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An ultrasonic study of superconducting and non-superconducting $GdBa_2Cu_3O_{7-x}$

D P Almond, Qingxian Wang, J Freestone, E F Lambson, B Chapman and G A Saunders

Schools of Physics and Materials Science, University of Bath, Claverton Down, Bath BA2 7AY, UK

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Abstract. Detailed measurements are presented of ultrasonic wave velocity and attenuation in the orthorhombic, superconducting and the tetragonal, non-superconducting forms of $GdBa_2Cu_3O_{7-x}$. The orthorhombic state data display a sharp elastic transition at about 240 K which is absent from that of the tetragonal state; however, x-ray diffraction measurements show no evidence of a structural phase transition. The lattice thermal expansion is found to be fairly isotropic. The elastic response in the superconducting state is found to be dominated by conventional anharmonic and anelastic phenomena: no effects that can be specifically attributed to the formation of the superconducting state have been detected. The ultrasonic velocity and attenuation data are explained by the presence in the tetragonal state of one and in the orthorhombic state of two thermally activated anelastic relaxation mechanisms which are attributed to various oxygen vacancy hopping processes.

1. Introduction

Although the elastic properties of the ceramic high-temperature superconductors have been investigated by numerous groups throughout the world, little consensus has emerged about the effect on them of the formation of the superconducting state. In the case of the A15 compounds, once described as the high-T_c superconductors, the elastic properties were strongly connected to the development of superconductivity, elastic mode softening acting as a precursor to superconductivity. A similar softening does occur in the lanthanum-based compounds (Bishop *et al* 1987a, Horie *et al* 1987, Luthi *et al* 1987) but it is not found in the higher-transition-temperature yttrium- and bismuth-based compounds. The yttrium compound, $YBa_2Cu_3O_{7-x}$ (YBCO) has been investigated the most extensively, yet for this compound there are wide variations between the experimental results. The earlier measurements, like our own (Almond *et al* 1987a, b), were performed on what had been assumed to be 'good' superconducting material. Samples were of high density—95% of the theoretical value—containing large well formed, well connected grains. Although excellent ultrasonic wave propagation was achieved in these samples, the results lacked reproducibility, showing significant run-to-run variations, and were characterised by extensive warming-versus-cooling hysteresis (Almond *et al* 1987a, b, Muller *et al* 1987, Ewert *et al* 1987, Lang *et al* 1988). It has since been established (Yamamoto *et al* 1988, Alford *et al* 1988) that such high-density samples are exceptionally difficult to anneal fully to achieve the desired O_7 state, and that residual

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internal stresses may significantly affect the elastic properties because of their extreme sensitivity to applied stress (Almond *et al* 1988b). Later work (Lemmens *et al* 1988, Bhattacharya *et al* 1988, Jerico *et al* 1988), on material of smaller grain size and often lower density, was more consistent, although there is still uncertainty about the influence of the superconducting transformation on ultrasonic wave propagation. This is caused in part by the absence of comprehensive data: the temperature range of the studies being too narrow, data for only one acoustic mode being presented, only one of either velocity or attenuation being presented, inadequate details being supplied of sample properties and superconducting characteristics. The confusion has also been caused, in our view, by a failure to recognise the characteristics of conventional, non-superconductive, phenomena that can also occur in the vicinity of T_c. The purpose of this paper is to present a comprehensive study of the elastic properties of a low-density, small-grain-size sample of $GdBa_2Cu_3O_{7-x}$ (GDCO) in a well annealed orthorhombic state and also in the non-superconducting tetragonal state. The data are found to be dominated by conventional anharmonic and anelastic relaxation phenomena which produce effects that have been previously described as either mode softening at T_c or modulus hardening below T_c. A strong elastic transition is also found in the range 210–230 K in the orthorhombic state but not in the tetragonal state. The data show no evidence of the superconducting phase transition having any effect on the elastic reponse.

2. Experimental techniques

The GDCO material studied was prepared by reacting appropriate proportions of Gd_2O_3, BaO and CuO at 940 °C for 48 h in air. The product was ground into a fine powder, pressed into cylindrical pellets (about 7 mm in diameter, and 9 mm long), sintered at 940 °C in an oxygen flow for 48 h and then cooled slowly to room temperature. The end faces of the sample used for ultrasonic measurements were polished flat and parallel to about 10^{-4} rad. The density of this sample was 5549 kg m^{-3}, indicating its mean porosity to be 0.22 (assuming an x-ray density of 7138 kg m^{-3} for GDCO). Microstructural examination revealed the material to be uniformly porous with pore sizes in the range 5–15 μm and to have a grain size of predominantly less than 5 μm. Subsequent to the completion of the study of the sample in its superconducting state, it was heated in vacuum to 700 °C for 24 h to reduce its oxygen content and to convert it to the non-superconducting tetragonal state.

Conventional ultrasonic pulse echo techniques were employed to make measurements of sound velocity and attenuation in the sample. Quartz transducers, bonded to a sample end face using Nonaq stop-cock grease, were used to generate and detect the ultrasonic waves. Sound velocity measurements were made by the pulse echo overlap method (Papadakis 1967) to an accuracy of better than 1 part in 10^4. The standard transducer correction (Kittinger 1977) was incorporated in the analysis. Changes in ultrasonic attenuation were monitored by the pulse comparison technique (Roderick and Truell 1952) to an accuracy of 0.1 dB in echo amplitude. At all times at least five well resolved ultrasonic pulse echoes were available for measurement, ensuring that true changes in sample attenuation were being recorded.

The sample was cooled to liquid helium temperature in a vacuum cryostat back-filled with a reduced atmosphere of dry nitrogen or helium exchange gas. The sample temperature was monitored with an accuracy of better than one degree using a gold–

iron thermocouple bonded to the sample and cooling and warming rates of less than one degree per minute were used throughout.

After the ultrasonic experiments had been completed the sample was characterised by four-lead resistivity and AC susceptibility measurements at temperatures down to 77 K.

GDCO powder from the same batch as that used to make the ultrasonic sample was analysed by x-ray diffractometry at temperatures down to 92 K. Extensive measurements were made between 200 and 250 K to seek evidence of any lattice parameter changes that might be consistent with a phase transition in this temperature range.

3. Experimental results

Measurements of the velocities and relative attenuations of longitudinal and shear waves in the temperature range 4.2 to 290 K of the sample in both the superconducting and the outgassed tetragonal state are shown in figure 1. Warming-versus-cooling hysteresis was found in the velocity data of the sample in the orthorhombic state but not in the tetragonal state. No hysteresis was found in the attenuation peaks in either state. Both longitudinal and shear wave attenuation peaks occurred at the same temperature for a particular frequency. The peak temperature was found in each case to rise in temperature with frequency, as is shown in the longitudinal wave data for the tetragonal state. The temperature dependences of the electrical resistance and the magnetic susceptibility of the sample in both states are shown in figure 2. The lattice parameters of the material in the orthorhombic state measured between 92 and 293 K using x-ray diffractometry are shown in figure 3. The lattice parameters at 293 K were $a = 3.925 \pm 0.002$ Å, $b = 3.863 \pm 0.002$ Å and $c = 11.755 \pm 0.002$ Å; values of $a = b = 3.89$ Å and $c = 11.73$ Å were obtained by Hor *et al* (1987).

4. Thermal expansion tensor components

The lattice parameter temperature dependences have been fitted by a least-mean-square procedure which leads to the thermal expansion tensor components (table 1; measurements of α_{ii} are also reported here for YBCO). The mean linear thermal expansion coefficients are in good agreement with those measured dilatometrically for YBCO ($\alpha = 1.22 \times 10^{-5}\,K^{-1}$ at 300 K; White *et al* 1988) and GDCO ($\alpha = 1.2 \times 10^{-5}\,K^{-1}$ at 270 K; Kadowaki *et al* 1988). The lack of anisotropy shown by these thermal expansion tensor components gives useful insight into the relative strengths of the inter-atomic binding forces in different directions in these materials. A feature of anisotropic crystals is elastic cross linking between the thermal expansion in the principal directions. These contributions can be determined from Grüneisen functions but this requires knowledge of the single-crystal elastic constants. However, the similarity of α_{11}, α_{22} and α_{33} indicates that the anisotropy of the inter-atomic binding forces may not be large. In layer-like crystals binding between the successive layers tends to be weaker than that due to intra-layer forces; vibrational modes are more easily excited in the softer direction, so the thermal expansion and linear compressibility are greater in this direction. With increasing temperature the lower-energy phonons in the more weakly bound direction are excited first, so α_{33} would be expected to be larger than α_{11} or α_{22} if GDCO or YBCO were layer-like with weaker inter-layer bonding along the c-axis direction. However, the

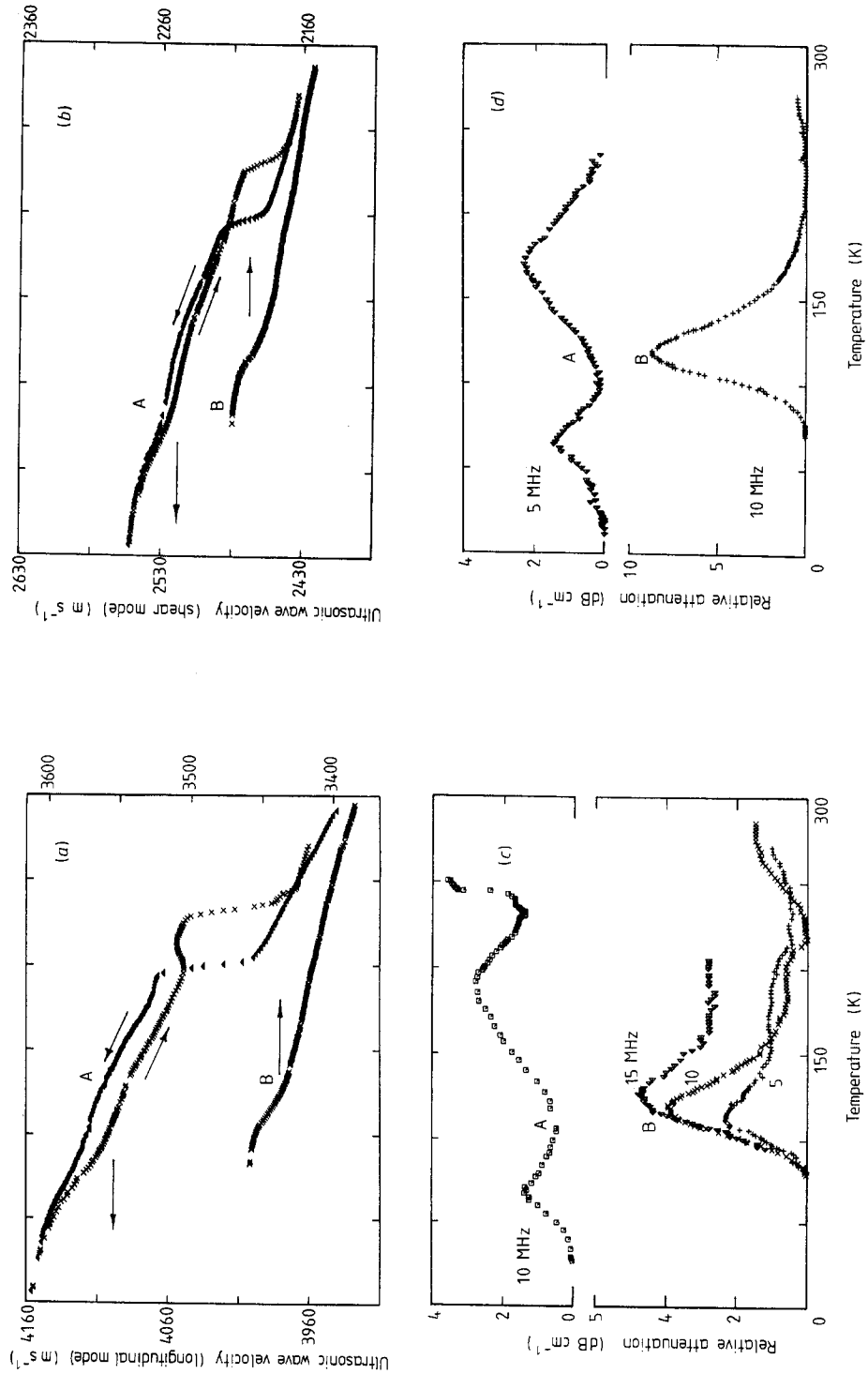

Figure 1. The temperature dependences of the longitudinal (*a*) and shear (*b*) wave velocities and the longitudinal (*c*) and shear (*d*) wave attenuations in both the (A) orthorhombic and (B) tetragonal states of GDCO.

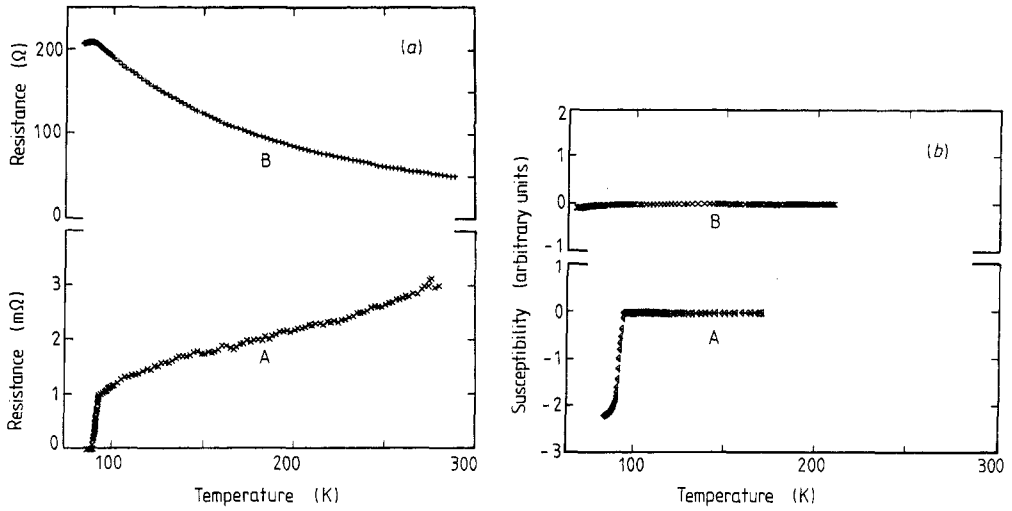

Figure 2. The temperature dependences of the electrical resistance (*a*) and the magnetic susceptibility (*b*) of GDCO in its (A) orthorhombic and (B) tetragonal states.

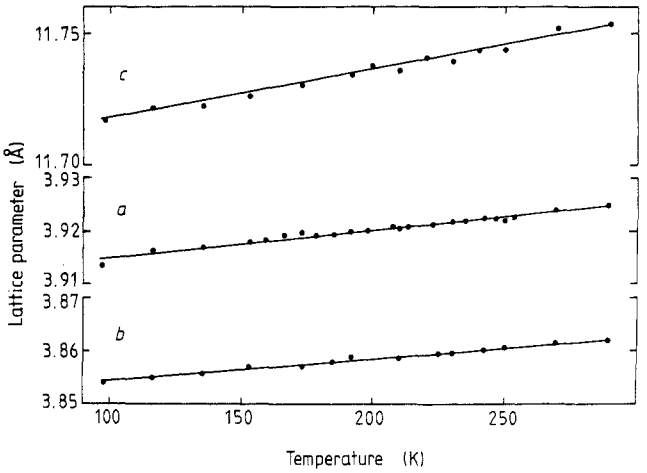

Figure 3. The temperature dependences of the lattice parameters of orthorhombic $GdBa_2Cu_3O_{7-x}$.

Table 1. The thermal expansion tensor components of orthorhombic $GdBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$.

	$GdBa_2Cu_3O_{7-x}$	$YBa_2Cu_3O_{7-x}$
α_{11}	$(1.22 \pm 0.03) \times 10^{-5}\,K^{-1}$	$(1.09 \pm 0.04) \times 10^{-5}\,K^{-1}$
α_{22}	$(1.12 \pm 0.03) \times 10^{-5}\,K^{-1}$	$(1.07 \pm 0.04) \times 10^{-5}\,K^{-1}$
α_{33}	$(1.64 \pm 0.03) \times 10^{-5}\,K^{-1}$	$(1.07 \pm 0.04) \times 10^{-5}\,K^{-1}$
Mean linear thermal expansion	$1.3 \times 10^{-5}\,K^{-1}$	$1.1 \times 10^{-5}\,K^{-1}$
Volume thermal expansion	$(3.98 \pm 0.09) \times 10^{-5}\,K^{-1}$	$(3.23 \pm 0.12) \times 10^{-5}\,K^{-1}$

similarity between the three tensor components implies that inter-atomic binding forces are probably similar in magnitude both between and within the layers as was found for $Bi_2CaSr_2Cu_2O_8$ (Almond *et al* 1988a).

5. The Debye temperature

Ultrasonic wave velocity measurements relate to the long-wavelength acoustic phonons, which are the only modes to be excited to any extent at liquid helium temperatures, and therefore enable the elastic Debye temperature θ_D^{el} to be obtained from

$$\theta_D = (h/k)(3N/4\pi)^{1/3} V_m. \tag{1}$$

Here V_m, the mean Debye velocity is given by

$$V_m = [\tfrac{1}{3}(1/V_L^3 + 2/V_S^3)]^{-1/3}. \tag{2}$$

Determination of θ_D^{el} requires knowledge of the elastic constants B^m and C_{44}^m and hence ultrasonic wave velocities V_L^m and V_S^m of the GDCO matrix. Thus the elastic constants measured in the porous ceramic need to be corrected for the effects of porosity ($n = 0.22$). To do this, a theoretical treatment of ultrasonic wave propagation in an isotropic solid containing a uniform distribution of pores (Cankurtaran *et al* 1988) has been applied to the experimental data for B^m and C_{44}^m measured at 4.2 K. This leads to low-temperature values of the bulk B^m ($=8.46 \times 10^{10}$ N m^{-2}) and shear C_{44}^m ($=6.45 \times 10^{10}$ N m^{-2}) moduli of the non-porous matrix of GDCO itself. These values correspond to a longitudinal velocity of 4937 m s^{-1} and a shear velocity of 3036 m s^{-1} and a Debye velocity V_m of 3350 m s^{-1} at 4.2 K and to an elastic Debye temperature of 426 ± 15 K. That of the tetragonal GDCO is 400 ± 15 K. Corrections for thermal contraction for sample length and density have been included. Specific heat measurements made between 240 and 290 K show Debye-type behaviour with θ_D equal to 614 K (Heremans *et al* 1987). Both optical and acoustic phonons (and possibly spin waves) in states across the Brillouin zone must contribute to the specific heat and hence to the Debye temperature in this temperature range. By comparing the limiting value C_∞ of the fitted Debye function to the Dulong–Petit value $3n_ik_B$, where n_i is the number of ions per mole, Heremans *et al* (1987) found a ratio $C_\infty/3n_ik_B$ of 1.38, and suggested that the elastic Debye function accounts for about 70% of the total specific heat.

6. Discussion of the anharmonic and anelastic effects in the orthorhombic and tetragonal forms of $GdBa_2Cu_3O_{7-x}$

The low-temperature ultrasonic characteristics that have been found in GDCO (figure 1) are similar to those that have been obtained in ultrasonic and lower-frequency internal friction studies of YBCO. A striking feature of the data is the abrupt change in the sound velocities in the temperature range 200–230 K, which is completely absent in the oxygen-reduced, non-superconducting sample. Rather similar, although not so distinctive, phenomena have been observed in internal friction measurements at kilohertz frequencies on YBCO (Cannelli *et al* 1988a, b). They were attributed to a possible phase transformation at about 240 K, evidence for which had been obtained by others (Toulouse *et al* 1988). In addition, there have been reports of superconductivity detected by the reverse AC Josephson effect (Chen *et al* 1987), electrical resistance drops (Ovshinsky

et al 1987), specific heat peaks (Laegreid *et al* 1987) and T_c enhancement effects (Bhargava *et al* 1987) associated with the same temperature. There have also been reports (Srinivasan *et al* 1988, Cheng *et al* 1988) of subtle lattice parameter changes at these temperatures in YBCO, indicating a structural phase transition. However, the detailed lattice parameter measurements made here in this temperature range (figure 3) show no evidence within experimental error of a structural phase transition in our samples of GDCO. Consequently, we do not attribute the high-temperature abrupt changes in the elastic response to an intrinsic structural phase transition. Rather our data seem consistent with suggestions, such as those of Cannelli *et al* (1988), that these phenomena, and the hysteresis, are associated with the twinned structure of the orthorhombic phase. Indeed, the obvious change in the microstructure of the sample, caused by oxygen reduction, was an elimination of the twinning of the crystallites and in the untwinned tetragonal state the sample shows no elastic anomalies at high temperatures.

The characteristics of the elastic response of GDCO in the vicinity of T_c and at lower temperatures again are similar to those that have been variously reported for YBCO (Bhattacharya *et al* 1988, Bishop *et al* 1987b, Levy *et al* 1989). Some of the velocity data below the higher-temperature elastic transition, discussed above, have been replotted in figure 4(*a*) to emphasise the effects about T_c. The data of the sample in its superconducting state show a distinct inflection, at first sight corresponding to a modulus softening, at a temperature corresponding closely to T_c. A similar effect is evident in recent single-crystal data for YBCO (Hoen *et al* 1988, Saint-Paul *et al* 1989) and GDCO (Saint-Paul *et al* 1989). However, the data on the oxygen-reduced, non-superconducting sample (figure 4(*b*)), also show an inflection at the higher temperature of about 118 K. An examination of the attenuation data for the sample in this state (figures 1(*c*) and 1(*d*)), reveals an attenuation peak at a similar temperature for both longitudinal and shear modes. Consequently, the inflection in velocity is attributed to the natural velocity change (Nowick and Berry 1972) that accompanies an elastic loss peak. This loss peak has been found to be associated with a thermally activated process, as will be discussed below. Similar attenuation peaks were found in the superconducting state data (figures 1(*c*) and 1(*d*)), again for both longitudinal and shear modes. The velocity increase below T_c can also be interpreted as being associated with the attenuation peak at about 65 K rather than the occurrence of superconductivity.

The temperature dependences of the velocities can be further clarified by consideration of conventional anharmonic effects. In general, an increase in sound velocity is expected in a crystalline solid as it is cooled to low temperatures. This is a consequence of the anharmonic nature of atomic oscillators which has been shown, phenomenologically, by Lakkad (1971) to lead to the temperature dependence given by

$$F(T/\theta_D) = 3(T/\theta_D)^4 \int_0^{\theta_D/T} \{x^3[\exp(x) - 1]^{-1}\} \quad dx. \tag{3}$$

This expression may be compared with a particular set of data if the Debye temperature θ_D ($\theta_D = \theta_D^{el}$, see § 5) of the solid is known. The full curves fitted to the data in figure 4 were obtained utilising the Debye temperatures for the non-porous matrix, obtained as discussed above, and the magnitudes of the velocities at the two points indicated, chosen well away from the anomalies. The deviations of the actual data from the anharmonic prediction emphasise their connections with the attenuation peaks. What is more, the initial part of the apparent softening associated with superconductivity at temperatures between about 80 and 120 K is seen to be no more than the natural change in slope as

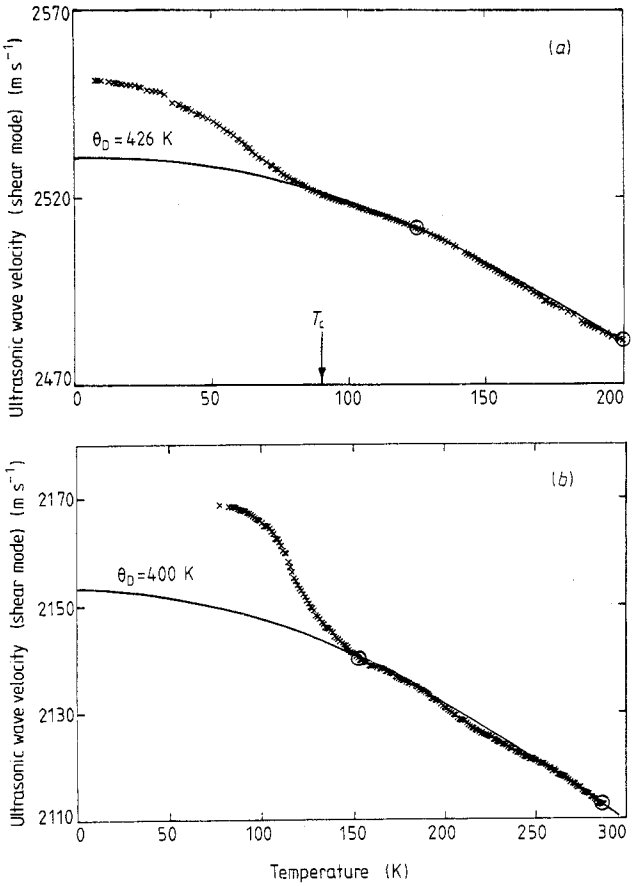

Figure 4. Fits of equation (3) to the temperature dependences of the shear wave velocities of (*a*) GDCO and (*b*) vacuum-annealed GDCO in its orthorhombic (*a*) and tetragonal (*b*) states. The expression was fitted to the data using the values of Debye temperature shown and the magnitudes of the data at the two points indicated.

the temperature falls well below the Debye temperature—i.e. it is exactly the effect that should be observed in any 426 K Debye temperature solid. The inflection in the curve is completed at lower temperatures by the additional stiffening of the lattice associated with the attenuation peak. This is a classical anelastic response in which the compliance of a thermally activated mobile entity is lost at low temperatures as its relaxation rate falls below the frequency of the probing elastic wave. The inflection, or the often reported change of slope or modulus hardening at T_c, seems to be no more than a confusing coincidence. At the often used ultrasonic frequency of 10 MHz, anelastic stiffening begins to become noticeable at temperatures below about 90 K.

Others (Sun *et al* 1988) have also reported attenuation peaks in YBCO at similar temperatures and demonstrated them to be thermally activated. In each case the peaks have been attributed to various possible atomic hops of mobile oxygen atoms; this will be discussed further below. The relaxation rates obtained here are shown plotted in an Arrhenius fashion in figure 5. These were obtained by assuming the attenuation peaks to be approximated by the simple Debye expression in which the peaks occur where

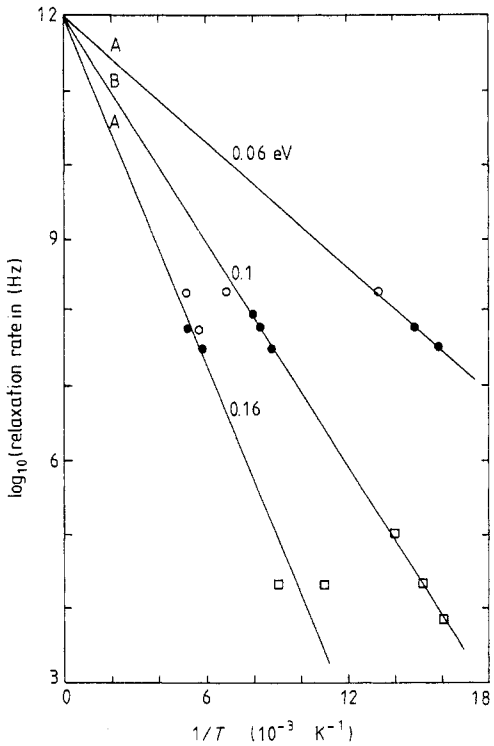

Figure 5. Arrhenius plots of the relaxation rates obtained as indicated in the text from the attenuation peaks (figures 1(*c*) and 1(*d*)). Ultrasonics: ●, this work; ○, Lemmens *et al* (1989). Internal friction: □, Cannelli *et al* (1988a). A: orthorhombic; B: tetragonal.

$\omega\tau = 1$ (ω is an angular frequency of the acoustic wave and τ is the relaxation time). The magnitudes of the relaxation rates of the species responsible are remarkable. The relaxation rate τ^{-1} in the superconducting sample at the 65 K peak is about 63 MHz. At the same temperature the ion hopping rate in sodium β-alumina, a notable fast-ion conductor having an exceptionally high diffusivity, is less than 100 Hz. The data for the tetragonal state are shown to agree well with those obtained by Cannelli *et al* (1988a) at much lower frequencies in YBCO and by Lemmens *et al* (1989) at similar frequencies in YBCO. A relaxation process characterised by the very low activation energy of about 0.1 eV and a reasonable attempt frequency of about 10^{12} Hz can be obtained from the data. For the superconducting state there are no equivalent low-frequency data but, if we may assume a similar attempt frequency, the higher recorded relaxation rate indicates the activation energy to have fallen to about 0.06 eV. The additional datum point is taken from the 30 MHz work of Lemmens *et al* (1989) which shows evidence of a lower-temperature relaxation peak at the temperature indicated. The higher-temperature attenuation peak is also thermally activated indicating a second anelastic process to occur in the orthorhombic state. Relaxation rates obtained from our data (figures 1(*c*) and 1(*d*) at 5 and 10 MHz and from those of Lemmens *et al* (1989) at 10 and 30 MHz are also plotted in figure 5. The line drawn through the data, assuming the same attempt frequency of 10^{12} Hz, indicates the second relaxation process to have an activation energy of about 0.16 eV. Extrapolation of the data for this second relaxation process to low temperatures leads to a prediction of absorption peaks near T_c for internal friction measurements that are made at frequencies of a few kilohertz. In fact, the 3.6 kHz data of Cannelli *et al* (1988a) show a twin absorption peak, with relaxation rates indicated in

figure 5, in the predicted temperature range. Other workers (Hoen *et al* 1988, Shi *et al* 1989) have also found internal friction peaks near T_c but unfortunately their measurement frequency was not reported so it is not possible to compare their data with ours. However, we again suggest that an alternative interpretation is that these effects found near T_c are caused by a classical relaxation process and not by the onset of superconductivity. It is indeed confusing that in these materials the two relaxation processes 'conspire' to produce from measurements made by both megahertz ultrasonic techniques and kilohertz internal friction techniques phenomena at temperatures of about 90 K that might well be attributed, albeit incorrectly, to the onset of the superconducting state.

Anelastic relaxation effects in solids appear where the strain fields of the probing elastic wave differentially alter the energies of the various atomic sites available to mobile species. Crystallographically identical sites are affected equally, so only diffusion processes involving hops between crystallographically different sites produce anelastic relaxation effects (Nowick and Berry 1972). Jorgensen *et al* (1988) have produced detailed measurements of the various oxygen site occupancies of YBCO. They find, as expected, the chain sites $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, 0)$ to have equal occupancies of about 0.25 when the material is in the tetragonal state. This high density of vacancies on these sites might be expected to be mobile but, since these sites are crystallographically equivalent, hops between them cannot be responsible for the observed anelastic relaxation phenomena. However, Jorgensen *et al* (1988) also reported the appearance of oxygen vacancies at (0, 0, 0.15), the pyramidal sites of the square-pyramidal-coordinated copper atoms that form the copper–oxygen planes. The discovery of these vacancies provides a possible explanation of the observed relaxation peaks in the form of hops between $(0, \frac{1}{2}, 0)$ and (0, 0, 0.15) sites.

A fully annealed sample with an O_7 oxygen content has an orthorhombic crystal structure with fully occupied $(0, \frac{1}{2}, 0)$ and (0, 0, 0.15) sites and unoccupied $(\frac{1}{2}, 0, 0)$ sites. Such a sample would have no oxygen vacancies and should not exhibit anelastic relaxation effects. However, real bulk samples are rarely produced fully oxygenated throughout and vacancies will be present. It is particularly interesting to find one of the anelastic relaxation effects occurring at lower temperatures in the superconducting sample. As explained above, this indicates the relaxation rate to be enhanced and this is a quite unexpected effect. Recently, Goodenough (1988) has suggested that the intrachain vacancies in YBCO may develop a series of ordered states, dependent on oxygen content. This possibility suggests both the need for a detailed study of anelasticity as a function of oxygen content and provides further reasons for the variability of the data to be found in the literature. It is not possible to identify precisely the processes responsible for the two relaxation processes found in the orthorhombic state but it seems that more than the one suggested for the tetragonal material may be possible. In the orthorhombic state $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$ are no longer equivalent leading to the possibility of anelastic processes involving the hopping between these two sites as well as between these two sites and (0, 0, 0.15).

7. Conclusions

This comprehensive study of both the attenuation and velocity of ultrasonic waves in GDCO has greatly elucidated the elastic response of this material. Measurements showing a softening of elastic constants near T_c or a stiffening below T_c have been found to have been caused by conventional anharmonic and anelastic phenomena. No effect that can

be directly attributed to the formation of the superconducting state has been detected. We believe that changes in slopes of velocity data that have been interpreted as a consequence of the properties of the superconducting state (Millis and Rabe 1988) should be reconsidered as these may well have the same origins as those found here. Measurements of the material in its non-superconducting tetragonal state show clear evidence of the presence of thermally activated entities which we suggest might be oxygen vacancies. Two similar relaxation processes have been identified for the material in the orthorhombic, superconducting state. Considerable further work is necessary to characterise the responses of these in superconducting materials of varying oxygen contents.

The absence of effects attributable to superconductivity is consistent with initial studies of superconductors of the bismuth–calcium–strontium–copper oxide family (Lemmens *et al* 1989). These show no elastic anomalies near T_c, a well behaved anharmonic response and no relaxation peaks at low temperatures.

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