High-resolution study of the supposed fourfold Nd spin-wave degeneracy of Nd_2CuO_4

N. M. Pyka*
Institut Laue Langevin, BP 156, F-38042 Grenoble Cedex 9, France

M. d'Astuto
Laboratoire Léon Brillouin, CE Saclay, F-91191 Gif-sur-Yvette Cedex, France

A. Metz†
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

A. S. Ivanov‡
Institut Laue Langevin, BP 156, F-38042 Grenoble Cedex 9, France

M. Loewenhaupt
Insitut für Angewandte Physik, Technische Universität Dresden, D-01062 Dresden, Germany

H. Casalta
Institut Laue Langevin, BP 156, F-38042 Grenoble Cedex 9, France

D. Petitgrand and P. Bourges
Laboratoire Léon Brillouin, CE Saclay, F-91191 Gif-sur-Yvette Cedex, France
(Received 2 November 1999)

Model predictions for the Nd spin-wave dispersion in Nd_2CuO_4 have been tested with high-resolution inelastic neutron scattering on a single crystal at $T=0.5$ K. A Heisenberg model in the random phase approximation has been previously proposed which predicts two dispersionless fourfold degenerate modes along the crystallographic *AM* direction. This particular feature is a consequence of the symmetry and of the type of interactions considered in the Hamiltonian. Our data unambiguously reveal additional peaks along *AM* which were previously unresolved. Possible origins for the lifting of the fourfold degeneracy of the modes along the *AM* direction are discussed.

In the last few years a large amount of experimental information was collected on the spin dynamics of R_2CuO_4 compounds which crystallize into a tetragonal T' structure. Such a structure is characteristic for the light rare-earth-based compounds ($R=$Nd, Pr, Sm, Eu) which exhibit superconductivity upon doping with more positively charged ions (Ce^{4+} instead of R^{3+} or F^- instead of O^{2-}) and corresponding injection of electrons into conducting CuO_2 planes. The relatively simple and highly symmetrical crystal structure of the T' phase leads to a situation where the Cu-Cu spin interactions of Heisenberg type between adjacent CuO_2 planes are frustrated and the other magnetic interactions and anisotropies, *a priori* considered to be weaker than the Heisenberg exchange, come into play to determine the ground state and lowest excitation spectrum as well as the low-temperature thermodynamics. An additional complication arises from the presence of magnetically active R ions whose role in the stabilization of the existing long-range magnetic ordering and excitation spectra is not yet fully understood.

The Cu spin structure of Nd_2CuO_4 (NCO) is antiferromagnetic and noncollinear below $T_N\sim 280$ K.[1] The ordered moment of Nd becomes sizable only at low temperatures ($T<5$ K).[2–5] It is believed that the Cu-Nd interaction causes a Zeeman splitting of the Nd crystal field ground state doublet and permits transitions within this ground state. The first detailed study of such low-energy (<1 meV) Nd spin-wave excitations were time-of-flight neutron-scattering measurements on polycrystalline samples.[6] It was found that the Nd excitations are split into two bands of magnon branches[7] at energies of about 0.2 to 0.5 meV and 0.5 to 0.7 meV, respectively. Inelastic-neutron-scattering measurements on single crystals by different groups have shown that both bands are split into several modes.[8–11] A mean field random phase approximation (RPA) Heisenberg model[12] predicts that the modes in the upper band have the same dispersion as the lower band modes. The only difference being that the upper modes are shifted upwards in energy and have a slightly reduced energy range due to the crystal field anisotropy. This means in particular that at any Q vector the number of modes in the lower band is identical to the number of modes in the upper band, see Figs. 5 and 6 of Ref. 12. From this model all eight expected modes should be observable only along ΓX while two fourfold degenerated modes should show up along *AM*, see dotted lines in Fig. 3 of the present paper. This highly degenerate regime is appropriate to test the theory because the particular choice of the model parameters induces only shifts in energy but does not remove the degeneracy itself. We will also refer to a different model, which calculates the spin waves in R_2CuO_4 and predicts a highly degenerate state at the M point as well.[13] Preliminary inelastic-neutron-scattering experiments on NCO, however, indicate that the supposed fourfold degeneracy of the spin-wave modes at the M and A points is partly lifted.[14,15]

The present inelastic-neutron-scattering experiment was carried out at the IN14 spectrometer of the high flux reactor of the Institut Laue-Langevin at Grenoble. A vertically curved PG002 monochromator and a horizontally curved PG002 analyzer were used with a 40′ collimator between monochromator and sample and no collimators between the sample-analyzer-detector. Appropriate diaphragms were installed instead. A Beryllium filter was used in front of the sample to suppress higher-order contaminations. The spectrometer was operated in the fixed final energy mode with $k_f = 1.10$ Å^{-1}, giving an elastic energy resolution of 49 μeV. Some scans were made with $k_f = 1.30$ Å^{-1} to compare with previous measurements. The sample (the same as in Ref. 15) was a 1-mm-thick platelike single crystal with almost perfect crystal structure, a volume of 0.15 cm^3, and a mosaicity smaller than 1 arc min. No misaligned crystals nor twinning were observed. The crystal was mounted in a ^{3}He-^{4}He-dilution cryostat and cooled down to 0.5 K to obtain saturated magnetic moments of Nd. All scans were performed in the {010} scattering plane to observe reflections of type $(h,0,1)$. We use the reciprocal lattice notation of the chemical cell. The notation used by the authors of Refs. 8 and 12 refers to the rotated magnetic cell. The A and M point read (0.5, 0, 0.5) and (0.5, 0, 0) in our notation and (0.5, 0.5, 0.5) and (0.5, 0.5, 0) in the latter notation. The magnon peaks are fitted with a Gaussian function.

In most Brillouin zones contributions from both magnon bands can be observed but with different structure factors. The dynamic structure factor is modulated as a function of Q_z (z component of momentum transfer in reciprocal lattice units), in such a way that at $Q_z = 0$ only the upper band is observed, while near $Q_z = 1.9$ the intensity of the lower band has its maximum. This is a direct consequence of the fact that there are two different Nd sites in the chemical unit cell. Figure 1(a) shows a scan at the M point at (0.5, 0, 2). Two distinct peaks are observed that are well resolved. The upper one at 0.38 meV has an energy width $\Delta E = 58$ μeV corresponding to the resolution of the focusing setup. The lower one at 0.25 meV is broadened to $\Delta E = 72$ μeV. This peak can as well be reproduced assuming a double peak with a resolution limited line width and about equal intensity for both individual peaks. No intensity is observed above 0.45 meV, i.e., the upper band modes do not contribute to this M point. Figure 1(b) shows a scan at the A point at (0.5, 0, 1.5) measured with $k_f = 1.3$ Å^{-1}. In this case the modes are not well resolved due to the worse resolution.

A scan at the M point measured at (0.5, 0, 3) is shown in Fig. 2(a). In this configuration the modes of the upper band can be observed. They yield a widely distributed signal between 0.4 and 0.8 meV with a structured plateau on top. Four peaks have been fitted to analyze the broad intensity distribution. In addition the two excitations at 0.25 and 0.38 meV of the lower band are observed at this M point. An independent test of the observed excitations would be the measurement of an equivalent M point in reciprocal space, e.g., at (0.5, 0, 1). This M point is expected to have a larger structure factor for the lower band than (0.5, 0, 3) as can be inferred from the relatively strong intensity of the two excitations of the lower band as shown in Fig. 2(b) for a scan measured at (0.5, 0, 0.75), halfway between M and A. In this scan the upper band still shows the four peak structure. At the A point at (0.5, 0, 0.5), Fig. 2(c), the structure factor of almost all modes has changed considerably: the two highest upper band magnons have decreased their intensity and the upper magnon of the lower band has vanished. The peak at 0.25 meV measured at (0.5, 0, 0.75) and at (0.5, 0, 0.5) has the same line width as measured at the (0.5, 0, 2) M point [see Fig. 1(a)] an indication that it possibly comprises two peaks. It should be noted that there is a weak additional intensity below 0.2 meV in some scans, see Fig. 2. Figure 3 shows all the observed dispersions along AM. The experimental observations are summarized in the following.

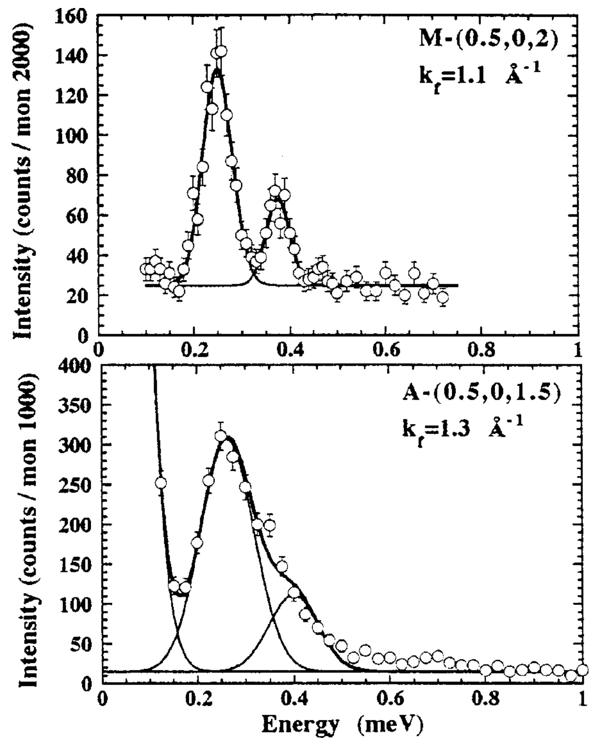

FIG. 1. Magnon groups in Nd_2CuO_4 at $T = 0.5$ K of the lower band at the M and A points at (0.5, 0, 2) and (0.5, 0, 1.5), respectively. The lower peak is broadened and probably comprises a double peak. The long tail above 0.45 meV stems from upper band modes which are weak in this configuration. The A point was measured with $k_f = 1.3$ Å^{-1} which leads to larger line widths than with $k_f = 1.1$ Å^{-1}.

For the frequency region of the lower band two excitations have been found, possibly three (in the latter case two of them must be very close to each other, $\Delta E = 35 \pm 7$ μeV). The total lower band splitting is 0.14 meV.

For the frequency region of the upper band the observed multiple peak structure is consistent with four excitations. They seem dispersionless between A and M. Obtained differences in the peak positions of 20 μeV or less are not significant because they could as well be due to changes in the structure factor. The total upper band splitting is 0.21 meV.

The lower and upper bands are not symmetric at and between A and M: the number of observed peaks is different and also their relative position in energy with respect to the position of the predicted two fourfold degenerate modes. The

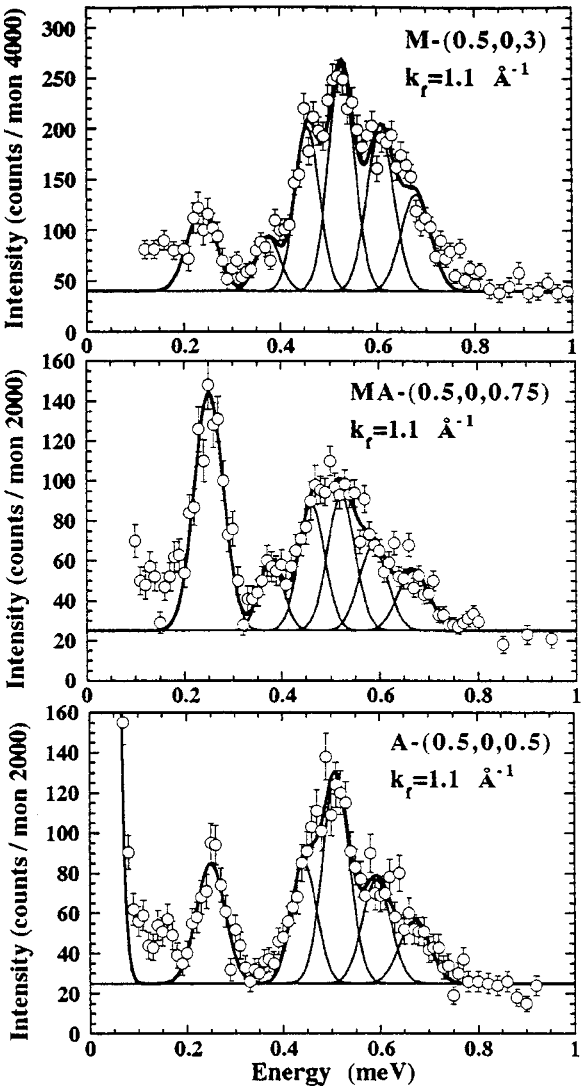

FIG. 2. Magnon groups in Nd_2CuO_4 at $T=0.5$ K of the upper band along *AM*. The upper band yields a broad intensity distribution above 0.4 meV and is fitted by four Gaussians. The lower band excitations at 0.25 and 0.38 meV are also clearly observed in the given configurations. Note also the extra intensity below 0.2 meV.

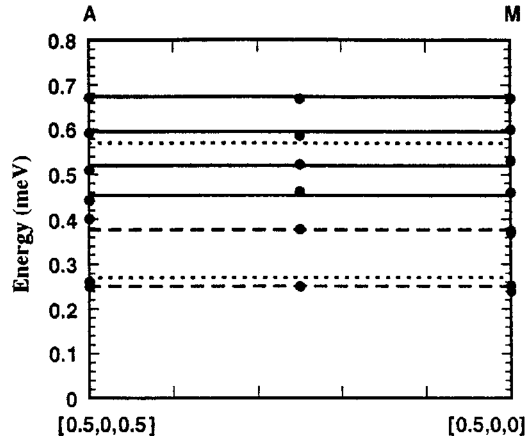

FIG. 3. Magnon dispersion in Nd_2CuO_4 at $T=0.5$ K along *AM*. Full lines correspond to the upper band excitations, dashed lines to the lower band excitations, full dots are data points. The dotted lines represent the model prediction[8] of the two, fourfold degenerate, dispersionless modes along *AM*.

structure factor of several modes has been found to change considerably between the *A* and *M* point. The mean separation between the lower and the upper band is 0.25 meV.

Preliminary experiments on NCO (Refs. 14, 15) already indicated that the fourfold degeneracy of the modes at the *A* and *M* point is partly lifted. This is in contradiction to the predictions of the Heisenberg model in the RPA treatment[12] that has been used to fit the experimental data of Ref. 8. The model[12] comprises an isotropic Nd-Nd exchange, while the Cu-Nd interaction is treated in the mean-field approximation as a staggered field on the Nd sites induced by Cu moments. The decoupling of Cu and Nd excitations is reasonable in view of the energy scales: below 5 K the energy gap of the Cu excitations determined by INS is larger than 10 meV (Ref. 16) while the energy of the Nd excitations is below 1 meV. An alternative approach to the Nd spin dynamics has been given in Ref. 13. Here the Cu spins are included explicitly. However, concerning the low-energy excitations due to the Nd spin dynamics the authors arrive at similar results as in Ref. 12.

Since both models[12,13] yield only two, fourfold degenerate, excitations along *AM* we will shortly discuss possible origins for the lifting of the degeneracy. One possible explanation lies in the nature of the spin interactions, which are involved within the Nd sublattices. Indeed, it has been shown that interactions of isotropic Heisenberg type cannot explain several magnetic properties of R_2CuO_4: the stability of the magnetic structure of the Cu spins in Nd_2CuO_4 and its development with field,[17] the sequence of magnetic phases as a function of temperature,[3,18] and the dispersion of low-lying magnetic excitations of the Cu spins in Pr_2CuO_4.[19] This is because isotropic Heisenberg interactions in a centered tetragonal structure are frustrated and cause a decoupling of the orthogonal Cu and Nd sublattices in a static mean field approximation. In contrast, it has been proposed[20] that pseudodipolar interactions might explain these observations because they are able to lift the degeneracies. This question has been discussed concerning the Cu-Cu (Ref. 19) interactions and the Cu-Nd (Ref. 21) interactions. It might apply to the Nd-Nd interactions as well, lifting also the degeneracy of magnetic excitations along the line *AM*.

Another explanation may arrive from the possibility that the symmetry of the chemical and magnetic lattice is lower than has been hitherto assumed. While at present there is no direct evidence for this assumption in NCO, there are a number of experiments that support this claim. Several heavy *R* cuprates, in particular Gd (Ref. 22) and Eu,[23] show weak ferromagnetism, which is explained as being due to distortions of the basal plane O(1) atoms. In fact, the corresponding phonon eigenmode, an O(1) in-plane rotation around Cu, shows rather anomalous behavior and tends to become soft.[24] In the case of NCO weak ferromagnetism has not yet been reported, but recently the magnetoelectric effect in NCO has been observed.[25] Since tetragonal symmetry does not allow a magnetoelectric effect, the observation of magnetic-field induced electric polarization might prove that the actual crystal and magnetic symmetry of this system is lower than it was thought to be. The lifting of the fourfold degeneracy by an external field is discussed in Ref. 26.

In summary, we have measured Nd spin waves along *AM* with high-energy resolution. The predicted fourfold degeneracy has not been observed. Instead the presented data are consistent with a multiple peak structure consisting of six or more peaks. All observed modes seem dispersionless between *A* and *M*. The lower and upper bands in that part of the Brillouin zone are not symmetric with respect to the number of observed excitations and their relative positions with respect to the position of the predicted two fourfold degenerate modes. It is likely that either the nature of the spin interactions is different and might be better described by pseudodipolar interactions or a symmetry breaking has to be assumed. Both mechanisms would be able to lift the degeneracy at and between the *A* and *M* points.

We would like to thank S. Pujol and F. Thomas from the Sample Environment Laboratory of the Institut Laue-Langevin for running the dilution cryostat, and A. Brochier for technical assistance during the experiment. We acknowledge financial support from the Institut Laue-Langevin for this experiment. This project was supported by the German Ministry for Education and Research (BMBF) under Grant No. 13N6606/0.

---

*Present address: ZBE FRM-II, Technische Universität München, D-85747 Garching, Germany.

†Also at Hahn-Meitner-Institut Berlin, D-14109 Berlin, Germany.

‡On leave from Kurtchatov Institute, Russian Research Center, 123182 Moscow, Russia.

[1] S. Skanthakumar, J. W. Lynn, J. L. Peng, and Z. Y. Li, Phys. Rev. B **47**, 6173 (1993).

[2] H. Casalta, P. Bourges, M. d'Astuto, D. Petitgrand, and A. S. Ivanov, Phys. Rev. B **57**, 471 (1998).

[3] M. Matsuda, K. Yamada, K. Kakurai, H. Kadowaki, T. R. Thurston, Y. Endoh, Y. Hidaka, R. J. Birgeneau, M. A. Kastner, P. M. Gehring, A. H. Moudden, and G. Shirane, Phys. Rev. B **42**, 10 098 (1990).

[4] J. W. Lynn, I. W. Sumarlin, S. Skanthakumar, W.-H. Li, R. N. Shelton, J. L. Peng, Z. Fisk, and S.-W. Cheong, Phys. Rev. B **41**, 2569 (1990).

[5] J. P. Hill, A. Vigliante, D. Gibbs, J. L. Peng, and R. L. Greene, Phys. Rev. B **52**, 6575 (1995).

[6] M. Loewenhaupt, P. Fabi, S. Horn, P. v. Aken, and A. Severing, J. Magn. Magn. Mater. **140-144**, 1293 (1995).

[7] M. Loewenhaupt, A. Metz, N. M. Pyka, D. McK. Paul, J. Martin, V. Duijn, V. H. M. Duijn, J. J. M. Franse, H. Mutka, and W. Schmidt, Ann. Phys. (Leipzig) **5**, 197 (1996).

[8] W. Henggeler, T. Chattopadhyay, B. Roessli, P. Vorderwisch, P. Thalmeier, D. I. Zhigunov, S. N. Barillo, and A. Furrer, Phys. Rev. B **55**, 1269 (1997).

[9] H. Casalta, P. Bourges, D. Petitgrand, and A. S. Ivanov, Solid State Commun. **100**, 683 (1996).

[10] D. Petitgrand, H. Casalta, P. Bourges, and A. S. Ivanov, Physica B **234-236**, 806 (1997).

[11] N. M. Pyka, M. Loewenhaupt, A. Metz, and N. T. Hien, Physica B **234-236**, (1997).

[12] P. Thalmeier, Physica C **266**, 89 (1996).

[13] R. Sachidanandam, T. Yildrim, A. B. Harris, A. Aharony, and O. Entin-Wohlmann, Phys. Rev. B **56**, 260 (1997).

[14] M. Loewenhaupt, A. Metz, N. M. Pyka, U. Stuhr, and P. Vorderwisch (unpublished) (in this experiment a different crystal was used than in the present study).

[15] M. d'Astuto, A. S. Ivanov, H. Casalta, D. Petitgrand, and P. Bourges, INS results at the *A* and *M* point measured at the LLB, Saclay (in this experiment the same crystal was used as in the present study).

[16] A. S. Ivanov, P. Bourges, D. Petitgrand, and J. Rossat-Mignod, Physica B **213&214**, 60 (1995).

[17] I. W. Sumarlin, J. W. Lynn, T. Chattopadhyay, S. N. Barilo, D. I. Zhigunov, and J. L. Peng, Phys. Rev. B **51**, 5824 (1995); D. Petitgrand, A. H. Moudden, P. Galez, and P. Boutrouille, J. Less-Common Met. **164-165**, 768 (1990).

[18] Y. Endoh, M. Matsuda, K. Yamada, K. Kakurai, Y. Hidaka, G. Shirane, and R. J. Birgeneau, Phys. Rev. B **40**, 7023 (1989).

[19] D. Petitgrand, S. V. Maleyev, P. Bourges, and A. S. Ivanov, Phys. Rev. B **59**, 1079 (1999).

[20] P. Bourges, L. Boudarene, and D. Petitgrand, Physica B **180&181**, 128 (1992).

[21] B. Gillon, D. Petitgrand, P. Galez, J. C. Castaing, and P. Schweiss, J. Magn. Magn. Mater. **104-107**, 583 (1992).

[22] A. A. Stepanov, P. Wyder, T. Chattopadhyay, P. J. Brown, G. Fillion, I. M. Vitebsky, A. Deville, B. Gailard, S. N. Barilo and D. I. Zhigunov, Phys. Rev. B **48**, 12 979 (1993).

[23] A. D. Alvarenga, D. Rao, J. A. Sanjuro, E. Granado, I. Torriano, C. Rettori, S. Oseroff, J. Sarrao, and Z. Fisk, Physica B **223&224**, 522 (1996).

[24] N. M. Pyka, N. L. Mitrofanov, P. Bourges, L. Pintschovius, W. Reichardt, A. Yu. Rumiantsev, and A. S. Ivanov, Europhys. Lett. **18**, 711 (1992).

[25] H. Wiegelmann, I. M. Vitebsky, A. A. Stepanov, A. G. M. Jansen, and P. Wyder, Phys. Rev. B **55**, 15 304 (1997).

[26] P. Thalmeier, Physica B **252**, 295 (1998).