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Ca-induced phase transition at 150 K in $Y_{1-x}Ca_xBa_2Cu_4O_8$ single-phase high-T_c superconducting material

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Elastic and specific-heat measurements have been performed on single-phase polycrystalline $Y_{1-x}Ca_xBa_2Cu_4O_8$ ($x = 0$, 0.025, 0.05, 0.1) in the temperature region from 100 to 180 K. Anomalies are detected in elastic and specific-heat measurements at 150 K for Ca-doped specimens. A reversible steplike change in sound velocity accompanied by an attenuation peak is observed in material with $x = 0.1$ doping at 150 K on cooling and heating, for both longitudinal and transverse modes. These elastic anomalies have a clearly observable counterpart in the specific heat. The anomalies in elastic and specific-heat measurements show dominantly the character of a mean-field-type phase transition. We observe similar anomalies at the same temperature even for $x = 0.025$ and 0.05, while for pure $YBa_2Cu_4O_8$ samples no anomalies are found in this temperature region. Thus we find a Ca-induced, but concentration-independent, transition temperature in the available range of x values. No magnetic anomaly is found by ac magnetic susceptibility. The transition is proposed to be of a structural type although x-ray powder diffraction did not reveal the origin.

INTRODUCTION

$Y_{1-x}Ca_xBa_2Cu_4O_8$ with x ranging from 0 to 0.1 has been shown to increase the superconducting transition temperature T_c continuously[1] from about 80 to 90 K without a change of the structure at room temperature. This substitution should be expected to affect not only the T_c value, but also other physical properties.

Following our previous elastic measurements of $YBa_2Cu_4O_8$,[2,3] we report here further measurements of $Y_{1-x}Ca_xBa_2Cu_4O_8$ ($x = 0$, 0.025, 0.05, 0.1) samples in the temperature region from 100 to 180 K. We find distinct evidence for the appearance of a phase transition at 150 K in the Ca-doped material. The evidence favors a phase transition of the structural origin.

EXPERIMENT

The samples were prepared by a solid-state reaction method using Ar and O_2 gases during hot isostatic pressing treatment.[4] X-ray measurements show that they are single-phase polycrystalline samples without any observable trace of $YBa_2Cu_4O_8$ or $Y_2Ba_4Cu_7O_{15-y}$ phases. Their superconducting transition temperatures T_c were measured by ac magnetic susceptibility, giving onset values as shown in Table I.

Elastic measurements were performed using standard Matec equipment with an automatic time-of-flight technique. Ultrasonic velocity and attenuation, with resolutions of 50 ppm and 0.1 dB/cm, respectively, were recorded during cooling and heating. The temperature was stabilized within 0.5 mK of the set value. Specific-heat measurements were made using an automatic ac calorimeter.[5] During specific-heat measurements, the temperature was regulated to within 5 mK of each set temperature for at least 200 s prior to measurements, to ensure that the sample had reached thermal equilibrium before data were taken during both cooling and heating.

Longitudinal and transverse waves of 10 and 15 MHz were employed in elastic measurements of $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. In the $Y_{0.95}Ca_{0.05}Ba_2Cu_4O_8$ case, only the longitudinal mode at 10 MHz was used. Specific-heat measurements were made on $YBa_2Cu_4O_8$, $Y_{0.975}Ca_{0.025}Ba_2Cu_4O_8$, and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$.

RESULTS AND DISCUSSION

As shown in previous papers,[2,3] we have detected no anomalies in the temperature region from 100 to 180 K in ultrasonic measurements on pure $YBa_2Cu_4O_8$. Here we make specific-heat measurements on the same sample, namely, $YBa_2Cu_4O_8$ (Y124-1), used in the ultrasonic

TABLE I. T_c values of the samples used in the ultrasonic and specific-heat measurements.

	Y124-1	$Y_{0.975}Ca_{0.025}Ba_2Cu_4O_8$	$Y_{0.95}Ca_{0.05}Ba_2Cu_4O_8$	$Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$
T_C (K)	76	82	87	89

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studies. No anomalies are found (see Fig. 1). This result is in good agreement with previous reports.[6,7] In contrast to the undoped $YBa_2Cu_4O_8$, distinct anomalies in specific-heat and elastic measurements are observed for all Ca-doped $YBa_2Cu_4O_8$ specimens. Taking $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, as an example, the results of specific-heat measurements are given in Fig. 1. During both cooling and heating runs, a large anomaly is found at 150 K, without any observable thermal hysteresis within the temperature resolution of 20 mK. Ultrasonic velocity of longitudinal waves measured at 10 MHz displays a step-like jump at 150 K accompanied by an attenuation peak both on cooling and heating [see Figs. 2(a) and 2(b)]. The change in velocity at 150 K is 450 ppm which is sufficiently above the noise level to be considered significant. Reproducibility was confirmed. No thermal hysteresis is seen in the location of the attenuation peak or velocity step. Similar elastic features appear in the measurements of transverse waves at 10 MHz (Fig. 3) where the step change in velocity is 240 ppm. The elastic and specific-heat anomalies at 150 K are also observed at other concentrations of Ca doping at the same temperature.

We performed further ultrasonic measurements on $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ using a longitudinal excitation at 15 MHz, in order to check whether the temperature of the anomaly changes with probing frequency. The results, not shown here, are similar to those shown in Figs. 2 but with a step change in velocity of 410 ppm. This result points towards a phase transition rather than a relaxation phenomenon as the cause for the anomaly.

The occurrence of a step change in ultrasonic velocity with a corresponding attenuation peak is normally a signature of a mean-field-like phase transition.[8] This idea is corroborated by the analysis of the specific-heat data.

To analyze the specific-heat data C_p, we fit an effective lattice background consisting of a linear as well as an Einstein term to the data points between 160 and 180 K (the Debye model will not give a significantly better fit to the specific-heat data than the simple Einstein model in this temperature region). Fitting parameters are adjusted such that the background approached the measured curve smoothly well below the transition, as shown by the full line in Fig. 4. The subsequent anomalous part ΔC_p could be described quite well by mean-field Landau behavior[9] below 145 K (dashed line in Fig. 4) with $\Delta C_d = AT(T_d - T)^{-1/2}$. Here, A is a constant and T_d is the theoretical anomalous temperature to be determined from the fit. The magnitudes of the specific-heat jump at 150 K for $Y_{0.975}Ca_{0.25}Ba_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ determined from the mean-field fit are 11% and 5.8%, respectively. This result will be commented on later.

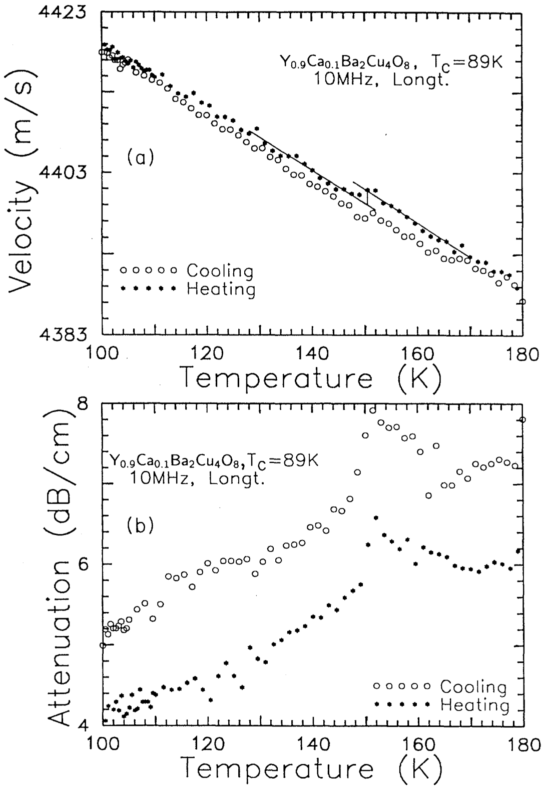

FIG. 2. Longitudinal sound velocity vs temperature for (a) $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ and (b) the corresponding attenuation data. The line in (a) is a guide to the eye.

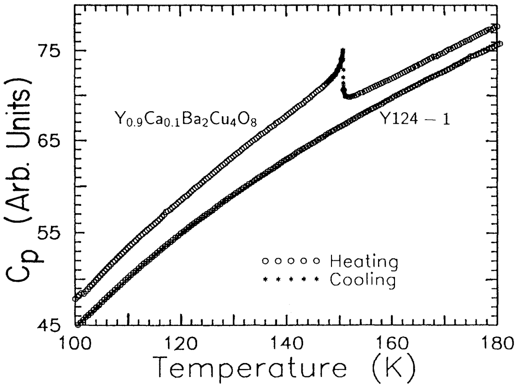

FIG. 1. Specific heat vs temperature for Y124-1 and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ samples during cooling and heating. Note that in the $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ case, cooling data are provided only near 150 K.

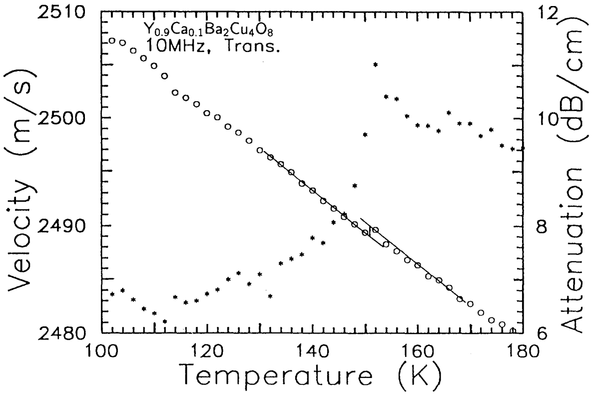

FIG. 3. Transverse sound velocity vs temperature for $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ on heating. The line in the figure is a guide to the eye.

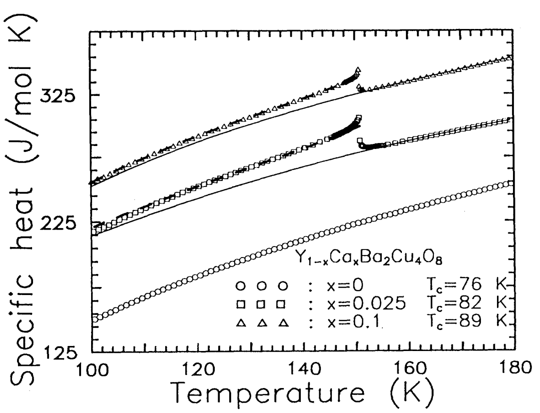

FIG. 4. Data analysis performed on the specific-heat measurements of $Y_{0.975}Ca_{0.025}Bu_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. All data have been calibrated at 180 K using measured value from Ref. 6. The plots for $Y_{0.975}Ca_{0.025}Ba_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ have been shifted by 50 and 100 J/mol K, respectively. Close to 150 K, only every tenth measured data is shown. Further away from 150 K, every second data is plotted (see text for more detail).

From Fig. 4, it is easily seen that, in addition to the mean-field behavior, there is an extra anomalous contribution just below and above the transition temperature. This part may be due to a very small amount of impurities.[10] It is unlikely to be caused by order parameter fluctuations, since only a steplike anomaly in ultrasonic velocities is found at the corresponding temperature (see Figs. 2 and 3).

Since the phase transition temperature is the same within the temperature resolution of 20 mK during cooling and heating runs, we interpret it as a second-order one (see Fig. 1). Comparing the experimental results for pure $YBa_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, we can conclude that the phase transition is induced by the Ca substitution.

Before suggesting possible mechanisms which might be responsible for the observed anomalies, let us address the question as to whether there are impurities in the samples. From our x-ray data we do not observe any extra peaks other than those belonging to $YBa_2Cu_4O_8$. It has been shown by Miyatake *et al.*[1] that no impurity phases existed for Ca-doped samples with Ca concentration less than 10% in materials of the same origin as are used here. For $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, only very small amounts of CuO were included in the sample.[11] Since the observed effect on specific heat is so large (see Fig. 4), the possibility that the anomaly is caused by an impurity phase is highly unlikely.

One possible explanation for the observed anomalies is the change of the crystallographic structure at 150 K. To investigate this possibility, we performed x-ray measurements on $Y_{0.975}Ca_{0.025}Ba_2Cu_4O_8$. We were unable to detect any structural changes from room temperature down to 20 K within the angular resolution of 0.5°. ac magnetic-susceptibility measurements on the same sample also revealed no detectable anomaly near 150 K. This result implies that the effect may be limited only to a static or dynamic rearrangement of some atomic positions, either on a long or a short length scale.

One naive interpretation of the elastic and specific anomalies at 150 K is that they are due to the ordering of the Ca ions alone. If so, then the magnitude of the jump in specific heat at 150 K should increase with increasing Ca concentration. This is, however, in contradiction with the experimental data (see Fig. 4). On the other hand, the step change in velocity at 150 K measured on $Y_{0.95}Ca_{0.05}Ba_2Cu_4O_8$ using a longitudinal wave of 10 MHz is 370 ppm, which is smaller than what is observed for $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. However, we point out that, unlike specific heat, the magnitude of the elastic anomaly does not necessarily increase with increasing concentration of the substituent.

Other possible mechanisms responsible for the anomalies are suggested as follows:

When Y is partly replaced by Ca, one obvious effect is that the amount of charge carriers in the conduction planes increases. The possible oxygen ordering in the CuO chains[2] could hardly be affected by this substitution because of the crystallographic location of the Ca ions. Thus it is expected in this case that the main influence of the substitution is on the CuO_2 planes. The elastic and specific-heat anomalies are caused by the charge-carrier induced second-order phase transition originating from the interaction between the Ca ions and the CuO_2 planes. The microscopic origin of this phase transition could be the same as that of the phase transition from Cmca to $P4_2/ncm$ in $La_{2-x}Ba_xCuO_{4-y}$ at Ba concentration of $\frac{1}{16}$.[12] Another possibility is the local correlated flipping of the buckled structure of Cu-O-Cu links in the CuO_2 plane from downward direction to upward direction or vice versa. Since the ionic radius of Ca is slightly larger than Y (0.92 Å) and the valence of Ca is one unit of charge less than that of Y, the interaction force between Ca^{2+} and O(2) or O(3) is different from that between Y^{3+} and O(2) or O(3). Consequently, at the places where *Y* is replaced by Ca, the buckled structure of Cu-O-Cu links will be changed, inducing a lattice instability at 150 K. Since each Cu-O-Cu link is associated with an electric dipole, the interactions between Cu-O-Cu links are, therefore, of long range. This means that the correlated flipping of the buckled structure of Cu-O-Cu links in the CO_2 planes at 150 K is governed by a long-range force, leading to the observed mean-field-like phase transition.

Clearly, a model intended to explain the anomalies at 150 K has to answer why only a simple shift of the velocities of shear and compressional waves was observed at that temperature. Extension of the above ideas to take this velocity effect into account is certainly not a trivial task. It is plausible, due to the long range nature of electric dipoles, that the system has an upper critical dimensionality d^* less than 3. Such systems are mean-field like.[13]

We cannot at this point provide a definite link between the phase transition at 150 K and the superconducting properties, but we can offer the following observations. We first recall the anomalies in attenuation and velocity found in $YBa_2Cu_3O_7$ and in La-based cuprate high-T_c superconductors in the temperature region from T_c to

T_c+100 K.[14] For $La_{2-x}Sr_xCuO_{4-y}$, it was suggested that the existence of the structural instability associated with the compressional deformation in the conduction planes at a temperature several degrees of Kelvin above T_c may be in favor of higher T_c,[15] while for $YBa_2Cu_3O_7$ a possible phase transition in this temperature region was also found.[14] Therefore, it is difficult to conclusively exclude the possibility that the phase transition at 150 K has an effect on the superconductivity, although we see that $Y_{0.975}Ca_{0.025}Ba_2Cu_4O_8$ has almost the same T_c value as that of $YBa_2Cu_4O_8$ (Ref. 3) and our resistivity measurements on $Y_{0.95}Ca_{0.05}Ba_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ detect no anomaly near 150 K. The probability for this is large, in particular, if the phase transition at 150 K is indeed induced by the additional charge carriers introduced by the partial substitution of Y by Ca. It is worth mentioning that a charge-carrier instability triggered structural phase transition has been proposed[13] to account for the anomalous suppression of superconductivity in LABCO near a Ba concentration of $\frac{1}{16}$.

CONCLUSIONS

Ca substitution of Y in the starting composition of $Y_{1-x}Ca_xBa_2Cu_4O_8$ leads to a phase transition at 150 K, independent of Ca-doping concentration in the range $x=0.025-0.01$. This transition is absent in the pure $YBa_2Cu_4O_8$ material. Ultrasonic and specific-heat data point unambiguously to such an interpretation of our data, although structural analysis has not yet identified what atomic displacements are involved.

The data are consistent with an interpretation involving a phase transition of the mean-field type, possibly of dipolar origin.

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