Kinetic properties of ceramic $YBa_2Cu_3O_x$ at various oxygen concentrations ($6 < x < 7$)

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The temperature dependence of the thermal conductivity κ, the resistivity ρ, and the thermal emf α of the compound $YBa_2Cu_3O_x$ has been studied experimentally as x was varied. The behavior of ρ and α at $T = 300$ K has also been studied as a function of the pressure up to 12 kbar. An estimate of the time scale of the relaxation of phonons with electrons $\tau_{ph,e}$, yields 10^{-12} s ($T = 100$ K). This value would be typical of ordinary superconductors.

The increased interest in the new superconductors has spurred a large number of studies of various properties of these materials, including kinetic properties. Since the very first publications called attention to a substantial dependence of the superconducting transition temperature T_c on the oxygen concentration, it seemed worthwhile to carry out an experimental study of the changes which occur in the kinetic characteristics of ceramic samples of the compound $YBa_2Cu_3O_x$ as x is varied.

The temperature dependence of the thermal emf was measured in Ref. 1 as x was varied from 7 to 6.1. As x was reduced, it was found that the thermal emf increased sharply (it was positive in sign), while for a sample with $x = 6.1$ the thermal emf was negative. Kwok and Cheong[1] attributed this behavior of the thermal emf to a transition to a region of a hopping conductivity.

We know of no studies of the thermal conductivity as x is varied. For the most part, all of the investigators (e.g., those in Ref. 2) have restricted their study to a measurement of κ of superconducting samples with $x = 7$. Experiments of this sort have revealed a clearly defined maximum in the thermal conductivity at temperatures below T_c. This maximum has usually been linked with an increase in the photon relaxation time $\tau_{ph,e}$ due to a sharp decrease in the number of electronic excitations at the transition to the superconducting state.[3]

The kinetic characteristics were measured over the temperature range 4.2–300 K in a vacuum container in a liquid-helium bath. The temperature gradient along the sample (< 5 K) and the average temperature of the sample were measured by manganin(~ 30 μm)-constantan(40 μm) thermocouples. The thermocouples were calibrated in independent experiments. The potential leads were also made of manganin wire (30 μm). The errors in the measurements of all of the coefficients were less than 5%.

Samples with a density of 4.9–5.6 g/cm^3 had dimensions of $20 \times 1.5 \times 2$ mm. The oxygen content was varied by heating to temperatures above 400 °C, either in vacuum (10^{-2}–10^{-4} Torr) or in oxygen. The oxygen content of the samples was determined from the change in the weight of the samples before and after the annealing and/or

through a condensation of the oxygen liberated into a helium sorber, with subsequent measurement of the pressure of gaseous oxygen when the latter was heated.

Before and after an experiment, we carried out an x-ray diffraction analysis, which indicated a significant change in the lattice constants of the material, in quantitative agreement with the data of Ref. 4. The uniformity of the oxygen distribution along the cross section of the samples with $x < 7$ was checked on the basis of x-ray diffraction patterns from the outer and inner parts of a control sample. The agreement within $\sim 0.2\%$ of the lattice constants is evidence that the uniformity is acceptable (the values of x calculated by the method of Ref. 4 for the inner and outer parts of the sample differed by 0.1).

Figure 1 shows the temperature dependence of the thermal conductivity [$\times 10^{-2}$ W/cm·K)]. The different curves correspond to successive changes in the thermal conductivity of the same sample as x was varied through annealing in vacuum and in oxygen.

The thermal conductivity of the samples is predominantly a lattice conductivity. The electron component is less than 10–15%, according to estimates based on measurements of ρ (0.5 mΩ·cm for the better samples with $x = 7$ near T_c). The maximum on the curve of $\kappa(T)$ for the original sample can be explained in terms of a sharp decrease in the number of electronic excitations by which phonons may be scattered, at the transition to the superconducting state.[3] As the oxygen concentration is reduced, the maximum shifts down the temperature scale, gradually spreading out. A maximum is not observed in the thermal conductivity of the nonsuperconducting samples. If we assume that the different phonon scattering mechanisms are indepen-

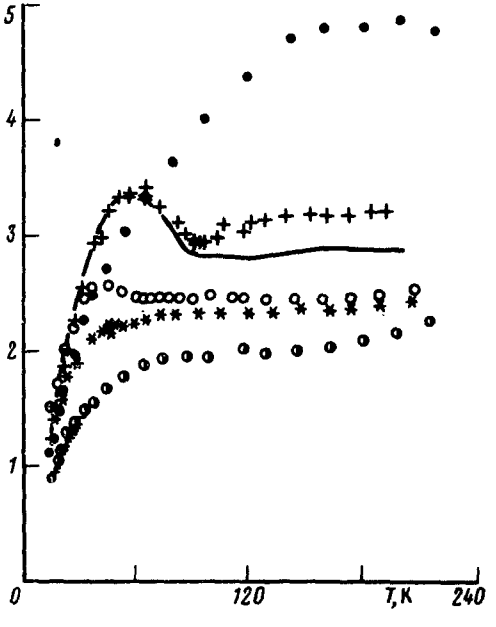

FIG. 1. Temperature dependence of the thermal conductivity κ [$\times 10^{-2}$ W/(cm·K)]. +—sample 4, original material, $x = 7$, $T_c = 92$ K; ○—sample 4/1, original material after annealing for 6 h at 435 °C, $x = 6.7$, $T_c = 70$ K; +—sample 4/2, further annealing in vacuum for 6 h at 455 °C, $x = 6.53$, $T_c = 56$ K; ◑—sample 4/3, 6 h at 470 °C, $x = 6.31$, nonsuperconducting; solid line—sample 4/5, annealing in oxygen for 21 h at 540 °C, $x = 6.77$, $T_c = 91$ K; ●—sample 4/7, after annealing in vacuum for 40 h at 675 °C, $x = 6.0$, nonsuperconducting.

dent, we can write

$$\kappa \sim Cs^2\tau,$$

$$\tau^{-1} = \tau_{ph,b}^{-1} + \tau_{ph,d}^{-1} + \tau_{ph,ph}^{-1} + \tau_{ph,e}^{-1}$$

where C is the phonon heat capacity, s is the sound velocity, and the times τ_{ph} are the relaxation times associated with the scattering of phonons by grain boundaries, lattice defects, phonons, and electrons, respectively.

The sound velocity for $x = 6$ is about 9% higher than that for $x = 7$ (Ref. 5), while the heat capacities are approximately the same. We can thus offer the following explanation for the experimental data. As the oxygen is removed, the vacancies which appear in the Cu–O chains (in the case of orthorhombic samples) and in Cu–O planes (for tetragonal samples) cause an intense scattering of short-wave phonons, which are characteristic of temperatures $T > \Theta/4$, where Θ is the Debye temperature. This process is reversible: One can saturate a sample with oxygen, and the thermal conductivity will increase again (see the line corresponding to sample 4/5), while during annealing in vacuum it will decrease again. The reversibility of this process suggests that the sample does not "disintegrate" and that the phenomenon stems from a change in the oxygen concentration, rather than an increase in the thermal resistance between grains. According to Wang *et al.*,[7] the thermal conductivity of single-crystal samples of the compound $YBa_2Cu_3O_7$ is 0.02 W (cm·K), lower than that of our samples.

An important fact is that a sample with $x = 6$ has a thermal conductivity at high temperatures which is far higher than in any previous case. The probable explanation is the essentially complete absence of electrons and oxygen vacancies which would scatter phonons. Comparing the thermal conductivities for sample 4 and 4/7, we can estimate the phonon relaxation time in scattering by electrons: $\tau_{ph,e} \sim 10^{-12}$ s at $T = 100$ K. This estimate is vastly longer than the estimate from Ref. 2, and it agrees with the values of $\tau_{ph,e}$ for ordinary superconductors (e.g., lead[2]) above the superconducting transition temperature.

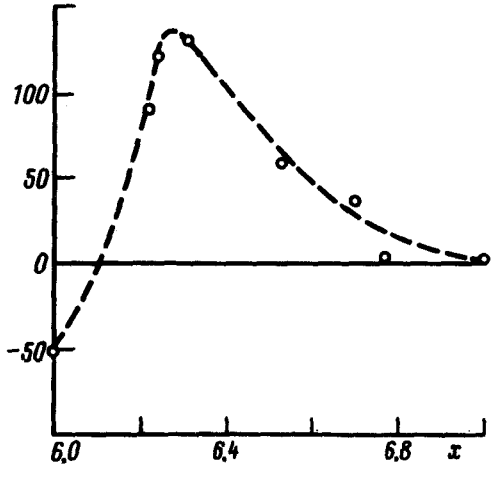

FIG. 2. The thermal emf α (μV/K) of the samples at $T = 120$ K versus the oxygen concentration x.

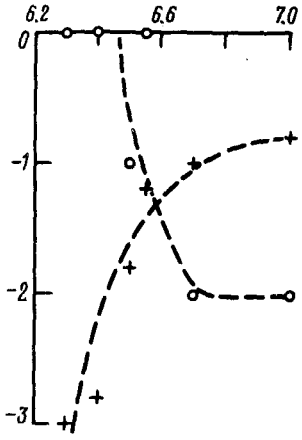

FIG. 3. Relative change in the thermal emf (O) and the resistance (+) with the pressure (in units of %/kbar) versus the oxygen concentration x.

Figure 2 shows the thermal emf of the samples at 120 K versus the oxygen concentration. At $x = 7$, the thermal emf is low ($\sim 3\,\mu$V/K), as it typically is of pure metals. With decreasing x, the thermal emf increases, reaches 150 μV/K, and then falls off, to negative values at $x = 6$. At $x = 6.4$, there is a structural transition from an orthorhombic phase to a tetragonal phase.[4] Another possible explanation for this behavior of the emf is a transition to a region of a hoppiong conductivity.[1,8] As x is reduced, oxygen vacancies are left in a random distribution in the Cu–O chains and planes, so there are an aperiodic potential and thus (at a low carrier density) a hopping conductivity.

Figure 3 shows measurements of the thermal emf and the resistance up to 12 kbar at room temperature. The sharp x dependence of the relative changes in the thermal emf and the resistance is probably due to a transition to a tetragonal phase at $x = 6.4$. The Hall constant for the compound $YBa_2Cu_3O_7$ does not depend on the pressure anywhere up to 10 kbar (Ref. 9).

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[1]R. S. Kwok, S.-W. Cheong *et al.*, Phy. C: **152**, 240 (1988).
[2]J. Heremans, D. T. Morelli *et al.*, Phys. Rev. **B37**, 1604 (1988).
[3]B. T. Geĭlikman and V. Z. Kresin, Zh. Eksp. Teor. Fiz. **36**, 959 (1959) [Sov. Phys. JETP **9**, 677 (1959)].
[4]J. M. Taraskon, L. H. Greene *et al.*, in: Proceedings of the International Workshop on Novel Mechanisms of Superconductivity (1987, Berkeley, California), Plenum, New York, 1987, 720.
[5]M. Suzu Ki, Y. Okuda *et al.*, Jpn. J. Appl. Phys. **27**, L308 (1988).
[6]K. S. Gavrichev, V. E. Gorbunov, *et al.*, Izv. Akad. Nauk SSSR, Neorg. Mater. **24**, 343 (1988).
[7]Z. Z. Wang, S. J. Hagen, and N. P. Ong, in: The International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, Abstracts, 1988. p. 229.
[8]N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Materials, Oxford Univ. Press, New York, 1979.
[9]I. D. Parker and R. H. Friend, J. Phys. **C21**, L345 (1988).

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