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Anelastic relaxation evidence of very low activation energy processes in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: magnetic chain excitations?

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Abstract. Relaxation rates obtained from a wide range of acoustic loss measurements are explained by introducing three thermally activated processes controlled by activation energies of 0.06, 0.14 and 0.2 eV in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The ultrasonic attenuation peak magnitudes indicate that the interactions responsible originate in at least 10% of unit cells in the bulk of the material. An analysis of spin excitations on the copper–oxygen chains is presented that leads to a series of discrete excitation energies matching those obtained experimentally.

There is now a substantial body of experimental data relating to mechanical relaxation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ which has been recently reviewed by Dominec (1989). These data have been obtained from a variety of techniques covering a frequency range from less than 1 Hz to 1 GHz. In most cases these investigations have been reported as characterisations of the material as determined by the technique concerned. The bulk of the lower frequency (less than 1 MHz) data obtained using classical internal friction monitoring techniques, take the form of a series of internal friction peaks, some of which are found close to T_c . At higher frequencies, where ultrasonic methods are employed, the majority of investigators have concentrated on the variation of sound velocity near T_c and less attention has been paid to ultrasonic attenuation. The ultrasonic sound velocity data have been variously interpreted as showing anomalous modulus hardening below T_c (Bishop *et al* 1987) or as showing reentrant softening at T_c (Datta *et al* 1988). However, recently (Almond *et al* 1989) have suggested that these effects are associated with thermally activated anelastic relaxation processes and that their appearance at T_c is coincidental. These conclusions point to the possibility of rationalising ultrasonic and internal friction data but also raise questions about the origins of the processes responsible for the effects observed. The purposes of this note are: to demonstrate the extent to which much of the mechanical relaxation data may be rationalised; to draw attention to the surprisingly low activation energies of the processes concerned and to the large magnitudes of the effects observed and to investigate the possibility that these effects are caused by an interaction with magnetic chain excitations.

Our earlier work comprised a comparative study of the temperature dependences of ultrasonic attenuation and sound velocity in a superconducting orthorhombic state and in an oxygen reduced, non-superconducting, tetragonal state of a sample of

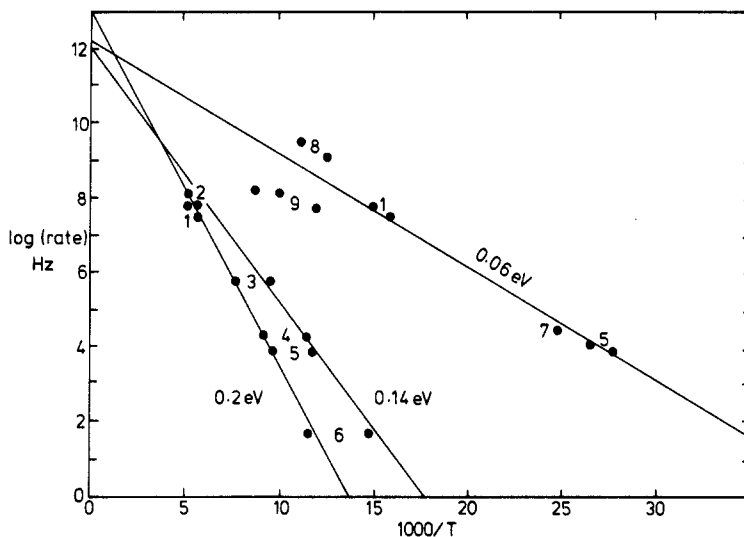


Figure 1. Arrhenius plots of relaxation rates deduced from mechanical loss peaks of: (1) Almond *et al* (1989); (2) Lemmens *et al* (1990); (3) Cheng Xiaohua *et al* (1988); (4) Cannelli *et al* (1988); (5) Duran *et al* (1988); (6) Weller *et al* (1989); (7) Mizubayashi *et al* (1988); (8) Saint-Paul and Henry (1989); (9) Sun *et al* (1988).

$\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$. In the tetragonal state, a single anelastic relaxation attenuation peak was found whose peak temperature rose with ultrasonic wave frequency, indicating an origin in a coupling to a thermally activated entity. Similar phenomena were reported by Cannelli *et al* (1988) in much lower frequency (a few kHz) internal friction measurements of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Both sets of data were found to be consistent with a process characterised by an activation energy of about 0.1 eV and an attempt frequency of about 10^{12} Hz. The ultrasonic data (Almond *et al* 1989) of the sample in its superconducting, orthorhombic, state exhibited two attenuation peaks at temperatures of about 65 and 200 K which were also attributed to thermally activated entities characterised by activation energies of about 0.06 and 0.16 eV and the same attempt frequency of 10^{12} Hz. The widely reported anomalies in sound velocity at T_c were seen to be caused by the anelastic stiffening associated with the lower temperature attenuation peak.

Much of the acoustic loss data of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ obtained by other groups is found to be consistent with the suggested low activation energy anelastic processes. Figure 1 is an Arrhenius plot of relaxation rates obtained from a wide range of data sets collected at frequencies from 8 Hz to 600 MHz. The relaxation rates have been obtained by making the assumption that the various acoustic loss peaks may be approximated by the well-known Debye function, for which the peak occurs where $\omega\tau = 1$ (ω is the angular frequency at which the measurements are made and τ is a characteristic relaxation time). Thus figure 1 shows the variation of relaxation rate (τ^{-1}) versus inverse peak temperature. The many low frequency internal friction studies are characterised by a pair of internal friction peaks at temperatures fairly close to T_c and, in those experiments extended below nitrogen temperature, by a further peak at a much lower temperature. Individually too narrow a frequency range was studied to confirm thermal activation but the collective picture, shown here, is convincing evidence of three low activation energy processes. The 0.16 eV process suggested earlier by us, based on

Table 1. Estimates of concentration N obtained from longitudinal wave attenuation data (Almond *et al* 1989) assuming $B = 1$ eV. Na β -alumina data (Almond and West 1988) are included for comparison.

	Peak temperature (K)	Activation energy (eV)	NB^2 (10^{20} eV cm $^{-3}$)	B (eV)	N (10^{20} cm $^{-3}$)
GdBa $_2$ Cu $_3$ O $_{7-x}$, orthorhombic	65	0.06	1.05	1	1.05
GdBa $_2$ Cu $_3$ O $_{7-x}$, tetragonal	185	0.14, 0.2	5.3	1	5.3
GdBa $_2$ Cu $_3$ O $_{7-x}$, tetragonal	120	0.1	3.0	1	3.0
Na β -alumina	235	0.16	8.4	0.44	43.0

our ultrasonic data, is seen in fact to be caused by a pair of processes whose relaxation rates become similar in the frequency range covered by ultrasonics but that are well resolved by the lower frequency internal friction techniques. Some of the ultrasonic data of other groups fall significantly off the three lines. This is understandable in the case of the very high frequency measurements of Saint-Paul and Henry as these were obtained from a single-crystal sample whilst all the other data are from polycrystalline samples. Sun *et al* (1988) also considered their attenuation data to comprise thermally activated peaks but their relaxation rates are a poor fit here. The reasons for this are unclear, but we suggest the possibility of their samples having a rather different oxygen content from those of the other groups. There is no doubt that, as for many of the other properties of this material, oxygen content has a marked effect on the magnitude and temperature of the acoustic loss peaks (Lemmens *et al* 1990). However, overall there is clear evidence of three thermally activated processes, activation energies 0.06, 0.14 and 0.2 eV, being present in YBa $_2$ Cu $_3$ O $_{7-x}$ in its superconducting, orthorhombic state to add to the 0.1 eV process found earlier (Cannelli *et al* 1988) for it in its non-superconducting tetragonal state.

The magnitudes of the various acoustic loss peaks provide both an indication of the significance of the effects and a means of eliminating some suggestions that might be put forward to explain them. A widely used expression for an anelastic attenuation peak is

$$\alpha = \Delta\omega^2\tau/(1 + \omega^2\tau^2) \quad (1)$$

in which the relaxation strength, Δ , determines the amplitude of the peak and the expression following it is the familiar Debye equation in $\omega\tau$. Δ is related to the physical properties of the material by:

$$\Delta = NB^2/4\pi\rho v^3kT \quad (2)$$

in which N is the concentration of entities contributing to the loss effect, B is the strain dependence of their site energy (a deformation potential), ρ is the density of the solid, v is the velocity of the sound wave concerned, k is the Boltzmann constant and T is absolute temperature. Of these quantities, those in the denominator of equation (2) are all known so the amplitude of the acoustic loss peaks can be taken to provide an estimation of the product NB^2 . Estimates of NB^2 from the attenuation peaks reported (Almond *et al* 1989) are presented in table 1. Also shown in table 1, for comparison, is an estimate of NB^2 for the ionic conductor sodium beta-alumina. It has been well established (Almond and West 1988) that in beta-alumina the acoustic loss peaks are

thermally activated and attributed to interactions with the mobile sodium ions. Since the concentration, N , of these is known, the effective deformation potential B can be assessed. Similar values of B up to about 1 eV are common in other materials. It is notable that the values of the NB^2 product obtained from the attenuation peaks in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ are comparable in magnitude to that produced by the very high concentration of mobile ions in beta-alumina. Conservative estimates of the concentrations of entities responsible for the attenuation peaks in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$, obtained assuming $B = 1$ eV which is at the upper end of values found in materials studied to date, are also listed in the table. Recognising the concentration of unit cells in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ to be $5.6 \times 10^{21} \text{ cm}^{-3}$, we conclude that the entities concerned are present in 10%, or more, of the unit cells.

Anelastic relaxation peaks, of the type under consideration here, are commonly associated with the thermally activated hopping of atoms or ions. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ oxygen is the mobile species and it is natural to consider first the possibility of it being responsible for the effects observed. However, it is now well established (Tu *et al* 1988) that an activation energy of over 1 eV, an order of magnitude larger than those discussed here, controls the diffusion of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. This diffusion process has recently been studied by classical internal friction techniques (Xie *et al* 1989) (a 1 Hz inverted torsional pendulum) and distinctive absorption peaks have been found at temperatures of about 500 K, as expected for a process controlled by an activation energy of about 1 eV. In that work, samples having a range of oxygen contents were studied and the amplitude of the absorption peak was found to increase rapidly with oxygen deficiency. It is of interest to note that the sample having an oxygen content closest to our superconducting $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ sample, one annealed at 400 °C in the usual way, exhibited an absorption peak amplitude (expressed in units of inverse Q) of 11.4×10^{-3} whilst our ultrasonic attenuation peaks correspond to Q^{-1} of 2.5 and 4.4×10^{-3} .

Several conceivable explanations of the low activation energy absorption peaks may be eliminated by their large magnitudes, i.e. by the large magnitude of the NB^2 products. Surface, grain boundary or twin sources could not possibly produce such large effects. The hopping of absorbed impurities, including hydrogen, can be eliminated for the same reasons. There remain intrinsic effects that must be found in at least 10% of the unit cells. Now, in addition to being superconducting, these materials also exhibit a range of intrinsic magnetic properties. It is well established (Lüthi *et al* 1970) that ultrasonic waves interact strongly with magnetic excitations. Below we consider the feasibility of such excitations explaining the effects introduced here.

In order to explain the low activation energies above, we now consider intrinsic atomic excitations at these low energies. Most of the atoms in these high T_c superconductors are non-magnetic closed-shell and unable to participate in the low energy excitations. Only the planes and chains of copper and oxygen are likely candidates. There is little evidence of these discrete excitations in the lanthanum compounds which suggests that they are associated at least in part with the chains. Firstly, let us consider the planes and the excitations present in them.

At oxygen concentrations below 6.5, the system is an antiferromagnetic insulator and the gap to charged excitations is the order of 1 eV and therefore too large to explain the observed excitations. The copper atoms in the planes have ordered spin- $\frac{1}{2}$ moments and the low energy excitations are spin waves. The energy scale of $J \approx 0.1$ eV is certainly the right order of magnitude, but the spin waves yield a smooth density of states without the discrete characteristics required. At oxygen concentrations above 6.5, the system

becomes a superconductor and there are charged excitations at low energies above the superconducting gap. These excitations have been studied using photoemission (Olson *et al* 1989) and a coherent band of about the required energy scale has been observed. Although the coherent excitations are fairly flat, it is also true (Sawatzky 1988) that the hybridisation matrix element controlling the delocalisation is larger than the spin exchange constant, and would be expected to yield excitations at higher energies (≈ 0.5 eV).

The chains have the same interaction mechanisms as the planes, but the local connectivity is very different and explains the discreteness of the required spectrum. As the oxygen concentration is increased, various other species and chain segments form. Up to oxygen concentration 6.5, whilst the system remains insulating, we expect to find Cu^{2+} , $\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}$ and $\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}$ species, where the first and third have equal concentrations—in order to maintain charge conservation. As soon as concentration 6.5 is reached, the Cu^+ is used up, and we expect to start making oxygen holes O^- , which lead to the superconductivity. Above 6.5 we expect to find longer chain segments, namely $\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}$ and $\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}$, segments which cannot be excluded above 6.75 and 6.8 respectively. The first holes are expected to migrate into the planes in order to make use of the extra hybridisation from the higher coordination, but the Coulomb energy will also play a role and soon holes will also be found in the chains. It is the discrete nature of the possible chain segments that is to be expected to yield the discrete spectrum required, but which excitations would be expected to contribute?

There are two reasons to believe that the charged excitations may be irrelevant. Firstly, the effect is observed in the insulating compound for which the gap to charged excitations is an order of magnitude too large, ≈ 1 eV (Nucker *et al* 1987). Secondly, the hybridisation energy, which sets the scale for the hole energy on a chain segment, is too large ≈ 0.5 eV (Sawatzky 1988).

Now let us explore the possibility of spin excitations in the chain segments as the source of the low activation energies. The exchange constant is not expected to change dramatically between spins in the planes, where it was determined by spin wave measurements (Rossat-Mignod *et al* 1989), and the chains, in which we are currently interested. We expect $J \approx 0.1$ eV which is precisely the desired energy scale.

In table 2 we present low energy excitation energies of Heisenberg chain segments. These energies have been calculated numerically using exact diagonalisation of the relevant clusters, both directly, for small clusters, and using the Lanczos algorithm for the larger clusters.

Although at the temperatures of experimental interest the chain segments will be found predominantly in their ground state, there will be well-defined equilibrium populations of chain segments in excited states. It is conceivable that the modulation of the exchange constants, by the elastic strain fields of acoustic waves, will disturb these populations. Where such effects occur, the conditions are essentially identical to those of the perturbed 'two-level systems evoked by Jackle *et al* (1976) to explain acoustic loss and dispersion at low temperatures in glasses. Here, the excitations of interest are likely to be a spin fluctuation exchanged between two neighbouring chain segments, by modulation of the small exchange constant between them, or perhaps a direct excitation on a single chain segment mediated by the modulation of the bond lengths themselves. In order to deduce the possible excitation energies, it is crucial to consider the *selection rules*. The spin is required to be conserved in an excitation, and this is a severe constraint on the possible excitations allowed.

Table 2. Heisenberg spin chain excitations in units of J .

Number of spins	Ground state		First excited state		Second excited state	
	Spin	Energy	Spin	Energy (versus GS)	Spin	Energy (versus GS)
1	$\frac{1}{2}$	-0.0000				
2	0	-0.7500	1	1.0000	—	—
3	$\frac{1}{2}$	-1.0000	$\frac{1}{2}$	1.0000	$\frac{3}{2}$	1.5000
4	0	-1.6160	1	0.6589	1	1.3660
5	$\frac{1}{2}$	-1.9279	$\frac{1}{2}$	0.7208	$\frac{3}{2}$	1.1189
6	0	-2.4936	1	0.4916	1	1.0721
7	$\frac{1}{2}$	-2.8362	$\frac{1}{2}$	0.5573	$\frac{3}{2}$	0.8848
8	0	-3.3749	1	0.3927	1	0.8712

For direct transitions this restricts attention to odd chain segments that have spin- $\frac{1}{2}$ ground states and the only relevant transitions that conserve total spin are listed below

Number of spins	Excitation energy (units of J)
3	1.0000
5	0.7208
7	0.5573

Although these excitations are theoretically permissible, it is unlikely that they are the cause of the observed effect. Once again it is a sort of selection rule that leads to the problems. This time it is inversion symmetry about the centres of the chain segments that causes concern. The Hamiltonian is conserved under inversion symmetry and so the eigenstates exhibit the symmetry. The $2 + 4n$ -membered chain ground states are odd while the other chain segment ground states are even. The fact that causes the problems is that for all situations the first excitation has opposite inversion symmetry to the ground state. In order to excite a direct transition, the probe (in our case a sound wave) must break the local inversion symmetry. The truth is that sound waves are very long wavelength objects which, considered as strains, maintain the local symmetries changing only the local scale. The sound waves are very unlikely to excite modes directly and so we now consider excitations involving neighbouring chain segments, excitations that are not restricted by any inversion symmetry problems.

For exchange between neighbouring chain segments, *both* segments need to be excited. An odd chain has a degenerate ground state and so can exchange a spin fluctuation at zero energy, but an even chain must lose energy. There is a fair amount of experimental evidence for zero-energy spin excitations coming from quasi-elastic neutron scattering and we would explain these as some 'free spins' associated with odd chain segments. The permissible excitations are exhibited in table 3 where they are simply sums of pairs.

Table 3. Spin conserving excitations of pairs of chain segments in units of J , constructed from table 2 as explained in the text.

Number of spins	Spins	Energy of excitation	Number of spins	Spins	Energy of excitation
1, 2	$\frac{1}{2}$ 0	1.0000	2, 2	0 0	2.0000
2, 3	0 $\frac{1}{2}$	1.0000	3, 3	$\frac{1}{2}$ $\frac{1}{2}$	1.0000
1, 3	$\frac{1}{2}$ $\frac{1}{2}$	1.0000	3, 3	$\frac{1}{2}$ $\frac{1}{2}$	2.0000
3, 4	$\frac{1}{2}$ 0	0.6589	4, 4	0 0	1.3178
3, 4	$\frac{1}{2}$ 0	1.6589	5, 5	$\frac{1}{2}$ $\frac{1}{2}$	0.7208
4, 5	0 $\frac{1}{2}$	0.6589	5, 5	$\frac{1}{2}$ $\frac{1}{2}$	1.4416
4, 5	0 $\frac{1}{2}$	1.3797	6, 6	0 0	0.9832
5, 6	$\frac{1}{2}$ 0	0.4916	2, 4	0 0	1.6589
5, 6	$\frac{1}{2}$ 0	1.2124	3, 5	$\frac{1}{2}$ $\frac{1}{2}$	0.7208
			3, 5	$\frac{1}{2}$ $\frac{1}{2}$	1.7208

As the oxygen concentration varies from 6.0 to 7.0, so the concentration of the different chain lengths varies from dominantly short chains to dominantly long chains. The amplitudes of the observable excitations will vary accordingly. For tetragonal crystals with chain lengths of only 1, 2 and 3 we expect excitations of J and $2J$, whereas for orthorhombic crystals with chains lengths 2, 3, 4 etc we expect also to find $0.66J$ and modes near $1.5J$. These values are in quite remarkable agreement with the experimental activation energies.

Although we have demonstrated theoretically that excitations should be present with energies matching the activation energies obtained from the mechanical relaxation data, we do not regard this as being 'proof' that the mechanical relaxation effects originate in these excitations. Such a 'proof' requires detailed knowledge of inter-chain segment exchange coupling effects and a careful examination of the affect of mechanical strain on the energies of the various cluster states. This amounts to a quantification of the deformation potential B being necessary to determine the plausibility of experimental effects, of the magnitude reported here, originating in cluster excitations. Whilst such a task is feasible, in principle, the paucity of experimental information about inter-chain coupling leads us to consider it beyond the scope of this note.

In conclusion, it has shown that data obtained in a wide range of mechanical relaxation studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ may be interpreted by anelastic couplings to particularly low energy intrinsic excitations. An analysis of spin excitations in the chains reveals a series of discrete excitations with energies that match those obtained in mechanical relaxation experiments. Such a discrete spectrum is rather unusual in crystalline solids.

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