The lines correspond to a fit $a f_{Nd}^2(Q)\sin^2(\pi z q_l) + b$ where $f_{Nd}(Q)$ is the Nd^{3+} spherical form factor. Bottom: temperature dependence of the fitted parameter a (modulation amplitude), which increases strongly below 10 K.

III. DISCUSSION

By comparing the three systems, we see that for Pr_2CuO_4 and La_2CuO_4, the $(0.5,0.5,q_l)$ contribution is the same (Fig. 3) and corresponds to critical scattering near the AF transition. This is entirely attributed to the Cu sublattice. Critical scattering is also observed for Nd_2CuO_4 peaked at the three Cu spin transitions, but in contrast to Pr_2CuO_4 and La_2CuO_4, there evidently exists an additional signal. This contribution (shown as dotted line in Fig. 1) builds up below T_N, remains largely temperature independent down to 70 K, and vanishes at a temperature above 20 K. The precise determination where this component vanishes in temperature is difficult because it is masked by the critical scattering around the two Cu spin reorientation transitions. This extra contribution is two-dimensionally correlated, energy-resolution limited (see inset in Fig. 4), and Q resolution limited in the a-b plane (Fig. 2). The fact that this signal is maximum at $q_h = q_k = 1/2$ confirms its magnetic origin and the influence of the Cu sublattice on this two-dimensional ordering. The comparison with Pr_2CuO_4 and La_2CuO_4 leads to the conclusion that this extra contribution is directly linked to the presence of Nd moments. This conclusion is strengthened by the fact that it decreases around 40 K where the Nd absorption edge x-ray scattering becomes measurable.[19] From our experiment and the x-ray data, it is probable that the intensity correlated in the a-b plane and associated with Nd moments collapses into Bragg reflections below 40 K.

In the inelastic scattering investigation performed on Nd_2CuO_4 at low energy transfers ($\hbar\omega \leqslant 2$ meV) we found, in addition to the quasistatic signal described in the previous paragraph, a quasielastic signal present at any wave vector that corresponds to paramagnetic fluctuations. This Lorentzian-like quasielastic component (see Fig. 4), which exists already above T_N, has an energy width proportional to the temperature above 40 K. This dependence of the energy width can be seen as the slowing down of the paramagnetic fluctuations with decreasing temperature. The modulation along the c^* direction clearly observed below 10 K (Fig. 5) shows that the quasielastic signal is associated with the Nd moments and rules out a possible origin from paramagnetic impurities.

Nd_2CuO_4 is a complex system where the strength or even the symmetry of the magnetic interactions taking place inside and in between the two Nd and Cu sublattices are not completely known. However, now there is enough experimental information to allow a tentative interpretation of the Nd magnetic behavior with temperature: Above T_N, the Nd subsystem is paramagnetic, i.e., there exists a decorrelated local moment on the Nd site that gives rise to the observed quasielastic signal. When one passes T_N, the 3D Cu long range ordering creates a magnetic field at the Nd site, and part of the Nd moment becomes polarized into the *a*-*b* plane, as revealed by the coexistence of the two Nd signals (two-dimensionally correlated static and quasielastic) we measured. Around 70 K, the in-plane macroscopic magnetic susceptibility ($\chi_\parallel$) departs from a $1/T$ dependence;[15] note that the macroscopic magnetic susceptibility is mainly attributed to the Nd sublattice (see Ref. 16). This coincides with the first Cu spin reorientation transition. At this temperature we still observe two components. Around 40 K, the Nd system undergoes a 2D to 3D transition but the ordered Nd moment is very small, explaining the weak intensity detected at this temperature by resonant x-ray scattering.[19] Around this temperature the signal correlated two dimensionally in the *a*-*b* plane disappears and the line shape of the quasielastic signal is modified. The ''small'' ordered Nd moment (roughly $0.2\mu_B$ around 10 K measured by neutron diffraction[7,20]) can be understood[21] by considering the Nd crystal field levels.[22,23] A splitting of the Kramers doublet of the Nd crystal field levels was inferred by neutron scattering experiments[24] and is consistent with the low-temperature behavior of the specific heat:[11,21] The simple two-level Schottky specific heat anomaly with a maximum around 2 K corresponds to a splitting of about 0.4 meV≡4.6 K. The ordered Nd moment becomes significant only at temperatures comparable to the splitting value ($0.44\mu_B$ at 4 K and $1.3\mu_B$ at 0.4 K). It is worthwhile mentioning that the comparison between Nd_2CuO_4 and $Nd_{1.85}Ce_{0.15}CuO_4$ shows that this splitting seems to exist independently of the 3D Cu ordering[11,21] since there is no long-range AF Cu order in $Nd_{1.85}Ce_{0.15}CuO_4$. This is possibly due to the fact that in $Nd_{1.85}Ce_{0.15}CuO_4$, the Ce doping does not fully destroy the Cu spin correlations because of the strong superexchange Cu-O-Cu coupling in the *a*-*b* plane. At low temperature, direct Nd-Nd interactions are promoted by the development of the Nd moment due to an increasing occupation of the Kramers ground state. The overdamped contribution (paramagnetic at higher temperature) is replaced by low-energy spin waves, which have been extensively measured recently below 2 K.[12–14]

IV. CONCLUSION

This work has provided information about the behavior of the Nd moments in Nd_2CuO_4. We deduced from our neutron-scattering data the existence of two components, both related to the Nd sublattice. The coexistence of these two components is expected in the case of a paramagnetic system under the influence of a magnetic field. This is a new result since it was previously considered that a very small induced moment on the Nd site was three dimensionally ordered on account of the Cu spin sublattice below T_N. What characterizes the ordering of Nd in Nd_2CuO_4 is the fact that it occurs under the influence of the Cu sublattice, and the Nd subsystem goes from an ''induced'' ordering to a ''spontaneous'' one. This observation might help in identifying the relevant magnetic interactions present in Nd_2CuO_4, which is important for the microscopic description of the Cu spin transitions and the spin wave spectrum observed in Nd_2CuO_4.

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