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Raman study of Kramers doublets in Nd_2CuO_4

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Raman-scattering measurements involving the Nd^{3+}-ion crystal field Kramers doublets in Nd_2CuO_4 are reported. The observed splitting is attributed to the lifting of the Kramers degeneracy by the Nd-Cu exchange interaction. Below 150 K the splitting of these crystal-field excitations is nearly temperature independent. There are also small discontinuities in the amplitude ratio of the doublet components at 30 and 75 K. These discontinuities can be interpreted as arising from the direction reversal of the Nd magnetic moment following the direction reversal of the copper exchange field at these phase transitions.

I. INTRODUCTION

The $Nd_{2-x}Ce_xCuO_4$ compounds have recently attracted a lot of attention due to the fact that, for $x \approx 0.15$ and once reduced, they become an electronlike high-T_c superconductor (HTCS).[1] Like other HTCS's, the parent compound is a semiconducting antiferromagnet. In Nd_2CuO_4 the copper spins order in a noncollinear magnetic structure,[2] in which the spins that lie in the Cu-O planes, parallel to the crystal axis, are rotated by 90°, in opposite directions in adjacent planes. The copper spin system undergoes two orientational transitions. At 75 K, all spins rotate by 90° about the c axis, and they rotate back to their initial direction at 30 K.[2–4] For temperatures between 75 and 30 K this corresponds to a 180° spin rotation in alternate planes (Fig. 1). The origin of these phase transitions is not well understood, even though it has been suggested that it might arise from a competition between the Nd-Cu and Nd-Nd spin interactions.[5] Furthermore, an exotic heavy-fermion state has been recently inferred from specific heat measurements in the Ce-doped samples.[6] In view of these properties, it seems very important to refine our understanding of the Nd-Cu interaction.

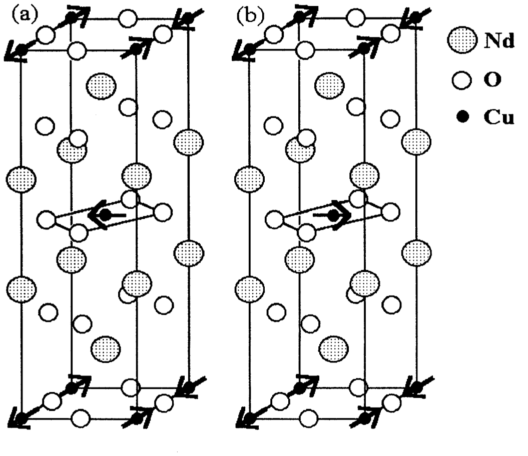

FIG. 1. Magnetic structure of Nd_2CuO_4: (a) above 75 K and below 30 K, (b) between 30 and 75 K.

The sensitivity of the neodymium crystal-field levels to both the local electric and magnetic fields, combined with the high resolution of the optical techniques, makes Raman scattering by these crystal-field excitations a valuable probe for the magnetic interactions. In that context, we have performed Raman-scattering experiments that involve transitions from the ground state doublet of the $^4I_{9/2}$ configuration to the first ($^4I_{11/2}$) and second ($^4I_{13/2}$) excited configurations. Transitions between the $^4I_{9/2}$ and the $^4I_{11/2}$ levels have been reported previously.[7]

II. EXPERIMENT

Single crystals of Nd_2CuO_4 were grown from the CuO flux by spontaneous nucleation, as described in Ref. 8. Typical crystals were $2\times2 \times 1$ mm^3 in size.

Raman spectra were measured as a function of temperature with a Dilor XY triple spectrometer equipped with a charge-coupled-device camera. The 4880 and 5145 Å argon-ion laser lines were used and the typical resolution was 1.5 cm^{-1}. The splitting of the 2000 cm^{-1} transitions was, however, determined in the triple additive mode with the 5145 Å laser line leading to a 0.5 cm^{-1} spectral resolution. The temperature of the sample was

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varied between 8 and 300 K using a closed-cycle refrigerator. The laser power used was 10 mW focused on a 20 μm spot on the sample. The sample heating due to the laser power is estimated to be about 10 K from the known temperature for the copper spin reorientations (30 and 75 K) observed at 22 and 63 K, respectively. Since the sample temperature is important in the analysis of the results, we performed a linear correction on the temperature scale to bring back the observed transition temperatures to their known values. Both temperature scales are indicated in Figs. 2 and 3. From now on, all temperatures cited in the text will be the corrected ones. The selection rules for the crystal-field transitions have been discussed in Ref. 7. It should be mentioned that the assignment of Ref. 7 differs somewhat from another recent publication.[9] We will assume that the ground state has symmetry Γ_6 in labeling the transitions.[7,9] In most cases, only the A_1 symmetry transitions lead to a detectable intensity. We will therefore present spectra for the $Y(ZZ)\bar{Y}$ configuration allowing the observation of the A_1 symmetry transitions of the C_{4v} point group. Attempts to observe transitions from the $^4I_{9/2}$ levels to the $^4I_{11/2}$ levels and the $^4I_{13/2}$ levels were successful only for the $Y(ZZ)\bar{Y}$ configuration. We did not succeed in observing transitions from the ground state Γ_6 level to some of the $^4I_{15/2}$ levels.

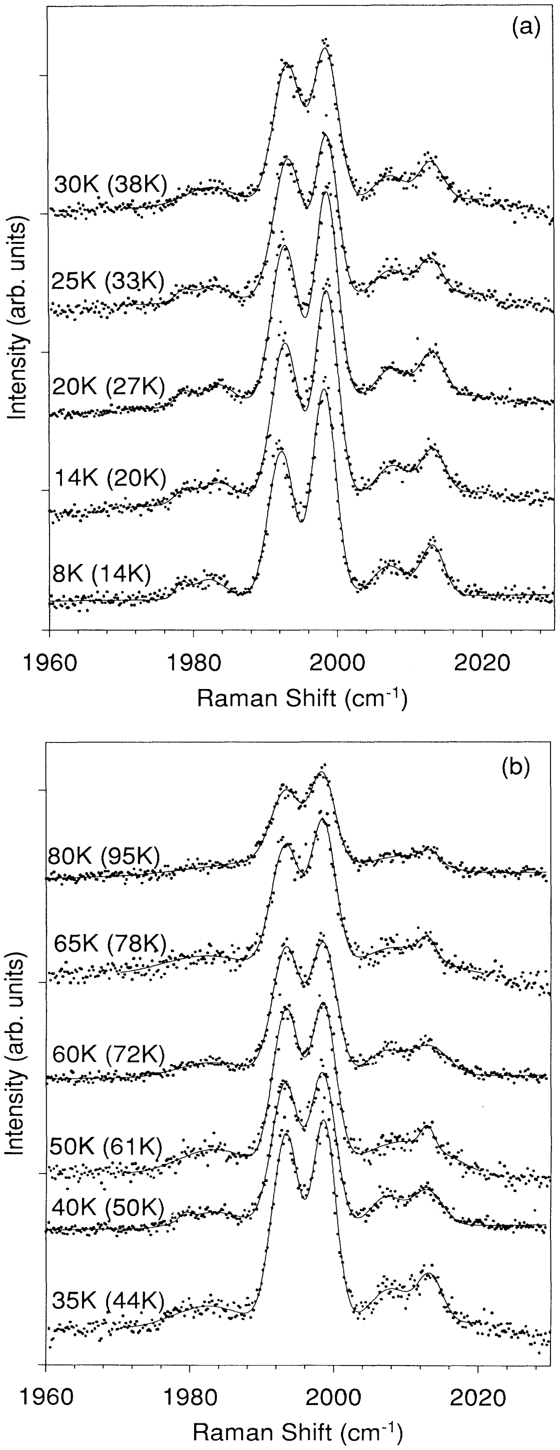

FIG. 2. Raman spectra of the 2000 cm^{-1} Kramers doublet at different temperatures: (a) 14–40 K, (b) 40–100 K. The corrected temperatures are indicated within parentheses.

III. RESULTS

The Raman spectra of excitations from the $^4I_{9/2}$ to the $^4I_{11/2}$ configuration are presented in Fig. 2. Three doublets are observed. These doublets correspond to the three expected Γ_6 to Γ_6 transitions. The other doublets, corresponding to Γ_6 to Γ_7 transitions (B_1, B_2, and E symmetry), have not been observed by Raman scattering. It has been suggested previously that these doublets

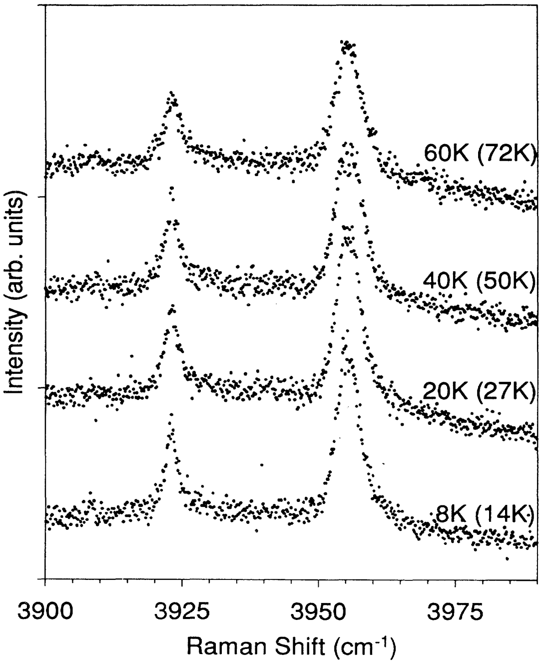

FIG. 3. Raman spectra of the 4000 cm^{-1} transitions at different temperatures. The corrected temperatures are indicated within parentheses.

may arise either from a Davydov splitting, due to the presence of two Nd atoms in the unit cell, or from a lifting of the Kramers degeneracy by the Nd-Cu exchange interaction.[7] As will be discussed below, the observation of the strong effect that reorientation of the copper spins exerts on these levels strongly favors the second hypothesis. We therefore believe that the origin of the doublets is the lifting of the Kramers degeneracy by the Nd-Cu exchange interaction as has been proposed on the basis of neutron and specific heat measurements.[10,11]

The energy splitting of the ground state, however, must be determined indirectly because it is not known, *a priori*, whether the observed splitting is the sum or the difference of the ground and excited state splittings. The important observations concerning these spectra (Fig. 2) consist of an overall decrease of the intensity of the higher-frequency doublet component relative to the lower-frequency one, with increasing temperature. Moreover, discontinuities in these intensities accompany the copper spin reorientations at 30 and 70 K.

In Fig. 3 we present the other transitions that have been observed by Raman spectroscopy. In these cases a splitting of the peaks is not clear, even though the peak at 3955 cm^{-1} is nearly twice as broad as the peak at 3923 cm^{-1}. It can be suggested, although not in a conclusive way, that for these transitions we are observing the difference between the splittings of the ground and excited states. In this case, a near-zero splitting will be observed if the excited state splitting is comparable to that of the ground state. For this set of transitions, there are one Γ_6 to Γ_6 and four Γ_6 to Γ_7 transitions missing in the measured spectra.

IV. DISCUSSION

We have fitted the Raman spectra with a sum of Gaussian line shapes. This type of profile was chosen because it gave an excellent fit to the experimental data. A Gaussian profile frequently suggests that the width of the peak is dominated by a distribution of frequencies (inhomogenous broadening) and not by the lifetime of the excitation (homogenous broadening), i.e., that the crystal-field transitions have slightly different frequencies in different unit cells due, possibly, to local electric-field variations. This interpretation of the line shape justifies the use of the amplitude instead of the area of the peaks in the analysis of the results. From the fits to the spectra, we have extracted the peak positions, widths, and amplitudes. These results are summarized in Figs. 4, 5, and 6 where the temperature evolution of these parameters is shown. Note that the widths [Fig. 6(a)] are independent of temperature within error. The ratio of the amplitudes is displayed in Fig. 4 since it is more reliable than the absolute values. Of particular interest here is the ratio of the amplitude of the main doublet at 1993 cm^{-1} and 1999 cm^{-1}. As can be seen in Fig. 4, this amplitudes ratio exhibits a nonmonotonic behavior with a clear slope change at 30 and 75 K. The 30 K discontinuity is also clearly visible in the doublet splitting. These discontinuities (Figs. 4 and 5) seem to be related to the two

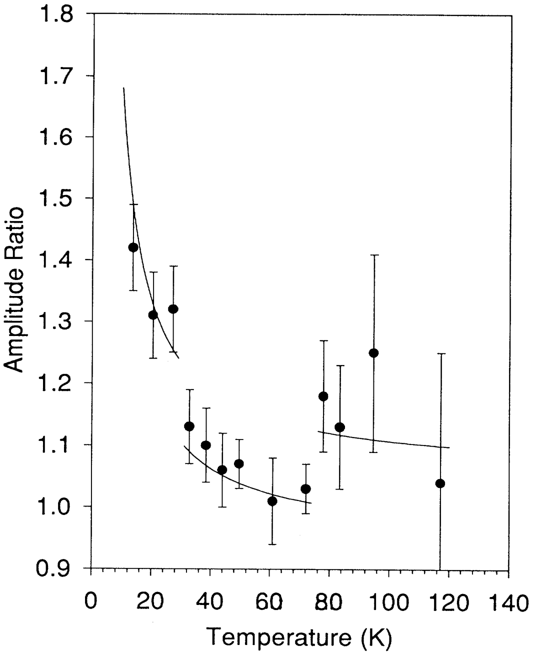

FIG. 4. Amplitude ratio of the main doublet around 2000 cm^{-1}. Notice the slopes change (nonmonotonic behavior) at 30 and 75 K. The circles are the experimental data. The line is calculated with the model discussed in the text.

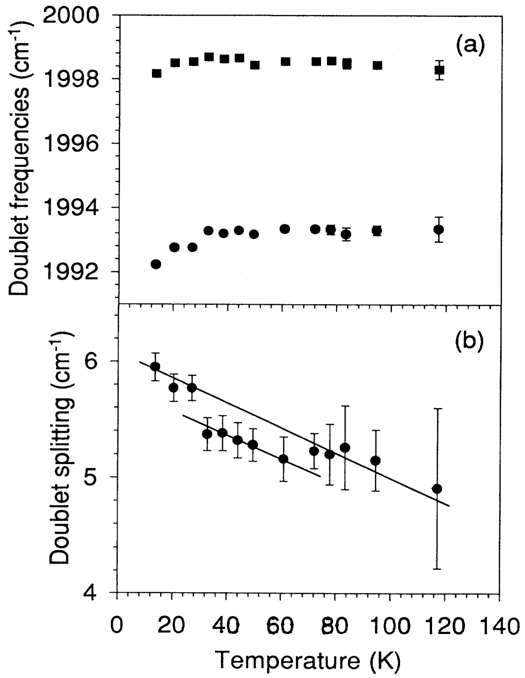

FIG. 5. (a) Temperature dependence of the frequencies of the observed crystal-field transitions. (b) Frequency difference of the two peaks of the central doublet around 2000 cm^{-1}. The line is a guide to the eyes.

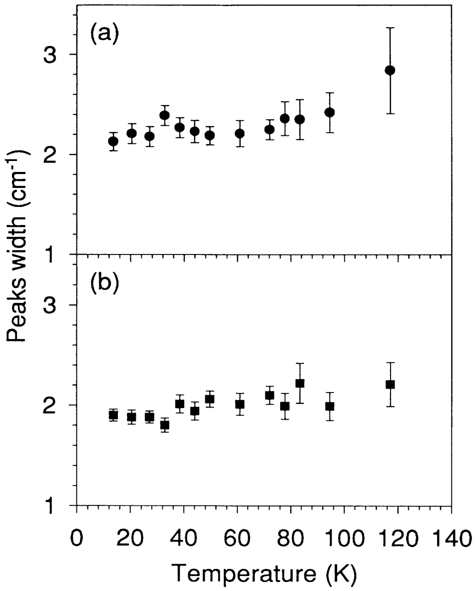

FIG. 6. Temperature dependence of the width of the observed crystal-field transitions (a) for the 1993 cm^{-1} peak and (b) for the 1998 cm^{-1} peak.

reorientations of the copper spin system.

The origin of these discontinuities can be quantitatively understood with three assumptions:

(1) The splitting of the Kramers doublets is mainly due to the Nd-Cu exchange interaction with a small contribution from the dipolar magnetic field induced by the copper at the Nd sites.

(2) The Raman-scattering efficiency for the two components of the doublet is not the same.

(3) The ratio of these Raman-scattering efficiencies is temperature independent and remains the same in the three phases.

The exchange interaction postulated in the first assumption has been used previously and has led to a good agreement between the experimental data and their modeling in both neutron[10] and specific heat measurements.[11] However, in the model of Ref. 10 the use of the exchange interaction was limited to the low-temperature phase. There was no clear effect of the copper spins, except that a static field was needed, as expected for the copper exchange field well below the Néel temperature. Here, since there are two phase transitions the effect of which is to reverse the copper spins in alternating planes (see Fig. 1) and therefore the magnetic field at the neodymium site, the origin of the magnetic field is quite clear. The exchange fields of the nearest neighbor (to a given Nd ion) copper planes cancel at that Nd site. A noncanceling contribution results from the Cu ions in the second neighbor plane. In the representation of Fig. 1 this results in a reversal of the copper exchange field in every other Nd ion. Note that at the phase transition, those ions for which the exchange field reverses direction experience a dipole field (induced mainly by the *NN* planes) which does not change direction, and vice versa. The effect of a reversal of the total copper-induced magnetic field is a reversal of the Nd magnetic moment, inverting the two components of the crystal-field Kramers doublet.

If the exchange field is treated as an external magnetic field it is clear, on the basis of time reversal symmetry, that mixing among the Nd states would fail to reproduce the behavior observed for the amplitude ratio. The small difference in the transition amplitudes of the two different components of a Kramers doublet can be qualitatively understood on the basis of the first and second neighbor (planes) copper interaction. Interaction with the first neighbor coppers should induce an admixture of Cu wave functions on the Nd crystal field states. This admixture should be spin dependent and would lead to a difference in the intensities of the doublet components. Since the effect of the nearest neighbor plane is reversed at the phase transition, the effect of that admixture on the intensities is also expected to reverse (together with the effect of the dipole field on the splitting).

The dipolar magnetic field is needed to explain the observed discontinuities of the doublet splitting [Fig. 5(b)]. In phase I [Fig. 1(a)], the main component of the copper dipolar magnetic field at the Nd site is parallel to the exchange field and has the same direction leading to an increase in the doublet splitting. In phase II [Fig. 1(b)], the orientation of the dipolar field remains the same but the direction is now opposite to that of the exchange field leading to a decrease in the doublet splitting. Using a magnetic moment of $0.4\mu_B$ for the copper,[12] the variation of the dipolar magnetic field between the two phases is 750 G, leading to a change of the order of 0.1 cm^{-1} in the ground state Kramers doublet splitting. Assuming that the effect on the excited state is about the same (this should be so since the doublet splitting caused by the exchange field is of the order of 6 cm^{-1} and that of the ground state is 3 cm^{-1}) we expect a decrease of 0.2 cm^{-1} of the doublet splitting due to the dipolar magnetic field between phase I and phase II. This is in good agreement with the observed value of 0.3 ± 0.2 cm^{-1}.

The results of Fig. 4 are fitted with the following function:

$$f(T,\Delta,\beta) = \begin{cases} \beta e^{\frac{\Delta}{kT}} & \text{for } 14 < T < 30 \text{ K and } T > 75 \text{ K}, \\ \beta^{-1} e^{\frac{\Delta}{kT}} & \text{for } 30 < T < 75 \text{ K}, \end{cases} \tag{1}$$

where β is a temperature-independent amplitude ratio and Δ is the splitting of the ground state Kramers doublet induced by the temperature-independent copper magnetic field. In the intermediate phase, the amplitude ratio is inverted because the energy levels have reversed with nearly no change of the overall splitting. As can be seen in Fig. 4 this model reproduces the amplitude ratio very well over the whole temperature range, thereby giving the first direct evidence that the Nd magnetic moments are also inverted when the two copper spins reorient. From the model, we extract an amplitude ratio of 1.06 and a gap of 3 ± 1 cm^{-1}. This splitting is in very good agreement with the 4 K value that was obtained by specific heat measurements and high-resolution neutron spectroscopy.[11,13]

V. CONCLUSIONS

We have observed the copper spin reorientations associated with the magnetic phase transitions in Nd_2CuO_4 by Raman spectroscopy. The reorientations manifest themselves through the coupling of the Nd spins to the Cu spins, in the splitting of the crystal-field transitions. Our measurements allow us to confirm the previous hypothesis that the Nd magnetic moments flip to follow the copper spins at these phase transitions. We have also been able to extract an independent value of the splitting of the Kramers ground state from the evolution of the amplitude ratio of one of the Kramers doublets (3 cm^{-1}). Finally, our measurements provide further information on the energies of the crystal-field transitions that might be used to refine the value of the crystal-field parameters.

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