Acoustic measurement of the low-energy excitations in Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$

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The complex dynamic Young’s modulus of ceramic Nd$_{2-x}$Ce$_x$CuO$_4$ with $x = 0$, 0.05 and 0.20 has been measured from 1.5 to 100 K at frequencies of 1 – 10 kHz. In the undoped sample the modulus starts decreasing below $\sim$ 20 K, instead of approaching a constant value as in a normal solid. The modulus minimum has been interpreted in terms of paraelastic contribution from the relaxation of the Nd$^{3+}$ 4f electrons between the levels of the ground state doublet, which is split by the interaction with the antiferromagnetically ordered Cu sublattice. The value of the splitting is found to be 0.34 meV, in excellent agreement with inelastic neutron scattering, infrared and specific heat experiments. With doping, the anomaly shifts to lower temperature and decreases in amplitude, consistently with a reduction of the local field from the Cu sublattice.
I. INTRODUCTION

The crystal-field (CF) excitations of the Nd$^{3+}$ 4f electrons in Nd$_{2-x}$Ce$_x$CuO$_4$ have been extensively studied, mainly by inelastic neutron scattering (INS) and infrared spectroscopy. Although discrepancies exist between the proposed sets of phenomenological parameters in the CF hamiltonian, there is general agreement on the level scheme. The ground state multiplet of Nd$^{3+}$ has $J = 9/2$ and is split into five doublets, the separation of the first two being 14 meV; each doublet, in turn, is split by the interaction of the Nd magnetic moment with the local magnetic field, mainly created by the antiferromagnetic ordering of the Cu magnetic moments below $T_{N}^{Cu} \approx 260$ K. The magnetic separation of the first doublet has been determined by INS, and passes from 0.39 meV for the undoped case to 0.2 meV for $x = 0.15$. Such a low-energy excitation also appears as a Schottky anomaly in the low-temperature specific heat, with values of the level splitting in agreement with the INS results; in principle, it should also give rise to an anomaly in the elastic moduli, if the level separation can be modulated by strain. To our knowledge, only two experiments have been reported on the elastic properties of NCCO at liquid He temperatures, but no attempts have been made to relate those data to the elastic response of the ground state doublet. We made anelastic spectroscopy measurements in the kHz range on Nd$_{2-x}$Ce$_x$CuO$_4$ with $x = 0, 0.05$ and 0.20, and found a decrease of the Young’s modulus at liquid He temperatures, which can be identified with the paraelastic response of the ground state doublet of Nd$^{3+}$.

II. EXPERIMENTAL

The samples were prepared by solid state reaction, with repeated sintering and grinding of the powders up to obtaining X-ray diffraction spectra free of unwanted peaks; the methods used, together with a thorough thermodynamic study of the phase diagram and stability of the Nd-Ce-Cu-O system, are reported in Ref. The real part $E'$ of the Young’s modulus is given by $E = \rho \left(\frac{2}{\pi l^2 h}\right)^2$, where $\rho$, $l$ and $h$ are the sample density, length and thickness; a correction for the porosity should be necessary, but we are only interested in the relative variation of $E$ with temperature. The elastic energy loss coefficient $Q^{-1} = E''/E'$ was measured from the free decay of the vibration amplitude after switching off the excitation signal.

III. RESULTS

Figure 1 presents the complex Young’s modulus of Nd$_{2-x}$Ce$_x$CuO$_4$ at three doping levels, between 1 and 100 K; only the data of the first mode are presented, since those at higher frequency are identical. The elastic energy loss coefficient decreases monotonously with temperature and with increasing doping, without any particular feature except for a small peak at 15 K for the undoped sample. Such a peak disappears after annealing in vacuum at high temperature, and, although several reorientational transitions of the Nd and Cu spins have been observed at low temperature with various techniques, it does not seem to be associated to any of these magnetic transitions. We will not discuss this peak further. The elastic modulus presents a nearly linear stiffening on cooling below room temperature, which levels off below 30 K; contrary to a normal solid, however, the modulus does not stabilize on further cooling, but drops of several parts in 10$^3$. The drop actually saturates at the lowest temperatures reached in the experiments (see also Fig. 2), and in some cases we measured the beginning of a rise below 1.5 K. The temperature and amplitude of the drop decrease with increasing doping similarly to the Schottky anomaly in the specific heat, and therefore this feature might well be connected with the ground state doublet of the Nd$^{3+}$ ions.

IV. DISCUSSION

Most of the specific heat data below 10 K have been interpreted in terms of a Schottky anomaly arising from the ground state doublet with a splitting $\Delta (T) = 2\mu_B B_{Cu} (T)$ determined through Nd-Cu exchange by the staggered magnetization $B_{Cu} (T)$ of the AF Cu sublattice below $T_{N}^{Cu}$; since $T_{N}^{Cu} \simeq 260$ K, $B_{Cu}$ and the splitting $\Delta$ are practically constant below 50 K. The existence of two levels $\varepsilon_i$ separated by $\Delta$, whose internal energy is $U = (\Delta/2) \tanh (\Delta/2k_B T)$, contributes to the molar specific heat with the Schottky term

$$\delta C_p = \frac{\partial U}{\partial T} = k_B c \left(\frac{\Delta}{2k_B T}\right)^2 \frac{1}{\cosh^2 (\Delta/2k_B T)},$$

where $c$ is the molar concentration of the relaxing entities, in the present case the concentration $1 - x/2$ of Nd ions.
On the other hand, if the splitting can be modulated by a strain $\varepsilon$, paraelastic and diaelastic contributions to the elastic modulus $M = \partial^2 U / \partial \varepsilon^2$ are expected. Here we omit the tensorial character of the elastic properties, since we are dealing with the Young’s modulus of polycrystalline samples, which contains a combination of several elastic constants and we are not entering in the details of the effect of the strain symmetry on the Nd$^{3+}$ multiplets; then $M$ is identified with the Young’s modulus $E$ and $\varepsilon$ is the corresponding effective strain.

The paraelastic contribution can be written as:

$$\delta M_{\text{para}} = \sum_{ij} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \frac{\partial \varepsilon_i}{\partial n_j}$$

and is due to the relaxation of the populations $n_j$, perturbed by the vibration strain $\varepsilon$ through the modulation of the energies $E_i$. For only two levels $E_2 - E_1 = \Delta$, one obtains:

$$\delta M_{\text{para}} = -\frac{c}{v_0} \frac{\gamma^2}{4k_B T \cosh^2(\Delta/2k_B T)} \, ,$$

(2)

where $v_0$ is the molecular volume and $\gamma = \partial \Delta / \partial \varepsilon$ is the deformation potential. Such a relaxation occurs with a characteristic rate $\tau^{-1}$, and therefore the dynamic modulus $\delta M$ has to be multiplied by a factor $(1 + i \omega \tau)^{-1}$. The resulting real part of the dynamic modulus $M' (\omega, T)$ acquires a frequency-dependent dispersion, while the imaginary part produces absorption in correspondence with the modulus dispersion. The present data, however, do not exhibit any frequency dependence of $M' (\omega, T)$ or absorption peak, and this implies $\omega \tau \approx 0$, namely the rate $\tau^{-1}$ is much faster than the measuring frequencies $\omega \sim 10^4 - 10^6$ s$^{-1}$. Indeed, the Cu and Nd spin rates deduced from muon spin relaxation experiments in samples with $x = 0.20$ are faster than $10^{10}$ s$^{-1}$.

If the first derivative $\gamma$ of the energy split with respect to strain is null for symmetry reasons, than one remains with the diaelastic term, $\delta M^\text{dia} = \frac{c}{v_0} \sum n_j \frac{\partial E}{\partial n_j}$, which contains the second derivatives. The physical meaning of such a term is simply that the curvature of each energy level versus strain contributes to the corresponding elastic constant, and its contribution is weighted with the level population. For only two levels one obtains:

$$\delta M^\text{dia} = \frac{c}{v_0} \left( \frac{\partial^2 \Delta}{\partial \varepsilon^2} \tanh \left( \frac{\Delta}{2k_B T} \right) \right) .$$

(3)

The continuous curves in Fig. 2 are fits with $\delta M_{\text{para}}$ given by Eq. (2) and assuming that the background modulus depends on temperature like an insulating Debye solid $M (T) = M_0 (1 - aT^4)$. An additional term quadratic in $T$ is expected when the system becomes metallic, due to the energy of the free electrons, which increases quadratically with $T$; such a term, however, could be of importance only for the highest doping $x = 0.20$, and still at $x = 0.15$ some elastic constants have been found to be well described by the quartic term alone below 60 K. From the data at $x = 0$ and 0.05 we find that $M (T)$ is described by the coefficient $a = -2.1 \times 10^{-10}$ K$^{-4}$. The values of the splitting deduced from the fits of Fig. 2 are $\Delta/k_B = 4.0, 2.25$ and 1.3 K at $x = 0$, 0.05 and 0.20 respectively, while the amplitudes of the paraelastic contributions are in the ratios 1 : 0.6 : 0.05. The splitting found for the undoped case is in excellent agreement with the values deduced from INS $\Delta/k_B = 4.06$ K, infrared spectroscopy (3.8 K) and specific heat $\Delta/k_B = 4.5$ K. Doping by Ce substitution introduces electrons mainly of Cu 3$d$ character, which cancel the magnetic moments of those Cu ions and therefore reduce the Cu-Nd exchange responsible for the ground state splitting. As a result, the Schottky anomaly in the specific heat has been found to shift to lower temperatures to broaden and to decrease in intensity with doping. The present data confirm such a trend, but the reduction in intensity is more marked than in the specific heat measurements possibly because of a reduction of the strain dependence of the splitting with doping.

At $x > 0.15$ there is no long range AF order of the Cu spins, and the magnetic ground state splitting should disappear; nonetheless, the specific heat presents a peak up to $x = 0.20$. Our data at $x = 0.20$ also present a residue due to the doubling with reduced splitting, but the value deduced from the fit, $\Delta/k_B = 1.2$ K, should be considered with caution in view of the possible influence of an electronic quadratic term in the temperature dependence of the modulus.

In some cases the fits to the specific heat data have been improved by assuming an additional temperature dependence of the magnetic splitting attributed to the ordering of the Nd moments which however affects the splitting by less than 10%, or by assuming a three-level structure instead of a doublet. We chose not to over-interpret our data with additional parameters besides a simple Schottky anomaly with constant splitting below 50 K and the $T^4$ dependence of the background elastic modulus. In fact, the contribution of the doublet to the elastic response, Eq. (2) has a slower temperature dependence than the contribution to the specific heat, Eq. (1), in the high temperature limit, being proportional to $T^{-1}$ instead of $T^{-2}$; therefore, the elastic anomaly is spread to higher temperature where additional effects become important. In addition, the lowest temperature attained in our experiments was not sufficient to complete the low-temperature side of the curves, so that some uncertainty in the determination of the minimum of $\delta M_{\text{para}} (T)$ exists. This means that, while it is easy to improve the fit by adding a temperature dependence of the splitting, by taking into account the contribution of the excited doublets, and adopting more sophisticated expressions for $M (T)$, it is difficult to distinguish which of the improvements is the important one. Still, the data presented here, together with other results on reduced samples, are sufficient to indicate the presence of a minimum in the modulus due to a paraelastic response, rather than a step-like anomaly due to a diaelastic response. Fits to the diaelastic expression, Eq. (3), are less satisfactory and yield values of $\Delta$ about twice larger than those of Fig. 2, in contrast with the literature values. If both the di-
aelastic and paraelastic terms are considered, with both \( \gamma \) and \( \partial^2 \Delta / \partial \varepsilon^2 \) as free parameters, the splitting \( \Delta \) remains almost the same as reported here and up to half of the anomaly can be accounted for by the diastic term, without a significant improvement of the fit. We conclude that the anelastic response in the modulus is mainly due to the linear part of the response of the ground-state splitting to strain. The magnitude of the deformation potential \( \gamma \) can be extracted inserting in Eq. \( \ref{eq:deformation} \) the value obtained from the fit, \( (\delta M_{\text{para}}/M)_{\text{max}} = 0.0044 \) at 2 K for \( x = 0 \), and using \( M = 100 \) GPa, as determined from the resonance frequency (without corrections for the porosity); it turns out \( \gamma = 0.013 \) eV for \( x = 0 \) and 0.01 eV for \( x = 0.05 \).

As noted above, the absence of a rise of the absorption in correspondence to the decrease of the modulus implies that the relaxation rate for the Nd\(^{3+}\) spins to redistribute themselves within the ground states doublet is much faster than our measuring frequency, \( \omega \sim 10^8 - 10^5 \) s\(^{-1}\). Also, there are no signs of freezing of the Cu spins into a spin-glass or cluster glass states, which instead is observed in the hole-doped Cu\(_2\)O planes of La\(_{2-x}\)Sr\(_x\)CuO\(_4\) and YBa\(_2\)Cu\(_{3-x}\)O\(_{6+x}\) in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) the frozen spin domains produce a distinct rise of the acoustic absorption which is totally absent here. Similar conclusions have been drawn from \( \mu \)SR relaxation experiments.

To our knowledge, only two other experiments exist on the acoustic properties of Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\) at liquid He temperatures, which however cannot be compared with the present one in a straightforward way; in fact, they report some elastic constants of single crystals, while we measured the Young’s modulus of polycrystals, which contain a combination of all the compliances. Fill et al.\(^{11}\) found several anomalies in the elastic constants of undoped Nd\(_2\)CuO\(_4\) as a function of temperature and magnetic field. In particular, the \( c_{66} \) shear presented a minimum at 5 K with an amplitude nearly ten times larger than our minimum, and with a narrower shape, followed by a smaller decrease below 1 K tentatively attributed to a Schottky anomaly or magnetic ordering of Nd ions. Around 5 K also step-like changes have been found in other elastic constants, which have been interpreted as a ferroelastic transition driven by an ordering of the Nd spins.\(^{4,11}\) We cannot find a clear correspondence between those data and the ones presented here.

Regarding the doped material, Saint-Paul et al.\(^{12}\) measured the sound velocity of a single crystal of Nd\(_{1.85}\)Ce\(_{0.15}\)CuO\(_4\); the shear mode in the ab plane did not present any anomaly down to 10 K, but this is not in contrast with our data at \( x = 0.20 \), where the decrease of the modulus is hardly detectable above 10 K. Instead, the \( c_{33} \) mode exhibited an upward deviation below 10 K with respect to the \( -T^4 \) dependence, opposite to our measurements. A possible explanation for the discrepancy is that the major contribution to the \( c_{33} \) mode is diastic with positive \( \partial^2 \Delta / \partial \varepsilon^2 \), while the Young’s modulus of the polycrystal contains a predominant paraelastic contribution which cancels the diaelastic one.

**V. CONCLUSION**

The Young’s modulus and elastic energy loss coefficient of Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\) with \( x = 0, 0.05 \) and 0.20 have been measured from 1.5 to 100 K. On approaching the lowest temperature, the modulus presents a drop whose temperature and amplitude decrease with increasing doping. The data have been interpreted in terms of paraelastic contribution from the relaxation of the Nd\(^{3+}\) \( 4f \) electrons between the levels of the ground state doublet, which is split by the interaction with the antiferromagnetically ordered Cu\(^{2+}\) ions. Excellent agreement is found with the value of the splitting at zero doping deduced from INS, infrared and specific heat measurements, and the shift of the anomaly to lower temperature with doping is consistent with a reduction of the local field from the Cu sublattice. An effective deformation potential \( \gamma = 0.013 \) eV is found for the strain derivative of the splitting at \( x = 0 \), which decreases with doping. The absorption is very low and featureless, indicating that the relaxation rate for reaching equilibrium within the ground state doublet is much faster than the measuring frequency, \( \tau^{-1} \gg 10^5 \) s\(^{-1}\), and also excluding the occurrence of freezing phenomena of the Cu or Nd spins down to 1.5 K.

**VI. ACKNOWLEDGMENTS**

This work has been carried out within the framework of the CNR-CNPq cooperation project 2001-2002.

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FIG. 1. Elastic energy loss coefficient and relative change of the Young’s modulus $E$ of Nd$_{2-x}$Ce$_x$CuO$_4$ samples with $x = 0$ (0.9 kHz), $x = 0.05$ (2 kHz) and $x = 0.20$ (1.6 kHz).

FIG. 2. Fit of the relative change of the Young’s modulus of Nd$_{2-x}$Ce$_x$CuO$_4$ with the paraelastic contribution from a doublet with splitting $\Delta$, Eq. 2.
Nd$_{2-x}$Ce$_x$CuO$_4$

- $x = 0$
- $x = 0.05$
- $x = 0.20$
\begin{align*}
x = 0.20 & \quad \Delta = 1.3 \text{ K} \\
x = 0.05 & \quad \Delta = 2.3 \text{ K} \\
x = 0 & \quad \Delta = 4.0 \text{ K}
\end{align*}