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CRYSTAL-FIELD EXCITATIONS IN Nd_2CuO_4

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Inelastic neutron scattering has been employed to study the crystal-field interaction in Nd_2CuO_4. The energetic ordering of the crystal-field levels and the crystal-field parameters are determined from the observed transitions. J-admixture effects turn out to be important and are included in the calculations. At 1.5 K the ground-state doublet is found to be split by about 0.35 meV due to the long-range magnetic ordering of the Nd^{3+} ions.

INTRODUCTION

Compounds of the type R_2CuO_4 (R=Pr,Nd,Sm) crystallizing in the T'-type structure are of considerable interest, since n-type superconductivity is observed in the substituted isostructural systems $R_{2-x}Ce_xCuO_4$ [1] and $R_2CuO_{4-y}F_y$. [2] Recently, a comprehensive inelastic neutron scattering (INS) study of the crystalline electric field (CEF) interaction has been performed for $Nd_{2-x}Ce_xCuO_4$ with the aim to compare the electronic charge distribution of the CuO_2 planes in the insulating (x=0) and superconducting (x=0.15) state. [3] While the CEF energy levels have been unambiguously established for $Nd_{1.85}Ce_{0.15}CuO_4$, two possible CEF level schemes have been derived for Nd_2CuO_4. [3] Here we present our INS data obtained for Nd_2CuO_4 which are distinctly in favour of one of the two CEF level schemes proposed in Ref. 3. We have recently published the results of a similar investigation performed for Pr_2CuO_4. [4]

EXPERIMENTAL

The polycrystalline sample of Nd_2CuO_4 was obtained from the respective oxides by a standard sintering technique and regrinding the material several times. Neutron-diffraction measurements proved the single-phase character and the stoichiometry of the sample. The INS experiments were performed at the reactor Saphir of the Paul Scherrer Institute at Würenlingen with use of a triple-axis spectrometer. The energy of the scattered neutrons was kept fixed either at 5.00 or 14.96 meV, giving rise to energy resolutions (ΔE=0) of 0.2 and 1.0 meV, respectively. To gain intensity the measurements were carried out with use of a doubly bent graphite monochromator as well as a horizontally bent graphite analyzer, both with (002) scattering planes. Consequently no collimations were used from neutron source to detector. Pyrolitic graphite or beryllium filters were inserted into the outgoing neutron beam to reduce higher-order contamination. The experiments were performed for moduli of the scattering vector $\vec{Q}$, temperatures T and energy transfers ΔE in the ranges $0.9 < Q < 5.5$ Å^{-1}, $1.5 < T < 250$ K and $-1 < \Delta E < 105$ meV, respectively. The sample was enclosed into a cylindrical aluminium container of 15 mm diameter and 50 mm height, mounted either in an ILL-type helium cryostat or in a closed-cycle helium refrigerator.

RESULTS

Fig. 1 shows typical energy spectra observed below 30 meV in the neutron energy-loss configuration. At 10 K the scattering is dominated by two intense inelastic lines B and C at 20.5 and 26.7 meV, respectively, whose intensities are decreasing upon raising the temperature. They can thus immediately be interpreted as ground-state CEF transitions. At 150 K excited CEF transitions show up at 5 and 11 meV (lines D and E, respectively). We have confirmed the magnetic origin of all these lines by studying the peak intensities versus modulus of the scattering vector $\vec{Q}$ which exhibit the expected form factor behaviour. The resulting CEF level scheme is indicated on top of Fig. 1. According to this interpretation the first-excited CEF state is located at 15 meV; the corresponding ground-state excitation (line A), however, is rather weak and could hardly be detected because of appreciable phonon scattering contributions in that energy range. The high-energy range was not easily accessible in our experiments; nevertheless, we found the highest excited CEF state to lie at around 95 meV, [5] in good agreement with the values of 93 and 95 meV reported in Refs. 3 and 6, respectively.

We have also examined the low-energy part with improved resolution as shown in Fig. 2. In addition to the incoherent elastic peak there are at 1.5 K broad inelastic lines centered at $\pm$0.35 meV, with more intensity on the energy-

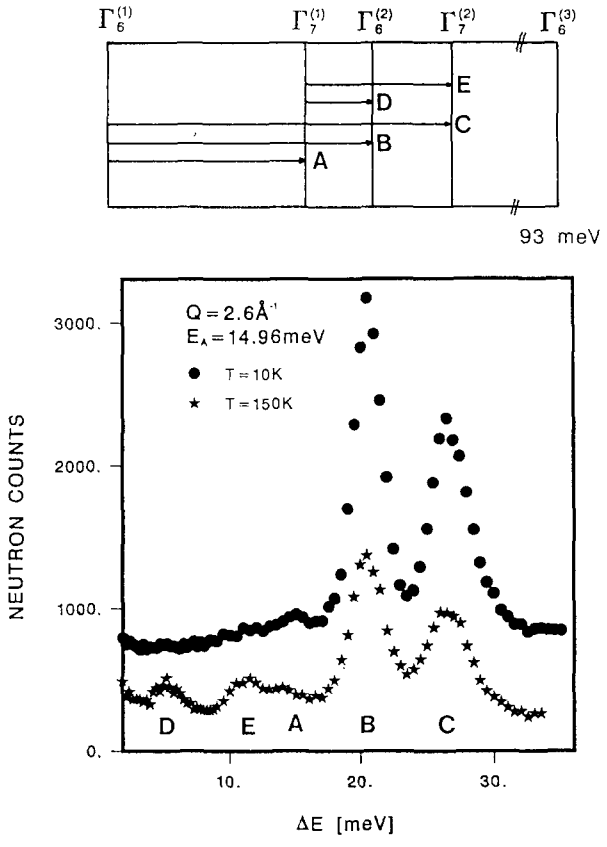

Fig. 1: Energy spectra of neutrons scattered from polycrystalline Nd_2CuO_4. The top of the figure shows the observed transitions and the resulting CEF level scheme.

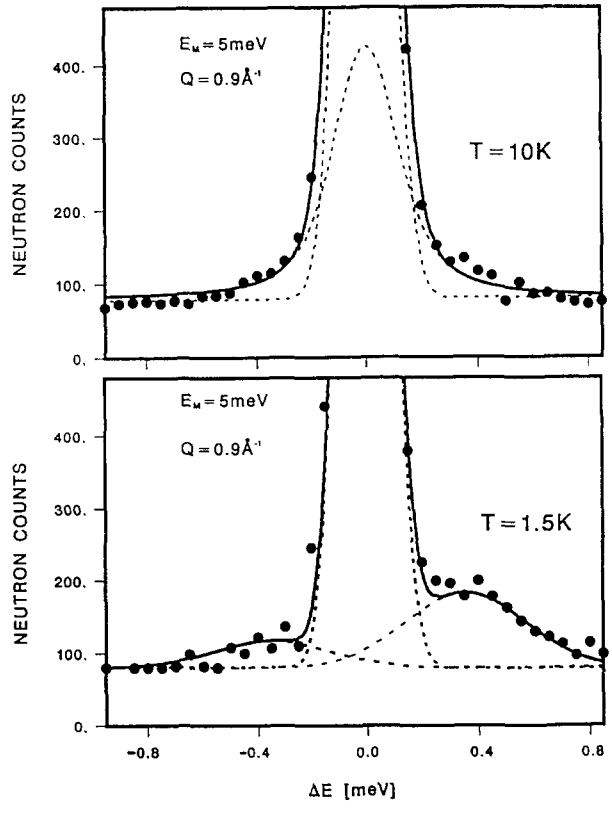

Fig. 2: High-resolution energy spectra of neutrons scattered from polycrystalline Nd_2CuO_4. The curves denote least-squares fits to the experimental data (Gaussian lines for the incoherent elastic peak and the inelastic peaks, Lorentzian line for the quasielastic peak).

loss side due to the thermal population factor. At 10 K the inelasticity of the spectral response disappeared, and the energy spectrum is characterized by a symmetric quasielastic line.

ANALYSIS

The tetragonal symmetry at the Nd^{3+} site in Nd_2CuO_4 gives rise to the following CEF Hamiltonian:

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4. \quad (1)$$

Here, the B_n^m denote the CEF parameters and the O_n^m are the corresponding Stevens operators. H_{CEF} splits the ground-state J-multiplet of $^4I_{9/2}$ of Nd^{3+} into five doublets, namely $3x\Gamma_6$ and $2x\Gamma_7$. The representation Γ_i of the ith CEF state with energy E_i can be identified by comparing the observed intensities of the CEF transitions with the differential neutron cross-section which is given in the dipole approximation by[8]

$$\frac{d^2\sigma}{d\Omega d\omega} \sim F^2(Q) \exp\left(-\frac{E_i}{k_B T}\right) M_{ij}^2 \, \delta(\hbar\omega + E_i - E_j), \quad (2)$$

$$M_{ij} = |\langle \Gamma_j | J_p | \Gamma_i \rangle|,$$

where F(Q) is the magnetic form factor and J_p the component of the total angular-momentum operator perpendicular to the scattering vector $\vec{Q}$.

Since there is no a priori information on the five independent CEF parameters B_n^m, an unambiguous interpretation of the experimental data is not at all straightforward. The most difficult problem of any nonlinear least-squares fitting procedure is a reasonable choice of the start values of the fitting parameters, which we have been able to assign[9] in a similar way as described for $HoBa_2Cu_3O_7$. Except for the 2nd order term the CEF potential at the Nd^{3+} site in Nd_2CuO_4 may reasonably be described by the coordination polyhedron determined by the eight nearest oxygen neighbours, which has the form of a tetragonally distorted cube. In a first approximation we can even start from the ideal cubic symmetry. The raising of the degeneracy of J-multiplets by a cubic CEF has been worked out in detail by Lea, Leask and Wolf (LLW).[10] Now we make use of the particular features of the CEF energy level scheme observed for Nd_2CuO_4, which is characterized by four low-lying states ($E_4 < 27$ meV) very much separated from the highest state at 93 meV (see Fig. 1). This situation can only be realized for the LLW parameters x = -0.6 and

W<0 (see Fig. 8 in Ref. 10), so that we are able to roughly estimate the diagonal 4th- and 6th-order CEF parameters B_4^0 and B_6^0, whereas the off-diagonal CEF parameters B_4^4 and B_6^4 are correlated by geometrical coordination. In principle, the 2nd-order CEF parameter B_2^0 can take any value between $-\infty$ and $+\infty$. After having fixed the start values of the CEF parameters in such a manner, we have performed a least-squares fitting procedure to the observed energies and intensities. The admixture of the excited J-multiplet $^4I_{11/2}$ situated at around 250 meV was taken into account. Perfect agreement with the available spectral information (energies and intensities) was obtained for the following CEF parameters:

$$B_2^0 = (-2.00 \pm 0.12)\times10^{-1} \text{ meV},$$

$$B_4^0 = (8.77 \pm 0.23)\times10^{-3} \text{ meV},$$

$$B_4^4 = (-6.52 \pm 0.04)\times10^{-2} \text{ meV},$$

$$B_6^0 = (-1.60 \pm 0.03)\times10^{-4} \text{ meV},$$

$$B_6^4 = (-4.57 \pm 0.03)\times10^{-3} \text{ meV}.$$

The resulting admixture effects due to the excited $^4I_{11/2}$ J-multiplet amount to about 20%. Since there is no upper limit in the number of J-multiplets which should be logically included in J-mixing calculations, we have also examined the effects of the third- and fourth-excited J-multiplets $^4I_{13/2}$ and $^4I_{15/2}$ situated at around 500 and 750 meV, respectively. However, the corrections to our results mentioned above were found to be rather small.

DISCUSSION

We have been able to unambiguously establish the energetic level ordering of the CEF split 4f-electron ground-state in Nd_2CuO_4. Our results essentially correspond to the CEF level scheme (b) proposed in Ref. 3, which is also favoured by Hoffmann et al.[6] based on the temperature dependence of the intensity of the strongest CEF transition. Another INS investigation of Nd_2CuO_4 carried out by Alekseev et al.[11] provided an incorrect CEF level scheme, since the high-energy CEF excitation was not taken into account. The CEF parameters resulting from our analysis are similar to those proposed by Nekvasil[12] and correctly reproduce the anisotropy of the magnetic susceptibility observed by Hundley et al.[13] The data analysis provided by Boothroyd et al.[3] has to be rejected for the following reasons: (i) The resulting CEF parameters are incompatible with any kind of geometrical coordination models, which are known to predict the CEF interaction in the high-T_c copper-oxide systems reasonably well;[14] (ii) The admixture effects due to higher-lying J-multiplets have been neglected; (iii) The analysis of the low-temperature data was based on the assumption of a molecular-field term that takes account of exchange interactions from Nd or Cu spin ordering. The molecular field was assumed to split the ground state doublet by 0.76 meV which, however, was determined in the present work to be only 0.35 meV (see Fig. 2).

The presence of low-energy inelastic lines at 1.5 K which condense into a quasielastic line at 10 K, is clearly due to the exchange-field resulting from Nd moment ordering. Indeed, the Nd sublattice in Nd_2CuO_3 becomes appreciably polarized below 10 K due to Nd-Cu interaction, which slowly increases with decreasing temperature down to about 1.5 K where the Nd moments spontaneously order.[15] In a high-resolution INS experiment Hoffmann et al.[6] even found two inelastic transitions at 0.3 and 0.6 meV, which may be interpreted in terms of acoustic and optic spin-wave excitations associated with the dynamics of the Nd moments. Thus the molecular-field approximation is likely to fail in the interpretation of the neutron spectroscopic data taken at low temperatures, and INS experiments on single crystals will be required to understand the dynamic magnetic behaviour of the Nd^{3+} ions in Nd_2CuO_4 in detail.

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