Thermal conductivity of oxygen-deficient $YBa_2Cu_3O_{6+x}$

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We have performed a systematic study of the temperature dependence of the in-plane thermal conductivity $K(T)$ in oxygen-deficient single crystals of $YBa_2Cu_3O_{6+x}$ $(0<x<1)$. An anomalous dependence of $K(T)$ observed in insulating $YBa_2Cu_3O_6$ below 200 K is evidence for the existence of unknown phonon relaxation process. This phonon relaxation seems to persist in superconducting samples. A strong temperature dependence of $K(T)$ in antiferromagnetic $YBa_2Cu_3O_6$ at $T>240$ K suggests a strong spin-phonon coupling. For underdoped superconducting crystals, we have found that features in metallic normal state $K(T)$ correlate with so-called spin-gap behavior of the spin and charge excitation spectrum. We interpret these features of $K(T)$ in terms of a spin-phonon interaction. [S0163-1829(96)05434-3]

I. INTRODUCTION

Measurements of the thermal conductivity K of high-temperature superconducting (HTS) cuprates as a function of temperature and applied magnetic field revealed generic behavior of the in-plane thermal conductivity parallel to the CuO_2 plane (for review, see Ref. 1): (i) $K(T)$ changes the slope $\partial K/\partial T$ near the superconducting transition temperature T_c. This can result in appearance of a peak in $K(T)$ at a temperature of about $T_c/2$. (ii) The thermal conductivity decreases in the applied magnetic field $H>H_{c1}$ at $T<T_c$. These observations demonstrate that the heat conduction increases with the superconducting order parameter rise and decreases with the Cooper pair breaking at a constant temperature. In other words, there is an intimate coupling between heat carriers and the order parameter in high-T_c cuprates. For this reason, thermal conductivity measurements provide with valuable information on the electronic structure of the HTS and, taking into account a layered structure of these materials, even on a spatial modulation of the order parameter.

In metals, usually two types of heat carriers, electrons and phonons, are responsible for the heat transport, and the total thermal conductivity is a sum of the electron (K_e) and phonon ($K_{\rm ph}$) contributions

$$K=K_e+K_{\rm ph}. \quad (1)$$

Estimations show that the electron contribution in crystals of high-T_c cuprates ranges from 10% to 50% of the total at $T>T_c$. Supposedly, both the electron and phonon thermal conductivities are weakly temperature dependent in the normal state. The problem of current interest is which type of heat carriers determines the behavior of the in-plane thermal conductivity in the superconducting state. More specifically, what are the temperature and magnetic field dependences of the electron and phonon thermal conductivity. There are two alternative interpretations of the thermal conductivity of high-T_c cuprates based on domination of either the phonon thermal conductivity (phononic scenario) or the electron one (see, e.g. Ref. 2).

The phonon thermal conductivity can be written as

$$K_{\rm ph}=\sum K_{{\rm ph},i}=\frac{1}{3}\sum \int_0^\infty \frac{C_i(\omega)v_i^2}{\tau_{i,c}^{-1}+\tau_{i,{\rm ph}\text{-}e}^{-1}}d\omega, \quad (2)$$

where $K_{{\rm ph},i}$ is the contribution of the phonon polarization i, $C_i(\omega)$ is the specific heat of the phonon mode ω with index i, v_i is the phonon velocity, $\tau_{i,c}^{-1}$ is the total relaxation rate due to the phonon scattering from boundaries, other phonons, lattice defects, etc. being independent of the gap function $\Delta(T)$, and $\tau_{i,{\rm ph}\text{-}e}^{-1}=A_{i,{\rm ph}\text{-}e}\omega g(\Delta,\omega)$ standing for the phonon-electron interaction.[3,4] In analysis of experimental data, it is usually assumed that scattering rates of the longitudinal and transverse modes are the same. Tewordt and Wölkhausen calculated the $K_{\rm ph}$ for high-T_c superconductors with different magnitudes of the electron-phonon coupling[5] and in the cases of s- and d-wave pairing.[6] Florentiev *et al.*[7] and Peacor *et al.*[8] found that the BCS variant of the model describes well the $K(T)$ data for $YBa_2Cu_3O_7$ single crystals. In both works, it was suggested that the electron thermal conductivity K_e is small at $T<T_c$. However, it is known that in conventional superconductors the $K_e(T)$ can show a pronounced maximum at $T<T_c$ in the weak-coupling and strong-coupling cases.[9,10] Generally, one should not associate the phononic scenario with phononic mechanism of high-T_c superconductivity. In fact, for phononic scenario to be valid, even a small value of the transport electron-phonon coupling ($\lambda_{\rm tr}\approx 0.1$) is enough.

In contrast, Yu *et al.*[11] proposed a different (electronic) interpretation of the superconducting-state thermal transport. They noted that the strong suppression of the quasiparticle scattering rate with decreasing temperature in $YBa_2Cu_3O_7$, which was inferred from microwave surface impedance measurements of Bonn *et al.*,[12] can result in large enhancement of the electron thermal conductivity in the superconducting state and, hence, is responsible for the peak in $K(T)$. Yu

TABLE I. Characteristic data and annealing conditions for $YBa_2Cu_3O_x$ single crystals.

No.	T_c K	ΔT_c K	Annealing conditions [a]	Dimensions [b] mm	x [c]	x [d]
54	89.25	0.15	O_2, 420 °C, 100 h	0.50×0.84×0.010	0.97	
7	91.0	0.32	O_2, 600 °C–300 °C	0.48×0.30×0.005	0.93	0.92
27	85.6	1.12	air, 510 °C, 30 h	0.73×0.50×0.050	0.83	0.87
44	73.3	0.95	air, 550 °C, 30 h	0.63×0.51×0.020	0.77	
22	62.0	0.39	air, 610 °C, 48 h	0.53×0.43×0.040	0.65	
45	51.0	0.73	air, 710 °C, 3 h	0.38×0.23×0.035	0.48	
50	<4.2		He, 800 °C, 3 h	0.50×0.80×0.010		0.05

[a]Gas pressure was 1 bar.
[b]Dimensions are given as (distance between thermocouple junctions)×(crystal width)×(crystal thickness).
[c]Oxygen content determined using the equilibrium concentration curves $x=x(T_{an})$.
[d]Oxygen content determined using the c-axis parameter curve $x=x(c)$.

et al.[11] assumed that the phonon contribution to the observed temperature dependence of $K(T)$ is insignificant below T_c. For this the authors pointed out that the data of Hagen *et al.*[13] on the in-plane thermal conductivity of insulating $YBa_2Cu_3O_{6+x}$ crystals and the out-of-plane thermal conductivity can impose the such constraint on the K_{ph}. However, no attention was given to the antiferromagnetism of insulating $YBa_2Cu_3O_{6+x}$, whereas the spin-phonon interaction may strongly influence the phonon thermal conductivity of paramagnetic dielectrics.[14] Previously we have found manifestations of the spin-phonon interaction in the thermal conductivity of antiferromagnetic cuprates.[15,16]

The data on the phonon thermal conductivity of antiferromagnetic insulating cuprates, even though being complicated by the spin-phonon interaction, appear to be a good starting point for an investigation of the mechanisms of heat transport in HTS. Thus motivated, we have studied the heat transport in single crystals of oxygen-deficient $YBa_2Cu_3O_{6+x}$. With increasing oxygen content the $YBa_2Cu_3O_{6+x}$ undergoes a transition from antiferromagnetic insulating state $0<x<x_{MI}$ to superconducting one $x_{MI}<x<1.0$, where $x_{MI}\approx 0.4$. The changes in the electronic and spin systems produce significant modifications of the temperature and magnetic field dependencies of thermal conductivity.

In this paper, we report the temperature dependence of thermal conductivity along the a-b plane for crystals of $YBa_2Cu_3O_{6+x}$ with different oxygen content in the whole range $0<x<1$. The effects of the magnetic field on thermal conductivity will be discussed in a following paper.[17]

II. EXPERIMENT

A. Single-crystal preparation

A master batch of $YBa_2Cu_3O_{6+x}$ single crystals was grown by the CuO flux method in a platinum crucible.[18] The crystals were grown under the melt cooling from 1150 °C to 860 °C in air. After this the crucible was removed from a furnace and the liquid flux poured out from the crucible. By this the crystals were isolated from the flux and rapidly cooled to room temperature. Typical dimensions of the platelet-like crystals were 1–3 mm in the a-b plane and 10–40 μm along the c axis. Analysis of the chemical composition of our crystals by an electron microscope with x-ray microanalyzer showed less than 0.1 at. % of Pt impurities. For post-growth annealing we selected the crystals without any defects (such as cracks, solidified flux, etc.) on their surface visible under an optical microscope.

To obtain $YBa_2Cu_3O_{6+x}$ crystals with different oxygen content, the crystals from the master batch were annealed at different temperatures. Few crystals were encapsulated into a small (<100 mg) ceramic $YBa_2Cu_3O_{6+x}$ container filled up with $YBa_2Cu_3O_{6+x}$ powder and annealed at T_{an} in 1 bar oxygen, air, or pure helium followed by a fast quenching into liquid nitrogen. The quenching was made by expelling the container out of the tubular furnace by means of pulsed helium jet from a nozzle located near the container. The single crystal No. 54 was annealed at 440 °C in 1 bar oxygen. We estimate that this crystal was overdoped (the oxygen concentration $6+x$ is about 6.97) with reduced transition temperature in accordance with data of Breit *et al.*[19] All our orthorhombic crystals were twinned, as seen under the optical microscope. The annealing conditions and properties of the samples are summarized in Table I.

The oxygen content in the crystals was determined using the dependence of lattice parameter c upon oxygen content [the $c(x)$ curve] (Ref. 20) or the dependence of x upon annealing temperature [the $x(T_{an})$ curve at $P_{O_2}=0.21$ bar].[21] The estimated total uncertainty in the oxygen content does not exceed ± 0.05.

The critical temperature for superconducting crystals was detected by measuring the temperature dependence of the ac magnetic susceptibility $\chi(T)$ in a configuration where the ac magnetic field is parallel to the c axis. The data taken at a frequency 667 Hz and amplitude of the ac field 0.1 Oe are shown in Fig. 1. It is seen that there are two regions near $x\approx 0.9$ and $x\approx 0.6$ where the superconducting transition is sharp and the peak in the imaginary component of the ac susceptibility $\chi''(T)$ is single and narrow. This result is consistent with that of Cava *et al.*[22] The samples with $x\approx 0.9$ and $x\approx 0.6$ are supposed to be close to the OrthoI and OrthoII phases, respectively. In the intermediate range $0.6<x<0.9$, the transition becomes broad, and multipeaks appear in the $\chi''(T)$. This can be interpreted as a result of the phase separation. The dependence of $T_c(x)$ upon oxygen content (Fig. 2) displays a well-known behavior with two plateaus at approximately 90 K and 60 K.

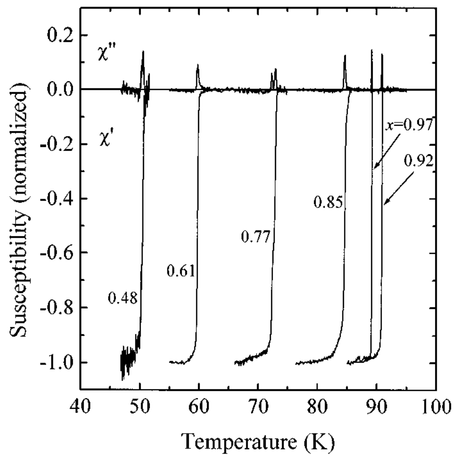

FIG. 1. ac susceptibility of the $YBa_2Cu_3O_{6+x}$ single crystals measured in a field of 0.1 Oe oriented parallel to the c axis.

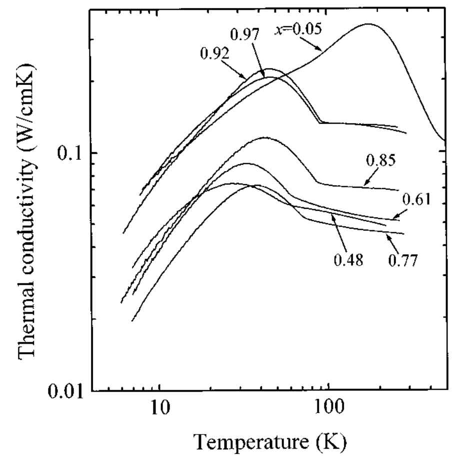

FIG. 3. Temperature dependence of the in-plane thermal conductivity for the $YBa_2Cu_3O_{6+x}$ single crystals.

B. Thermal-conductivity measurements

The thermal conductivity was measured by a temperature-wave method described in detail elsewhere.[23] The temperature wave in a sample was generated at a frequency ranging from 0.2 to 2 Hz by an electrical heater which was glued onto the end of the sample. The sample was clamped at another end to a temperature-controlled copper heat sink. Heat losses from the sample were minimized by evacuating a sample chamber and surrounding the sample with a copper shield which was thermally enchored to the heat sink. The temperature of the heat sink was measured with a carbon-glass resistance thermometer. An amplitude and phase of a temperature drop along the sample were measured using the differential manganin-constantan thermocouple. The amplitude of the temperature drop was approximately 1–3 % of current temperature. The random error in the magnitude of thermal conductivity was 0.1% at $T>20$ K, and it increased to 0.25 % at 6 K. The systematic error was less than 50 %. The latter is mainly due to the error in determination of the sample dimensions, irregularity of its form, finite size of the contact between thermocouple junctions and the sample, and uncertainty in the magnitude of heat current through the sample.

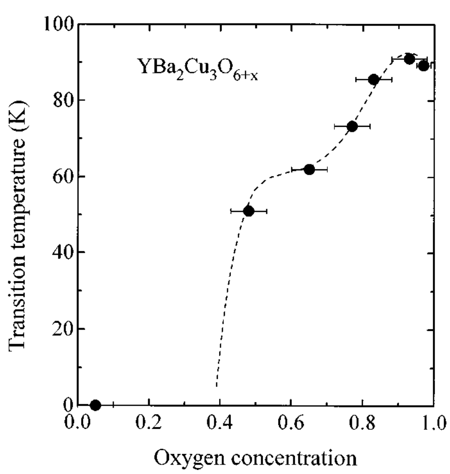

FIG. 2. Superconducting transition temperature vs oxygen concentration for the $YBa_2Cu_3O_{6+x}$ single crystals. The dashed line is a guide for the eye.

For insulating crystal of $YBa_2Cu_3O_6$ (No. 50) the thermal conductivity was measured at temperatures up to 500 K. At high temperatures radiation heat losses usually become essential and can cause substantial error in the measured $K(T)$. We estimated that in our measurements the radiation losses lead to a systematic error of 2% and 10 % at 300 K and 500 K, respectively. This is an upper bound for the effect of radiation losses. The relatively small effect is due to the small size and moderate thermal conductivity of this crystal.

III. RESULTS AND DISCUSSION

The temperature dependencies of the in-plane thermal conductivity for $YBa_2Cu_3O_{6+x}$ single crystals with various oxygen content are shown in Fig. 3. The general features of these data are as follows.

(i) The peak in the thermal conductivity is clearly observed for all the superconducting samples. With decreasing oxygen content, the position of the peak shifts to lower temperatures, and its relative magnitude becomes smaller.

(ii) The samples with maximum oxygen concentration show a sharp upturn of the thermal conductivity near the superconducting transition. The decrease in oxygen concentration results in the gradual upturn of $K(T)$ near T_c.

(iii) For all the studied crystals the temperature dependencies of thermal conductivity are approximately the same at low temperature $T<10$ K.

(iv) The magnitude of $K(T)$ tends to decrease down to its minimum for the samples with $x\approx 0.5$, near the metal-insulator transition at $x_{MI}\approx 0.4$.[20] The thermal conductivity of the insulating antiferromagnetic $YBa_2Cu_3O_6$ is higher than that of fully oxygenated crystals of $YBa_2Cu_3O_7$ in the normal state.

Similar behavior was observed in oxygen-deficient ceramic samples.[24–27] The main differences of our results from the most representative data of Zavaritskii *et al.*[26] consist in observation of the maximum in the thermal conductivity for our insulating sample ($x\approx 0$) at $T\simeq 175$ K and well-pronounced peak in $K(T)$ below T_c for superconducting crystals. It is naturally to connect these differences with higher quality of single crystals than of ceramics.

The temperature dependence of the in-plane thermal conductivity for insulating crystal of $YBa_2Cu_3O_6$ (Ref. 15) is anomalous as compared with that for normal dielectric crystals. These data differ essentially from the results obtained by Hagen *et al.*[13] for nonsuperconducting crystals. They observed a smooth monotonic dependence of $K(T)$ with magnitude of about 0.07–0.1 W/(cm K) at $T>100$ K. Our experimental data on the variation of the $K(T)$ with oxygen content suggest that in the crystals used by Hagen *et al.* the oxygen content was larger than in our crystal being within the range $0.1<x<0.4$. Recently, Cohn *et al.*[28] measured the in-plane thermal conductivity for lightly oxygen-doped $YBa_2Cu_3O_{6+x}$ crystals ($x\leqslant 0.11$) and found the maximum in $K(T)$ at approximately 200 K for the crystal with $x\approx 0.05$. Our data for $YBa_2Cu_3O_6$ are in qualitative agreement with Cohn *et al.*,[28] although we found the more pronounced peak in $K(T)$ and the stronger temperature dependence of $K(T)$ above the maximum.

In common dielectric crystals, the thermal conductivity varies approximately as T^{-1} at high temperatures. This dependence arises from the phonon-phonon interaction. Normally impurities and lattice defects result in a weaker temperature dependence of $K(T)$. We suppose that the heat transport in the insulating $YBa_2Cu_3O_6$ is due to the phonons. The thermal conductivity of $YBa_2Cu_3O_6$ varies stronger than T^{-1} in the temperature range 240 K $<T<$ 440 K and tends toward a T^{-1} dependence at higher temperatures. In some nonmagnetic dielectrics, the faster than T^{-1} dependence of lattice thermal conductivity at high temperatures (near the Debye temperature) can arise from such anharmonic effects as the volume thermal expansion and higher-order phonon-phonon interactions.[14] Using experimental data for the thermal expansion,[29] we estimate that the thermal conductivity may decrease by few percent with temperature increase from 300 K to 500 K due to the change in crystal density. Thus this small effect cannot account for the steep T dependence of $K(T)$ in $YBa_2Cu_3O_6$. Note that for $YBa_2Cu_4O_8$ Andersson and Sundvist[30] have found experimentally that $K(T)$ data obtained at constant pressure and constant volume differ only slightly at high temperatures. Generally, higher-order phonon-phonon interactions are much weaker than the three-phonon interactions and result in small additional term, $\sim T^{-2}$, in $K(T)$. We suppose that the higher-order phonon-phonon interactions also contribute a little to the thermal of $YBa_2Cu_3O_{6+x}$. Comparison of $K(T)$ for insulating $YBa_2Cu_3O_6$ with that for metallic $YBa_2Cu_3O_7$, which shows the weak temperature dependence near room temperature, supports the proposition that the discussed anharmonic effects are inessential.

We attribute the anomalous behavior of $K(T)$ near the Néel temperature, $T_N\simeq 420$ K, in the antiferromagnetic $YBa_2Cu_3O_6$ to a coupling between phonons and spin excitations in the CuO_2 planes. The observed strong dependence of $K(T)$ implies that the spin-phonon relaxation rate, τ_{sp}^{-1} is of the same order of magnitude as the sum of phonon-phonon and defect scattering rates, $\tau_{3ph}^{-1}+\tau_d^{-1}$, at $T\approx T_N$. The spin-phonon coupling becomes unimportant well far from the Néel temperature, i.e., above 440 K and below 240 K. This ''magnetic'' interpretation of the high-temperature anomaly in the $K(T)$ is supported by the recent doping studies of Taldenkov *et al.*,[31] where for $YBa_2Cu_3O_6$ the peak in $K(T)$ at $T\simeq 175$ K is dramatically suppressed at small concentration (<2.5 at. %) of Zn and Ni impurities. These impurities destroy locally the antiferromagnetic ordering in the CuO_2 planes and are not strong point-defect scatterers for phonons because of small difference between their and Cu atomic masses and ionic radii.

In $YBa_2Cu_3O_6$ the temperature dependence of $K(T)$ is anomalous at temperatures below 200 K. There is a maximum in $K(T)$ at unusually high temperature of 175 K. This behavior of $K(T)$ suggests that some additional process of phonon relaxation contributes substantially to the total scattering rate and almost entirely determines the $K(T)$ below 175 K. We have found that anomalous dependence of $K(T)$ can be qualitatively described within the Callaway model provided that there is a strong relaxation for the phonons having the energy (in the temperature unit) in the range from 20 K to 250 K. It means that the phonon-phonon and defect scattering are insignificant at $T<200$ K. From the above considerations we conclude that in $YBa_2Cu_3O_6$ the phonon-phonon and defect scattering processes may be important only within the temperature range from 200 K to 240 K. An estimation of scattering rate from the magnitude of $K(T)$ in this temperature range yields the upper limit for $\tau_{3ph}^{-1}+\tau_d^{-1}$

Let us compare the $K(T)$ data for crystals of $YBa_2Cu_3O_{6+x}$ with different oxygen content. In $YBa_2Cu_3O_{6+x}$, the specific heat[32] and sound velocity[33] do not change considerably to explain the variation of lattice thermal conductivity with the oxygen content. It is evident that changes in the relaxation rate of dominant heat carriers and in electronic properties are responsible primarily for the variation of $K_{ph}(T)$.

The in-plane thermal conductivity of $YBa_2Cu_3O_7$ is about two times smaller than that of $YBa_2Cu_3O_6$ at temperatures near 200 K. Assuming that the anharmonism and concentration of lattice defects in these crystals are approximately similar, we conclude that the contribution of phonon-phonon and phonon-defect scattering to the total phonon relaxation rate is less than 30% in $YBa_2Cu_3O_7$. For crystals of $YBa_2Cu_3O_{6+x}$ with approximately two times smaller magnitude of thermal conductivity, these scattering processes contribute even less and therefore are insignificant. Our conclusion about the small contribution of the phonon-phonon scattering is consistent with that of Cohn *et al.*.[34]

The question arises as to what are dominant phonon scattering processes in superconducting crystals of $YBa_2Cu_3O_{6+x}$ in the normal state? The suppression of the phonon thermal conductivity in metallic $YBa_2Cu_3O_{6+x}$ at high temperatures may be due to phonon scattering by charge carriers, spin excitations, and oxygen defects within the CuO_x chains. It is very difficult to separate the net effect of the oxygen defects by comparing the $K(T)$ data for pure crystals of $YBa_2Cu_3O_{6+x}$ with different oxygen content, because the changes in the electronic and spin excitation spectra accompany the change in the concentration of oxygen defects. Usually lattice defects (without internal degrees of freedom) tend to produce the positive slope of the K_{ph}. Indeed, we have found that in-plane $K(T)$ for $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$ crystal, in which Er atoms are the strong point (mass) defects, shows the positive slope at $T>T_c$. The observed negative slope of the $K(T)$ for superconducting crystals, which becomes more pronounced with oxygen deficit, suggests that oxygen defects (as the point defects) are not strong phonon scatterers, though they can produce some overall suppression of the phonon thermal conductivity. Numerical estimations also shows that the phonon scattering rate from oxygen defects is small.[35]

It is well known that metallic $YBa_2Cu_3O_{6+x}$ demonstrates dynamic antiferromagnetic correlations.[36] One of the intriguing features of the normal-state excitation spectrum in underdoped $YBa_2Cu_3O_{6+x}$ is so-called ''spin gap'' (or pseudogap) opening: the loss of low energy spectral weight which sets in at temperature T^* above T_c. In overdoped samples the temperature variation of the excitation spectrum is qualitatively different: there is no spin-gap formation above T_c. Evidence suggestive of the spin-gap phenomena was obtained from NMR,[37] neutron scattering,[36] electrical resistivity,[38] specific heat,[32] reflectivity,[39] and thermoelectric power.[40] It is important that Litvinchuk *et al.*[41] have found a correlation between the temperature dependencies of phonons and spin excitations in the oxygen-deficient $YBa_2Cu_3O_{6+x}$. This observation indicates that there is a sizable spin-phonon coupling at least for some infrared and Raman-active phonons. Above we concluded that in the antiferromagnetic $YBa_2Cu_3O_6$ the interaction of acoustical phonons with spin excitations strongly suppress the thermal conductivity near T_N. On this basis, one may expect a finite magnitude of phonon scattering from spin excitations in metallic $YBa_2Cu_3O_{6+x}$ which could result in the increasing of the phonon thermal conductivity with temperature decrease due to the spin-gap opening.

To gain some insight into the effect of spin-gap opening, we would have to use the normalized data, $\kappa(T)=K(T)/K(300\text{ K})$, in order to exclude the relatively large experimental uncertainty in the absolute value of thermal conductivity which hampers the analysis of the $K(T)$ evolution upon doping. Shown in Fig. 4 are the temperature dependencies of normalized thermal conductivity $\kappa(T)$ for crystals of $YBa_2Cu_3O_{6+x}$ with $x>0.5$. Two features have to be pointed out. First, for underdoped samples the $\kappa(T)$ systematically deviates from the nearly T-linear dependence, the deviations emerging at higher temperature as the oxygen concentration decreases. Secondly, the overdoped sample demonstrates completely different behavior, namely, the monotonic increase of the $\kappa(T)$ with decreasing temperature down to 120 K and a plateau in the temperature range from 120 K to 98 K. It is very likely that these features arise from characteristic behavior of the excitation spectrum in $YBa_2Cu_3O_{6+x}$, and the data in Fig. 4 suggest that the opening of the spin gap at temperatures below T^* results in a decrease of heat carriers scattering rate.

Recently Ito *et al.*[38] found a spin-gap effect on the in-plane electrical conductivity $\sigma(T)$ of $YBa_2Cu_3O_{6+x}$. Our experimental data can be tested for conformity to electrical conductivity data. For this we estimated an upper limit to the electron thermal conductivity K_e using the data of Refs. 38

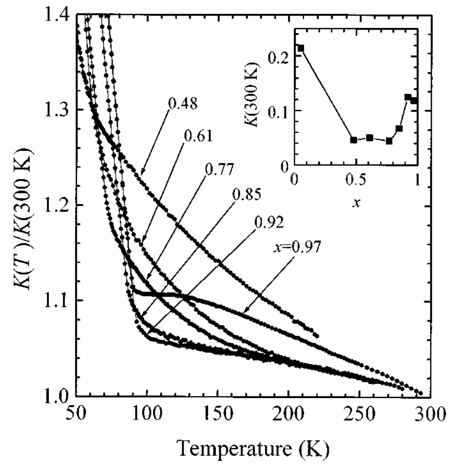

FIG. 4. Temperature dependence of the normalized in-plane thermal conductivity for the $YBa_2Cu_3O_{6+x}$ single crystals. The insert is plot of the thermal conductivity at $T=300$ K as a function of the oxygen concentration. The lines through the data are a guide for the eye only.

and 42 for the in-plane $\sigma(T)$ and the Wiedemann-Franz low $K_e=L_0\sigma T$. It appears that the features of $\kappa(T)$ discussed above can be ascribed to the rise of $K_e(T)$ due to systematic deviation of the electrical conductivity from the T-linear dependence, provided that $K_{ph}(T)$ has a slight negative curvature at T well above T_c, but rises with decreasing temperature near T_c in underdoped crystals. The latter is due to the flattening out and weak dependence of $\sigma(T)$ on temperature near T_c. At room temperature the ratio of K_{ph}/K_e increases from approximately 2 to 6 as the oxygen deficiency increases from 0.08 to 0.5. However, in spite of this consistent picture at $T\sim T^*$, the rise $K_{ph}(T)$ near T_c suggests that the spin-gap formation results in decreasing of the phonon scattering rate. It is noteworthy that in underdoped stoichiometric crystals of $YBa_2Cu_4O_8$ the in-plane thermal conductivity[43] and electrical conductivity[44] exhibit the deviation from T-linear dependence at $T<180$ K similar to those found in the underdoped metallic $YBa_2Cu_3O_{6+x}$.

For crystals of $YBa_2Cu_3O_{6+x}$ with oxygen concentration near optimal value, the temperature dependence of $K(T)$ shows an almost abrupt change of the slope $\partial K/\partial T$ in narrow temperature interval near T_c. Note that superconducting fluctuations might contribute to the increase of $K(T)$ above T_c.[45] Cohn *et al.*[46] attributed the slight enhancement of $K(T)$ in $YBa_2Cu_3O_{6+x}$ ($x\approx0.9$) at temperatures about 20 K above T_c to the effect of superconducting fluctuations. Thus one can expect that without superconducting fluctuations the increase of $K(T)$ would be even sharper at T_c. The observed behavior of $K(T)$ does not seem consistent with theoretical results. Wermbler and Tewordt[47,48] calculated $K_{ph}(T)$ and $K_e(T)$ for high-T_c superconductors with s-wave pairing in the framework of strong-coupling theory and two-dimensional Hubbard model for electrons interacting via exchange of phonons, charge fluctuations, and spin fluctuations. The pair-breaking caused by spin fluctuations results in a gapless density of states near T_c and a gradual upturn of the $K_{ph}(T)$ below T_c. For $K_e(T)$, even more smoothing off upturn was obtained. For the d-wave pairing, the $K_{ph}(T)$ (Ref. 6) and $K_e(T)$ (Ref. 49) exhibit similar gradual variations near T_c. The same results are expected for superconductors with extended s-wave gap having nodes on the Fermi surface. For optimally doped crystals, the experimental data suggest that the scattering rate of heat carriers changes abruptly at T_c. We suppose that this is a result of a rapid spin-gap opening below T_c. The diminishing of the sharp upturn with oxygen deficit may be due to a gradual opening of the spin gap, which sets in well above T_c, with a small change in the rate of gap formation at T_c. This behavior of $K(T)$ correlates well with that of low-frequency c-axis optical conductivity[39] and Knight shift.[50] In addition, the above-mentioned T dependence of electrical conductivity, which flattens out as T_c is approached from above (this is just the opposite of what is expected of the superconducting fluctuations), suggests that in the underdoped crystals the effect of superconducting fluctuations on the $K(T)$ is small.

In the superconducting $YBa_2Cu_3O_{6+x}$ crystals with oxygen content near optimal, the sharp upturn of $K(T)$ at T_c seems to us to suggest that the phonon interaction with spin excitations and charge carriers contributes insignificantly to the phonon relaxation at temperatures below the peak in $K(T)$. This is a consequence of rapid opening of the energy gap in both charge and spin excitation spectra at $T<T_c$ (for optimally doped YBCO, recent neutron experiments[51] shows almost zero spectral weight of low energy spin excitations at low temperatures). Therefore, it appears that at low temperatures the phonon thermal conductivity in the superconducting crystal is almost completely determined by the relaxation processes which operate in the insulating analog. Since the values of thermal conductivity for superconducting $YBa_2Cu_3O_7$ and insulating $YBa_2Cu_3O_6$ are the same within experimental uncertainty at temperatures below the peak, we conclude that the unknown phonon relaxation process persists in superconducting crystals of $YBa_2Cu_3O_{6+x}$ as well. We suppose that in the underdoped crystals the electron-phonon and spin-phonon interactions may contribute significantly to the phonon damping at low temperatures.

Valuable information about phonon spectrum can be gained from inelastic neutron scattering measurements, Raman and far-infrared spectroscopy. For $YBa_2Cu_3O_{6.6}$, a slight decrease in the linewidth of an in-plane transverse acoustic phonon mode below T_c was observed by Harashina *et al.*[52] The authors attributed the linewidth narrowing to the reduction of the electron-phonon scattering rate due to the Cooper pair formation. This effect implies the increase of the phonon thermal conductivity below T_c with decreasing T. Far-infrared reflectivity studies of the $Y_2Ba_4Cu_{6+n}O_{14+n}$ ($n=0,1,2$) (Ref. 53) showed a decrease in the linewidth of some infrared-active phonons at superconducting transition. Recently, the spin-phonon coupling in HTS was studied theoretically by Normand *et al.*[54] within slave-boson, mean-field treatment of the extended t-J model. This theory predicts that optical-phonon anomalies in underdoped $YBa_2Cu_3O_{6+x}$ should show evidence of the spin-gap phenomena with the same characteristic temperature as that found in NMR studies. While optical phonons do not contribute to the heat transport, the changes in their linewidth near T_c support the conclusion that some phonon modes couple to spin excitations and charge carriers. Moreover, Yagil *et al.*[55] reported an experimental evidence for strong electron-phonon coupling to selected phonon modes in point-contact spectroscopy of $YBa_2Cu_3O_{6+x}$. The authors pointed to the probable "existence of additional excitations which are strongly coupled to the phonons, and are also involved in the pairing mechanism."

From the available experimental data, we cannot deduce unambiguously which scattering processes are responsible for the suppression of phonon thermal conductivity in superconducting $YBa_2Cu_3O_{6+x}$ with respect to the insulating counterpart. Apart from the obvious candidates, electron-phonon and spin-phonon scattering, the unknown relaxation process, which determines the behavior of $K(T)$ in the insulating $YBa_2Cu_3O_6$ at $T<200$ K, may contribute a lot to the phonon damping in metallic crystals. It seems likely that this unknown process may be required to explain the $K(T)$ within any scenario of the heat transport. Note that recently Cohn *et al.*[28] tentatively attributed the anomalous phonon damping in insulating $YBa_2Cu_3O_{6+x}$ and $PrBa_2Cu_3O_{6+x}$ to a lattice structural instability (local tilt distortions of the CuO polyhedra) and argued that this phonon damping may be weaker in superconducting $YBa_2Cu_3O_7$.

IV. CONCLUSIONS

In conclusion, we have carried out a systematic investigation of the in-plane thermal conductivity for oxygen-deficient single crystals of $YBa_2Cu_3O_{6+x}$. We find that the temperature dependence of the thermal conductivity for insulating $YBa_2Cu_3O_6$ differs substantially from that for normal dielectric crystals. The strong temperature dependence of $K(T)$ in the broad vicinity of the Néel temperature suggests the strong spin-phonon coupling. The decrease of $K(T)$ below 175 K is attributed to the suppression of the heat transport by some unknown phonon scattering process. This scattering exists in superconducting crystals of $YBa_2Cu_3O_{6+x}$ having oxygen content up to 6.97 and contributes significantly to the phonon scattering in wide temperature range. The nature of this unknown phonon scattering is unclear. We have argued that oxygen vacancies within the CuO_x chains and other lattice defects play a minor role in scattering of phonons and quasiparticles confined in the CuO_2 planes.

The thermal conductivity peak is well developed both in OrthoI and OrthoII phase and is diminished under metal-insulator transition. Examination of the $K(T)$ data for metallic $YBa_2Cu_3O_{6+x}$ reveals the features in the temperature dependence of $K(T)$ which we attribute to the spin-gap behavior of the normal-state excitation spectrum. The change of the rate of spin-gap formation at transition from normal state to superconducting is likely to be responsible for the upturn in $K(T)$ near T_c. We have argued that in metallic $YBa_2Cu_3O_{6+x}$ the spin-phonon coupling may play an important role in the phonon thermal conductivity. It is notable that recently Cohn[56] found that the superconducting-state enhancement of the $K(T)$ is inconsistent with the electonic scenario of heat transport and could be predominantly phononic. The question of relative contributions of phonons and electrons to the thermal conductivity of superconducting

$YBa_2Cu_3O_{6+x}$ below T_c is still an open question.

We believe that this qualitative interpretation of the $K(T)$ data for $YBa_2Cu_3O_{6+x}$ including the existence of the unknown phonon scattering is appropriate in the cases of other superconducting and insulating cuprates. The present results should stimulate theoretical studies of the effect of spin excitations on the thermal conductivity of HTS.

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