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Variations of internal friction in $YBa_2Cu_3O_x$ superconductors

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The internal friction (Q^{-1}) spectrum of $YBa_2Cu_3O_x$ superconducting ceramic exhibits several peaks. It has been confirmed that the high-temperature peak (around 240 K) depends on structural changes and varies during subsequent cycles of cooling and heating. Q^{-1}, conductivity, X-ray spectra and the shielding effect have been measured on several samples having different superconducting properties obtained by various thermal treatments. Splitting is a characteristic feature of the high-temperature internal friction peak of the sample which exhibits good superconducting properties. In the case of the specimen exhibiting the worst properties the peaks decrease and overlap. In both cases an increase can be observed of this peak with the number of thermal cycles. After ageing at 470 K, the high-temperature peak disappears. Subsequent thermal cycles slightly recover it. Hysteresis of the Young modulus is also observed. The results are interpreted as transition of the O4 oxygen atom between two energy minima in the O4–Cu–O4 chain.

1. Introduction

Internal friction is a suitable tool for investigation of the structural changes and phase transitions in various materials. It has been confirmed that superconducting $YBa_2Cu_3O_x$ ceramic shows structural changes during several cycles of cooling and heating. Cannelli *et al.* [1] have reported a peak of internal friction at 240 K and interpreted it as a phase transition. The shape of this peak depends on the thermal history of the sample. The same peak has been observed by other authors [2–4].

A high-temperature specific heat anomaly has been found near 220 K by Laegreid *et al.* [5]. The neutron diffraction study by Francois *et al.* [6] has shown that $YBa_2Cu_3O_x$ reveals structural anomalies near T_c and near 240 K [6]. There are also some suggestions of possible superconductivity transition near 240 K detected by a reverse a.c. Josephson effect [7] or a drop in electrical resistance [8, 9].

The aim of the present work was to obtain further evidence for the characterization of the structural change at 240 K by means of internal friction measurements. The interpretation was supported by resistivity, X-ray diffraction spectra and oxygen desorption measurements.

2. Experimental details

The samples were prepared from appropriate amounts of Y_2O_3, CuO and $BaCO_3$. The reagents were carefully powdered, mixed, pressed and sintered four times at 950° C in a flowing oxygen atmosphere (total time 40 h). In order to obtain samples with different superconducting properties, two sets of specimens (A and B), which varied in the final cooling rate, were prepared. Samples A were slowly furnace cooled (for $\sim$ 10 h); samples B were cooled relatively quickly (for 1 h). All samples had a density of 5.8 g cm^{-3} which was obtained from geometric measurements. We believe that the simple Archimedes method gives rather unreliable results due to the porosity of the sample.

The internal friction measurements were carried out with the vibrating reed technique. The measurement frequency was about 200 Hz. The samples were in the shape of a thin plate (30 mm × 5 mm × 0.3 mm). The amplitude of the oscillations was about 5 μm which corresponds to the value of strain amplitude of about 10^{-6}. The heating rate was 1 K min^{-1}.

Electrical conductivity measurements were performed using the four electrodes method applying low-frequency a.c. voltage. X-ray diffraction spectra measurements were taken with a DRON-3 spectrometer using the CuKα line. The oxygen desorption measurements were obtained using a time of flight (TOF) spectrometer.

3. Results

Our investigations and previously published data [1, 2, 4] indicate that internal friction spectra strongly depend on the quality of the sample, so special attention was paid to obtaining samples of the best possible superconducting properties. Fig. 1 presents the internal friction, the changes of Youngs modulus, and resistivity of sample A, which exhibits good superconducting properties. The midpoint of transition is 90.5 K, $\Delta_T = 1$ K and the slope of the resistivity curve

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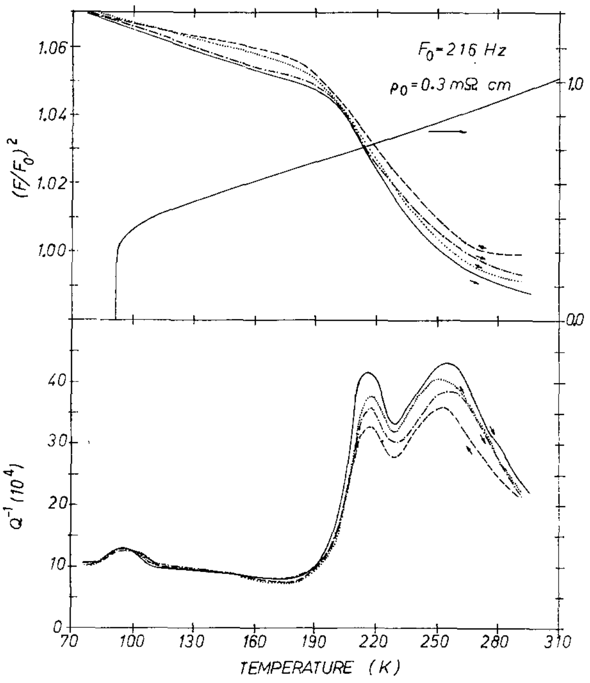

Figure 1 Variation of internal friction Q^{-1}, modulus and resistance with temperature for sample A. (– – –) first cycle, cooling; (–·–·–·–) first cycle, heating; (· · · ·) second cycle, cooling; (——) second cycle, heating.

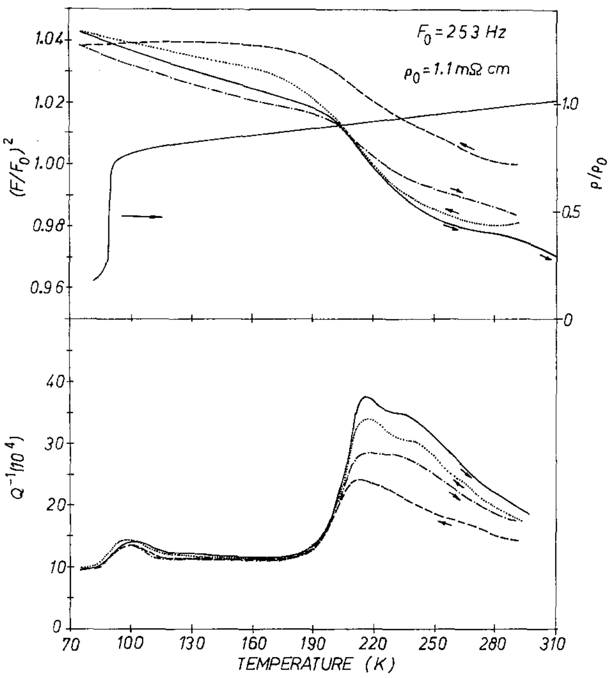

Figure 2 Variation of internal friction Q^{-1}, modulus and resistance with temperature for sample B. (– – –) first cycle, cooling; (–·–·–·–) first cycle, heating; (· · · ·) second cycle, cooling; (——) second cycle, heating.

$\varrho(300\,\mathrm{K})/\varrho(100\,\mathrm{K}) = 2.6$. X-ray diffraction spectra show the existence of only one orthorhombic phase. The internal friction (Q^{-1}) and modulus curves were obtained during subsequent thermal cycles. All the Q^{-1} curves display the previously reported peak [1–4, 10] at the transition temperature and two high-temperature peaks at 215 and 256 K. A distinct increase in both high-temperature peaks and a small hysteresis of modulus is apparent. There is no change of the low-temperature peak.

Fig. 2 shows the results of the same measurements for sample B. This sample, due to the method of preparation, exhibits much worse properties, but is still superconducting. It can be seen from the figure, that the resistivity does not vanish to zero and the slope of the curve is much lower ($\varrho(300\,\mathrm{K})/\varrho(100\,\mathrm{K}) = 1.3$). X-ray spectra show the existence of only an orthorhombic phase but there are some differences when they are compared to the ideal structure [9]. The most interesting feature of the Q^{-1} curve is the absence of splitting of the high-temperature peak. During thermal cycling the peak increases sharply and splits. The modulus shows a much greater hysteresis which tends to saturate.

After two cycles of measurements, sample B was heated to 470 K and aged in the apparatus (in vacuum) for 12 h. Fig. 3 shows two measurements of Q^{-1} carried out after this treatment. One can observe complete disappearance of the high-temperature peak during the first cooling and heating. However, after conditioning for 3 weeks at room temperature in vacuum the next cycle leads to the reappearance of this peak at 256 K, which is a higher temperature than previously found, before the heat treatment at 470 K. The modulus features a large hysteresis which decreases during the subsequent cycle.

In order to obtain information on the electrical conductivity and X-ray spectra, two further samples (C and D) were prepared in the same manner as sample B and aged in vacuum in 470 K for 12 h. Fig. 4 shows the conductivity and shielding effect of one of these samples. The conductivity shows no indication of superconducting transition; however, the shielding effect confirms the existence of the superconducting phase. After several cycles of Q^{-1} measurements the resistance of the sample has significantly decreased.

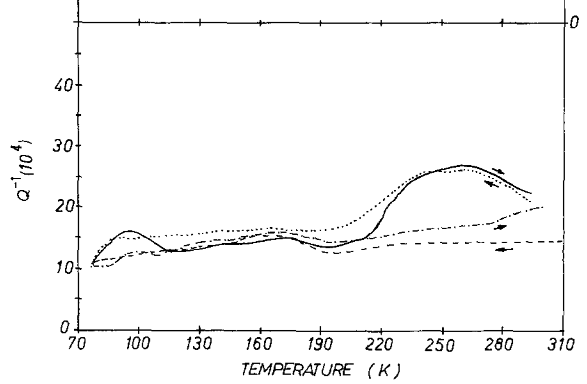

Figure 3 Variation of internal friction Q^{-1}, modulus and resistance with temperature for sample B after thermal treatment at 470 K for 12 h. (– – –) First cycle, cooling; (–·–·–·–) first cycle, heating; (· · · ·) second cycle, cooling; (——) second cycle, heating.

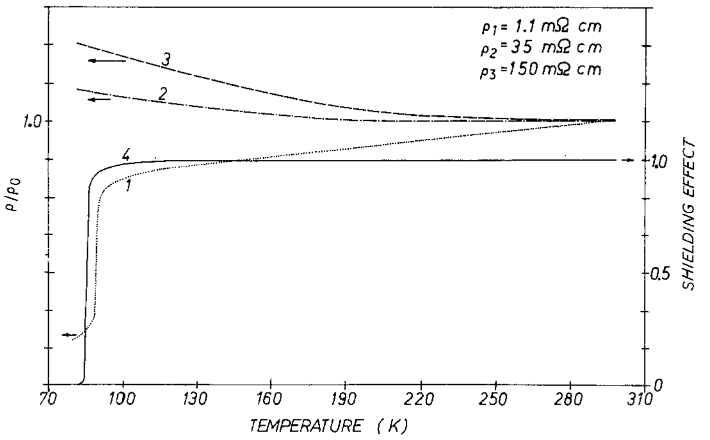

Figure 4 Resistivity and shielding effect of sample C. (· · · ·) resistivity before heat treatment; (- - -) resistivity after thermal treatment; (–·–·–·–) resistivity after heat treatment and two cycles of Q^{-1} measurements; (——) shielding effect after heat treatment.

The X-ray spectra data for samples A, B and C show that they consist of a single orthorhombic phase according to the experimental and theoretical data of Gallagher *et al.* [9]; however, there are some differences in the intensity of the main lines. Sample A has an almost ideal orthorhombic structure. Sample B exhibits differences from the ideal structure (for example, line 32.60 is too intense when compared with 32.88). After ageing at 470 K (sample D) the differences increase. Subsequent Q^{-1} measurements lead to a change in the X-ray spectra towards better orthorhombic structure.

4. Discussion

It is noticeable that the internal friction spectra depend on the quality of the sample. Sample A, which has the best superconducting properties, shows splitting of the high-temperature Q^{-1} peak. Sample B, which is a worse superconductor, displays overlapping of the 215 and 256 K peaks. Moreover, the peak is lower. In both cases, an increase of this peak with the number of thermal cycles can be observed. This is consistent with the improvement of superconducting properties with thermal cycling. A similar behaviour of internal friction has been observed by Cannelli *et al.* [1] and was interpreted as non-recoverable defects introduced by a phase transformation.

Another interpretation of the high-temperature Q^{-1} peak was given by Laegreid and Fossheim [2] and supported with vibrating reed, specific heat and ultrasonic attenuation data. They suggest that the observed behaviour is caused by an intrinsic structural instability related to the oxygen vacancies.

The studies of $YBa_2Cu_3O_x$ superconductor structure by high-resolution neutron diffraction by Francois *et al.* [6] show that no significant structural change is observed at the onset of superconductivity but the lattice dimensions and some of the structural parameters show small anomalies near 90 K and 240 K. Francois *et al.* observed large vibrational amplitudes of the O4 atoms and proposed a model in which these atoms are disordered between two potential minima at about 0.01 nm either side of the O4–Cu–O4 chain over the whole range of temperature (5 to 320 K).

We believe that the high-temperature Q^{-1} peak can be interpreted in terms of oxygen transition between the two minima. Splitting of this peak observed for good superconducting samples (Fig. 1) may suggest that two levels of these minima are possible or that two processes coexist. For samples with worse superconducting properties, this splitting tends to vanish, which means that these minima are not so well defined from the energetical point of view. The observation that ageing of the sample at 470 K causes the peak to disappear may be interpreted as the breaking of the O4–Cu–O4 chain. The reappearance of the peak after thermal cycling might suggest restoration of some of the O4–Cu–O4 chains. In this case, the electrical resistivity of the sample exhibits no superconducting transition; however, the magnetic shielding effect shows existence of the superconducting phase. The oxygen desorption measured by Keller *et al.* [11] and our data obtained by time of flight mass spectroscopy prove that no oxygen has been lost from the sample at temperatures up to 600 K. This is additional support for the interpretation of the ageing effects being internal to the sample.

5. Conclusions

A splitting is a characteristic feature of the high-temperature internal friction peak of the sample which exhibits good superconducting properties. In the case of the specimen with the worst properties the peaks decrease and overlap.

After ageing in 470 K the high-temperature peak disappears. Subsequent thermal cycles slightly restore it.

The results can be interpreted as transition of the O4 oxygen atom between two energy minima in the O4–Cu–O4 chain.

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