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Ultrasonic investigation of $Nd_2Cu_{1-x}Zn_xO_4$: magnetoelastic interaction in the antiferromagnetic and paramagnetic state

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Abstract

A pulse echo technique was employed to measure the ultrasonic attenuation and velocity in the 120–340 K temperature range on $Nd_2Cu_{1-x}Zn_xO_4$ with $x=0$, 0.02 and 0.05. A marked hysteresis in the velocity *vs.* temperature trend was observed. The Zn doping results in a reduction in the hysteresis loop area. Strong attenuation maxima were observed at 210 and 260 K. The results are discussed in terms of magnetoelastic interaction across the Néel temperature.

1. Introduction

Magnetic interactions are invoked by many workers to describe superconductivity in the copper-oxide-based high temperature superconductors [1]. The discovery of electron carrier superconductors such as $Nd_{2-x}Ce_xCuO_4$ [2] allowed comparison with analogous properties in La_2CuO_4 [3]. The common magnetic property is the quasi-two-dimensional antiferromagnetic long-range order of Cu^{2+} spins with a Néel temperature of around 300 K.

On the contrary, some specific peculiarities make Nd_2CuO_4 very interesting.

(i) It always displays a tetragonal structure and so a weak ferromagnetism as in La_2CuO_4 is symmetry forbidden [4].

(ii) Nd^{3+} ions have localized moments which can order, while La^{3+} ions in La_2CuO_4 are diamagnetic.

Ultra-acoustic techniques can be advantageously employed to characterise magnetic onset [5], particularly when measurements of the magnetic susceptibility cannot give unambiguous information about Cu magnetism, as in the case of Nd_2CuO_4. The aim of this work was to acquire preliminary results on the effect of Zn^{2+} substitution for Cu^{2+} on $Nd_2Cu_{1-x}Zn_xO_4$, through measurements of the ultrasonic attenuation and velocity by a pulse echo overlap technique. Zn was chosen because it is a particularly effective dopant that causes rapid decreases in both T_c and T_N in La–Cu–O and Y–Ba–Cu–O systems [6].

2. Experimental details

Polycrystalline $Nd_2Cu_{1-x}Zn_xO_4$ specimens in powder form for $x=0.02$ and 0.05 were obtained by solid state reaction procedures from the starting neodymium, copper and zinc oxides. The Nd_2CuO_4 powders were obtained instead by Nd_2O_3 and CuO powder diluted in an ethylenediaminetetraacetic acid water solution. Four cylindrical samples (10 mm in diameter and 0.5 cm high) were finally prepared by repeated consolidation and sintering stages. A pulse-echo Matec equipment operating at 10 MHz was employed for velocity and attenuation measurements in the longitudinal mode. Data acquisition and processing were completely automated.

All measurements were made during heating and cooling at 1–2 K min^{-1}. The temperature was controlled to within 1 K of the set value.

3. Results

The ultrasonic attenuation coefficient α on the pure and Zn-doped compounds, in the 200–340 K range, is reported in Fig. 1.

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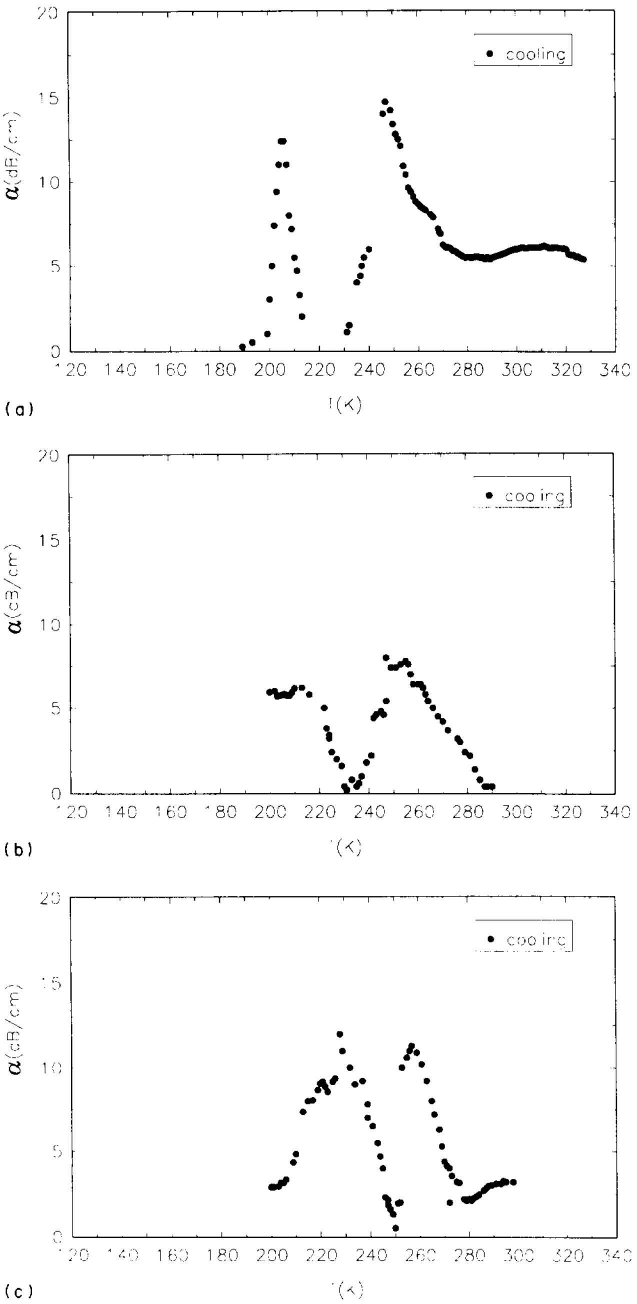

Fig. 1. Ultrasonic attenuation of (a) pure Nd_2CuO_4, (b) $Nd_2Cu_{0.98}Zn_{0.02}O_4$ and (c) $Nd_2Cu_{0.95}Zn_{0.05}O_4$.

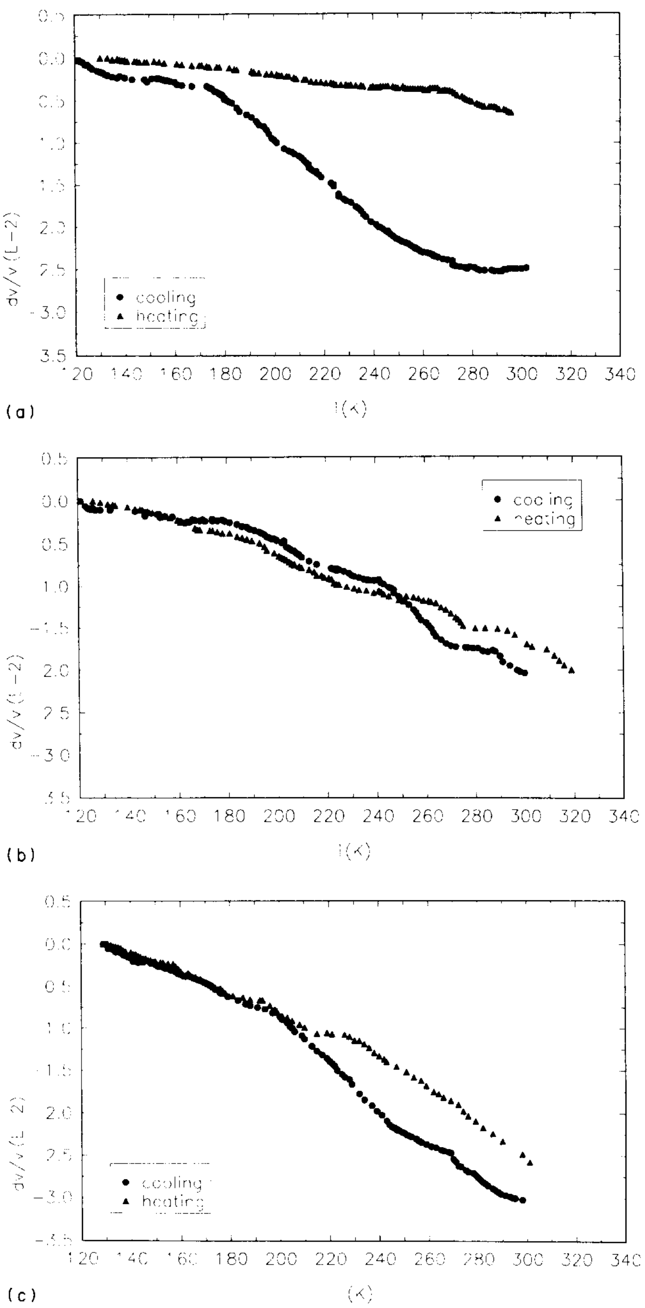

Fig. 2. Relative variation in velocity for (a) pure Nd_2CuO_4, (b) $Nd_2Cu_{0.98}Zn_{0.02}O_4$ and (c) $Nd_2Cu_{0.95}Zn_{0.05}O_4$.

Two peaks are visible at $T_1 = 260$ K and $T_2 = 210$–220 K. The peak at the higher temperature does not seem to be strongly affected by the Zn doping, while a broadening of the lower temperature peak can be detected.

Typical velocity *vs.* temperature trends during a sequential cooling and heating run, on the same samples as in Fig. 1, are reported in Fig. 2.

In Fig. 2(a) it is note worthy that a marked and not closed hysteresis is present in the pure compound. The Zn doping reduces the differences between the velocity trends on cooling and heating. A close inspection of these trends revealed that in the doped specimens during heating a stronger temperature dependence of the elastic constants is measured (Figs. 2(b), 2(c) and 3).

The hysteresis observed in the pure compound depends on the previous thermal history, as shown in Fig. 4 by the velocity *vs.* time evaluation after a stop at 293 K during a heating run, thus suggesting an intrinsic relaxation mechanism as its origin.

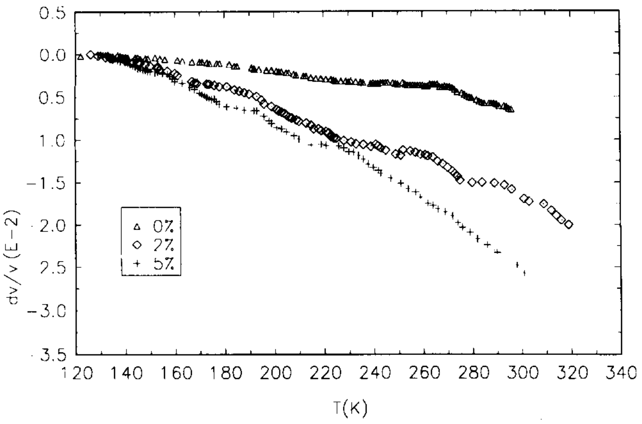

Fig. 3. Comparison of typical velocity trends on differently Zn-doped specimens.

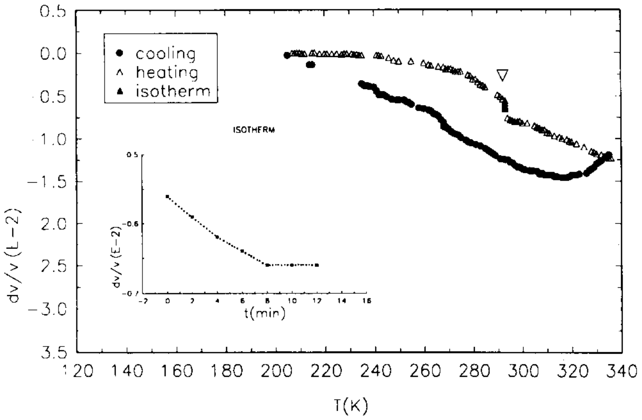

Fig. 4. Relative variation in velocity for pure Nd_2CuO_4 with a thermal stop at 293 K for 12 min (inset).

A similar hysteresis has been measured by Fanggao *et al.* [7] on a pure compound and it was not measured in superconducting $Nd_{1.85}Ce_{0.15}CuO_4$. In a similar way we note that Zn-doped compounds show a less marked mismatch between cooling and heating; furthermore, a larger Zn doping induces a more marked dependence of the elastic constants of $Nd_2Cu_{1-x}Zn_xO_4$ on temperature in heating measurements. Zn-doped samples show a slope velocity change *vs.* temperature at T_1 and T_2. In Fig. 4 we have another set of velocity measurements with a brief isotherm performed at $T=293$ K.

4. Discussion

Let us first take into account the attenuation peak observed at T_1 on the pure and doped specimens (Fig. 1).

In the pure Nd_2CuO_4 the Néel temperature occurs at 255 K [3]; thus anomalous behaviour in attenuation and velocity is expected [5].

Moreover, an attenuation peak in the temperature range 240–260 K has been recently observed by different workers on other cuprate systems such as $YBa_2Cu_3O_{7-x}$ [8, 9], $ReBa_2Cu_3O_{7-x}$ [9] and $YBa_2Cu_4O_8$ [10] and it has been attributed to structural transformations involving the formation of an antiferroelectric or ferroelectric state associated with the ordering of oxygen atoms in some off-centre positions of the structure.

On account of the reported T_N shift at lower temperatures following Zn doping and of the fact that we have not observed a systematic shift in the peak temperature with Zn content, it could seem that no direct correlation exists between this peak and the magnetic state of the specimens.

Indeed we observe a peak more pronounced in the pure compound than in the doped compounds so that a concomitant influence of dissipative phenomena of magnetoelastic and structural nature cannot be excluded. If so, the less pronounced peak observed at T_1 for the Zn-doped paramagnetic specimens could be identified with the similar peak observed for other cuprates [8–10]. This in turn should exclude attenuation mechanisms involving Cu–O chains not present in the Nd_2CuO_4 structure [2].

Two very different trends differentiate cooling from heating measurements and make our hysteresis similar to that reported by Fanggao *et al.* [3]. We believe that such mismatching trends could be caused through magnetoelastic interaction by the onset of magnetic order at $T=255$ K. In general, an increase in sound velocity is expected in a crystalline solid as it is cooled to low temperatures. This behaviour can be observed on cooling up to the onset of dv/v different temperature trend ($T=180$ K) in the undoped compound.

In this second regime ($T<180$ K, well below T_N), magnetoelastic interactions modify the elastic constants and change the temperature dependence (Fig. 2(a)); the new trend is kept for all the heating measurement up to temperatures above T_N where a tendency to close the hysteresis is observed.

5. Conclusions

Preliminary measurements of ultrasonic attenuation on pure and Zn-doped Nd_2CuO_4 compounds have confirmed that the $Zn^{2+} \rightarrow Cu^{2+}$ substitution substantially modify the attenuation and velocity spectra. In particular, we observed specific features including (a) a reduction in the hysteresis behaviour on the velocity *vs.* temperature between cooling and heating, attributable to the strong downward shift of the T_N; (b) a modification of the relaxation strength for the peak shown at T_1 and probably due to a suppression of magnetoelastic contribution to the attenuation in Zn-doped compounds and (c) a broadening of the peak observed at T_2.

Further measurements are in progress to gain further data and to clarify better the connections between the magnetic state and micromechanism at the origin of attenuation and velocity variations.

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