

Ultrasonic anomalies and phase transitions in the $Y_1Ba_2Cu_4O_8$ and the $Y_{1-x}Ca_xBa_2Cu_4O_8$ systems*

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Abstract

Ultrasonic and specific heat measurements have been performed on single-phase $Y_1Ba_2Cu_4O_8$ (Y1:2:4) and $Y_{1-x}Ca_xBa_2Cu_4O_8$ with $x=0.1$. In the temperature range from 65 K to 320 K several anomalies were recorded. Among these were a pronounced elastic anomaly near 260 K in the pure Y1:2:4, a phase transition at 150 K seen both in specific heat and in elastic behavior, and another phase transition at 81 K in $x=0.1$ substituted material. Thermal hystereses below 200 K were also studied.

1. Introduction

The $Y_1Ba_2Cu_4O_8$ superconducting compound is interesting for several reasons in the context of thermal properties of Y-based materials. One important reason for this lies in the similarities and differences compared with the $Y_1Ba_2Cu_3O_7$ (Y1:2:3) system. This offers a possibility of testing out ideas related to one of them against the other, in some cases because the results should be similar, in other cases because they should be different. An example of such a situation is the stability of oxygen in the Y1:2:4 compound [1] *vs.* the corresponding instability in Y1:2:3. Another example is the absence of twinning in Y1:2:4 [2] compared with the extensive twinning in Y1:2:3. Both of these examples are relevant to issues addressed in the present paper, which partly deals with structural aspects through their influence on elastic properties. When adding to this also the granularity and the consequent possibility for local reorientation of grains, one realizes that a host of effects may be expected in elastic measurements.

2. Experimental details

The pure Y1:2:4 samples were prepared by solid-state reaction using Ar and O_2 gases during hot isostatic pressure treatment [3]. One sample labeled Y124-1 had a T_c onset of 76 K as measured by magnetic susceptibility. The other one, labeled Y124-2, was prepared by the same method and had a sharp T_c onset of 81 K. Their bulk densities were 3.97 and 4.55 g cm⁻³ for Y124-1 and Y124-2, respectively. X-ray measurements showed

that both specimens were single phase without any trace of other Y-based phases.

The Ca-substituted samples were prepared in a fashion similar to the pure materials. In this case the absence of the Y1:2:3 and $Y_2Ba_4Cu_7O_{15-y}$ phases was confirmed. Again the materials were single phase superconducting with a T_c onset at 89 K for $x=0.1$.

Elastic measurements were performed using standard Matec equipment with automatic time-of-flight technique. Ultrasonic velocity and attenuation, with resolution of 50 p.p.m. and 0.1 dB cm⁻¹, respectively, were recorded during cooling and heating. The temperature was stabilized to within 0.5 mK of set value. Specific heat measurements were made using an automatic AC calorimeter. During specific heat measurements, the temperature was regulated to within 5 mK of each set temperature for at least 200 s prior to measurements, in order to ensure that thermal equilibrium had been reached before measurement.

Longitudinal and transverse waves of 10 MHz and 15 MHz were employed in elastic measurements of $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. Specific heat measurements were made on $Y_1Ba_2Cu_4O_8$ and on $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$.

3. Results and discussion

3.1. $YBa_2Cu_4O_8$

Since the pure Y1:2:4 material serves as a natural reference with respect to the Ca-substituted case, we discuss some results on this system first.

3.1.1. Anomalies near 260 K

The most important findings are shown in Figs. 1 and 2 for the Y124-1 sample. These results are quite

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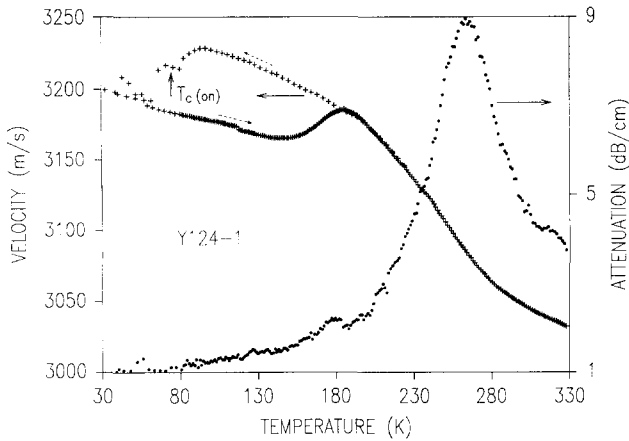


Fig. 1. Ultrasonic velocity and attenuation in Y124-1 measured with longitudinal waves at 14 MHz. The dashed-line arrows indicate the direction of the thermal cycle.

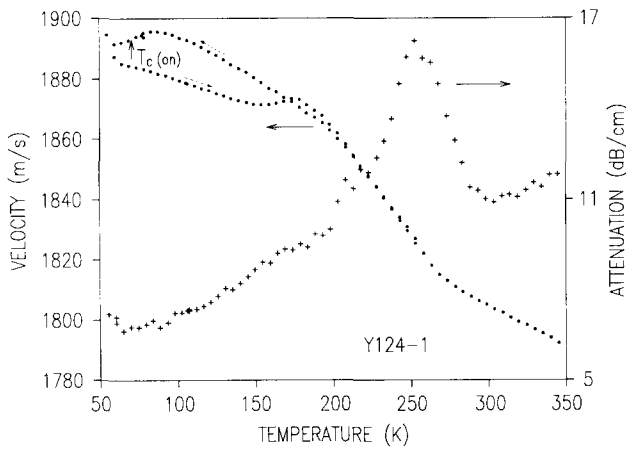


Fig. 2. Ultrasonic velocity and attenuation in Y124-1 measured with transverse waves at 10 MHz. The dashed-line arrows indicate the direction of the thermal cycle.

similar to those obtained in the Y124-2. Longitudinal mode attenuation is characterized by a very pronounced peak around 260 K, accompanied by an inflection point in the velocity vs. temperature curve. The change of curvature occurs on a steadily increasing velocity curve as the temperature is lowered from 330 K to about 180 K. Figure 2 shows that these features are in fact quite similar in the case of shear waves. They bear a striking resemblance to elastic anomalies found by many groups in the Y1:2:3 material near 240 K. Since, as we have previously pointed out [4], it is very unlikely that such similarities in so closely related compounds should occur accidentally, our results immediately rule out the possibility that the anomalies at 240 K in Y1:2:3 are caused by the ordering of oxygen vacancies in the CuO chains, or by oxygen breathing taking place at grain boundaries or crystal surfaces due to the well

known fact that there are no oxygen vacancies in Y1:2:4. Nor can twin structure effects be invoked since no twin structure is present in Y1:2:4.

To explain the effects seen here, we propose [4] a mechanism involving the ordering of oxygen in some off-center position of the structure, which can be effective in both cases. One such possibility is the random distribution of O(4) atoms between two potential wells in the direction transverse to the CuO chain direction. Due to the possibility that an electric dipole moment can be associated with each CuO pair, the ordering of these can be viewed as a phase transition between a paraelectric and an antiferroelectric state. This would mean that the elastic anomalies are created by piezoelectric or electrostrictive coupling between acoustic waves and the polarization of CuO dipoles. Independently, a similar idea was advanced to explain the dissipation peak observed at lower temperatures in Y1:2:3 [5].

3.1.2. Thermal hysteresis in velocity

As could already be seen in Figs. 1 and 2 hysteretic behavior is usually found, typically below about 200 K in the compounds under discussion here. These hysteresis phenomena have several features which deserve to be discussed. Again, some controversy exists regarding these phenomena. For instance, the idea has been promoted that hysteresis is related only to the grain size [6, 7], so that it will vanish if the grain size is small enough. Evidence to that effect [8] has been presented in Y1:2:3. It turns out that this explanation is too simple to apply to our data. Figure 3 shows an example of measurements performed on sample Y124-2, the one with largest grain size but smallest porosity of the two investigated here. It turns out that the

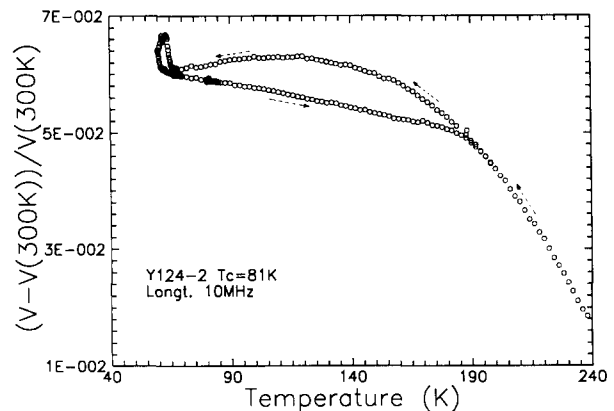


Fig. 3. The thermal hysteresis in velocity for the longitudinal mode in Y124-2, measured at 10 MHz. The dashed-line arrows indicate the direction of the thermal cycle. The origin of the "tail" at the lower end is not known.

hysteresis loop, which is found in both cases, is smaller in the sample with the *larger* grain size, contrary to the proposition referred to above. A clue to the cause we believe to have found in the porosity. The volume fraction of pores is smaller in the Y124-2 sample than in the Y124-1 sample. Thus it seems that the area of the hysteresis loop correlates more strongly with the volume fraction of pores than with grain size (Table 1). In reality we expect both to be important.

The physical picture we want to advance here is the following: Y1:2:4 has been observed to display large anisotropy of compressibility and expansivity along the three crystallographic directions [9, 10]. The compressibility and expansivity along the *a* direction were triple and double, respectively, of those along the *b* direction. The differences between *c* and *a* or *b* were even much larger. When the material is cooled down, the different thermal expansion along the three axes leads to anisotropic change of grain size, and each grain will change in a different manner due to their different dimensions and different orientation.

Due to the fact that each grain is confined to a surrounding matrix, the expansion or contraction is hindered, and a stress field is created near grain boundaries. This stress field increases gradually while cooling down to the temperature where the velocity reaches its maximum, T_h , where the stress becomes large enough to create some reversible defects near the interconnecting region so as to relieve part of the gathered elastic energy. Here, therefore, we observe a decrease of sound velocity. This process continues until at about 60 K, where the thermal expansion along the three principal directions becomes relatively stable.

When heating up again, the velocity remains relatively low until a temperature T_1 where reversible defects start to annihilate gradually. This process is completed near 200 K where the velocity is completely recovered. We find that our observations regarding these features in elastic properties are consistent with the ideas presented here. For instance, in sample Y124-1 the pore volume is larger than in the Y124-2 sample, facilitating the creation of reversible defects more in the former case. This property rather than grain size, which is smaller in this sample, favors greater hysteresis, in

TABLE 1. Some material parameters of investigated samples

	Y124-1	Y124-2
Grain size	3 μm	7 μm
Pore size	1-10 μm	0.5-12 μm
Pore volume (%)	35	25
Grain shape	~ rounded	~ rectangular
Hysteresis area* (K) (m s^{-1})	3580	1770

*Measured by longitudinal mode.

agreement with observation. We would like to add that we also propose that the same mechanism, at least partly, is involved in the hysteresis in Y1:2:3.

3.2. $Y_{1-x}Ca_xBa_2Cu_4O_8$

The Ca-substituted material was concluded to be clean and single-phase after careful X-ray analysis. In addition to displaying phenomena encountered in the Y1:2:4 material and discussed briefly above, qualitatively new features appeared. The most interesting of these were a phase transition occurring at 150 K causing a typical specific heat anomaly at this temperature (Fig. 4) and another phase transition below the superconducting transition (Figs. 5, 6). In both cases the anomalies could be observed both by specific heat and by elastic measurements. Attempts to reveal structural changes by X-ray measurements did not succeed. The mechanisms responsible for these anomalies is therefore unknown. Magnetic susceptibility also did not reveal any hint of magnetic ordering. We believe that rather subtle structural changes are responsible, but cannot at this moment point it out clearly. One possible suggestion: the immediate candidate is the ordering of Ca ions. However, measurements show no increase of the specific heat anomaly with increasing Ca-substitution. So this possibility seems to be ruled out. Some difference in the magnitude of elastic anomalies was found, depending on Ca-concentration, but we still consider the evidence inconclusive as far as mechanism is concerned. For a more detailed discussion of these phenomena we refer the interested reader to the original papers [11, 12].

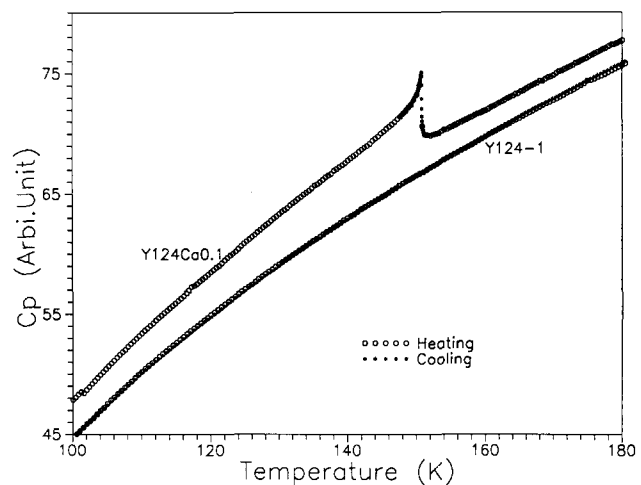


Fig. 4. Specific heat vs. temperature for Y124-1 and the $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. A phase transition is clearly seen in the latter at 150 K.

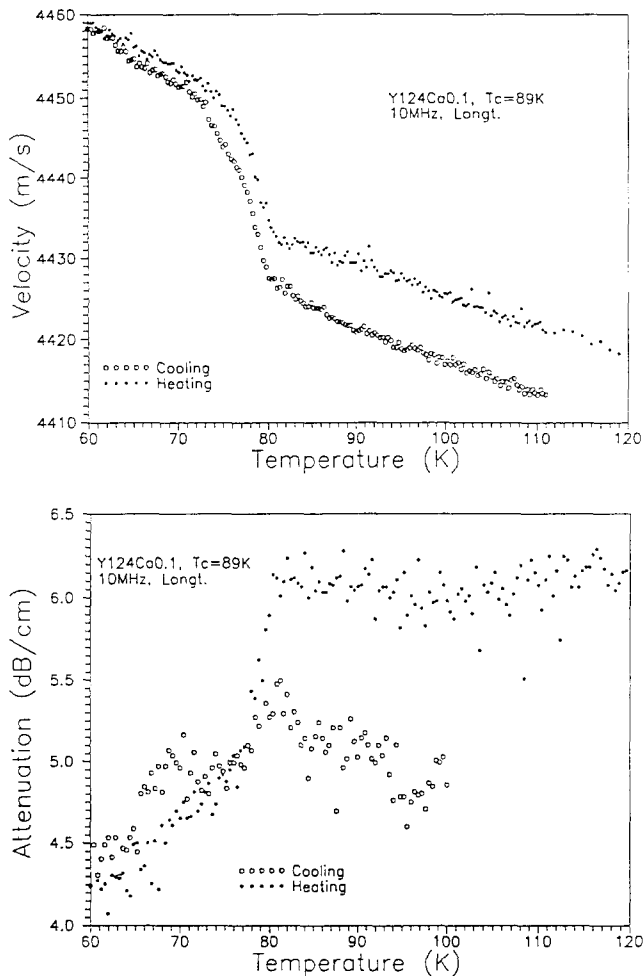


Fig. 5. Ultrasonic velocity and attenuation indicating the presence of a first-order phase transition below the superconducting transition in the $x=0.1$ Ca-substituted material. (The same material as in Fig. 4.)

Acknowledgments

The authors are indebted to The Superconductivity Research Laboratory/ISTEC for collaboration on the present research. Partial support by Norsk Hydro and The Norwegian Research Council is gratefully acknowledged.

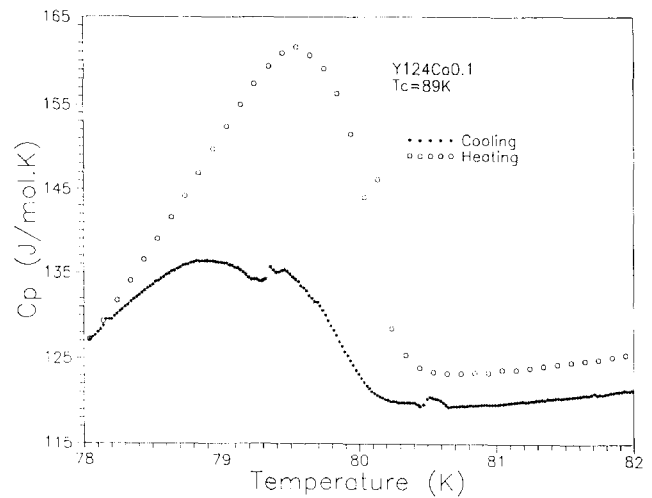


Fig. 6. Specific heat in the $x=0.1$ Ca-substituted material, the same material as in Figs. 4 and 5. The anomaly indicates the existence of a first-order phase transition.

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