Thermal conductivity of Bi-Sr-Ca-Cu-O superconductors: Correlation with the low-temperature specific-heat behavior

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Thermal conductivity has been measured on Bi-Sr-Ca-Cu-O high-T_c superconductors down to 70 mK. Samples included a sintered specimen as well as two hot-pressed samples cut from the same ingot parallel and perpendicular, respectively, to the pressing direction. Below 3 K the thermal conductivities of all samples follow an approximately quadratic temperature variation with no indication of the limiting T-linear dependence typically observed for the superconducting state of Y-Ba-Cu-O and La-Sr-Cu-O ceramics. We discuss the apparent correlation between the occurrence or absence at low temperatures of a T-linear thermal conductivity and a T-linear (γ) term in the specific heat in all high-T_c superconducting ceramics.

We have recently reported[1,2] on the anomalous thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ (1:2:3) and $La_{2-x}Sr_xCuO_4$ (La-Sr-Cu-O) ceramics at very low temperatures where a T-linear temperature dependence sets in below about 300 mK. Such a weak temperature variation is surprising for the temperature range far below T_c where the material might be expected to behave as an ordinary dielectric solid. Indeed, on destroying superconductivity by annealing the ceramics in a vacuum above 600 °C, the T^3-dependence characteristic of the phonon boundary scattering is invariably observed. As a consequence, the thermal conductivity of the insulating phase at 0.1 K is an order of magnitude lower than that of the superconducting phase of the same material. In order to account for this astounding difference in the behavior of the superconducting and insulating phases, we have postulated the presence of a small number of uncondensed carriers participating in the heat transport of superconducting ceramics. By extrapolating the resistivity data to below T_c and invoking the Wiedemann-Franz law, we have estimated the uncondensed carrier fraction in the 1:2:3 compound as $\sim 5\%$ of the total carrier concentration. This small normal carrier contribution would be sufficient to dominate the thermal conductivity below 0.2 K and it could account for the magnitude of the widely observed T-linear (γ) term in the specific heat of these two high-T_c superconducting ceramics.[3] The exact physical origin of the uncondensed carriers is as yet unspecified but models based on a Fermi surface with some gapless regions[4] would provide for coexistence of superconducting and normal bands and, therefore, for the electronic origin of the linear term in the specific heat. Other possible mechanisms frequently mentioned with regard to the specific heat are two-level tunneling systems[5] and impurity phases.[6,7] The latter in particular has been explored in some depth and it was found[8] that the $BaCuO_{2+x}$ impurity phase has a very high γ term that might influence the overall specific heat even if its volume fraction is very small, $\lesssim 1\%$. A linear term intimately tied to a superconducting state is also predicted by a resonating-valence-bond (RVB) model.[9] The major appeal here, of course, is an entirely new mechanism of superconductivity whose relevance to the high-T_c materials is yet to be firmly established.

While extensive experimentation worldwide confirms the presence of the unusual linear term in the specific heat of La-Sr-Cu-O, 1:2:3 and, more recently, also in Tl-Ca-Ba-Cu-O superconductors, any claim to universality of this behavior, or perhaps identifying this property as clearly distinguishing the new class of oxide superconductors from conventional superconductors, is rendered questionable by the specific-heat data on Bi-Ca-Sr-Cu-O. Regardless of annealing conditions and the exact stoichiometry, including the presence of either "85-K" or "116-K" phases or both, all high-precision specific-heat measurements show a persistent lack of a detectable linear term.[10–12] Since we have established that the anomalous linear variation of the thermal conductivity of the La-Sr-Cu-O and 1:2:3 materials is observed only when the ceramics are in their superconducting state and both of these oxides possess a linear specific-heat term, in this paper we inquire whether this reciprocity extends also to the Bi-based high-T_c oxides. The question posed is whether the missing linear term in the specific heat is reflected in the lack of a T-linear dependence of the thermal conductivity well below 1 K.

To test this premise we measured the thermal conductivity on three Bi-Ca-Sr-Cu-O samples down to 70 mK. Sample A was prepared from a mixture of powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO at the atomic ratio of Bi:Sr:Ca:Cu = 1:1:1:2. The mixture was thoroughly ground and annealed at 820 °C for 12 h, and this process was repeated. The material was then reground and isotropically pressed at 55×10^3 psi. The pellet was annealed at 865 °C for 120 h in air. Samples B and C were prepared with the same starting materials using a standard coevaporation process. Powders were mixed in an atomic ratio of Bi:Sr:Ca:Cu = 2:2:1:2 and dissolved in HNO_3. The solution was heated on a hotplate until thick and then baked at 200 °C in an alumina crucible until a dry powder was obtained. The powder was reground and annealed for 12 h at 850 °C. This process was repeated twice for a total anneal time of 36 h. Finally, the material was hot pressed in an argon atmosphere at 1 MPa at 800 °C for 30 min. Samples B and C were cut from this pellet with their long axes perpendicular and parallel to the pressing direction, respectively. The bulk density of the hot-pressed samples is 6.3 g cm^{-3}. To characterize the samples and to establish their superconducting and normal-state parameters, we have first measured the Meissner signal and the electrical resistivity.

Field-cooled magnetization (Meissner effect) was carried out in a Quantum Design magnetometer at a field of 150 Oe and the data are presented in Fig. 1. Sample A shows clearly the presence of two phases, one undergoing a transition near 106 K and the lower one near 85 K. The hot-pressed samples show a dominant transition near 90 K with a trace of a lower phase near 20 K. Little difference between the two orientations is seen.

The electrical resistivity of the samples determined by a four-probe technique is shown in Fig. 2. We note that sample A has a strong metallic dependence and its resistance changes by a factor of 2.7 between room temperature and 114 K. Because of the large superconducting fluctuation contribution to the resistivity, it is difficult to pinpoint exactly the upper superconducting transition temperature but it occurs in the vicinity of 110 K. It is clear that the higher-T_c phase is quite well connected throughout the sample; nevertheless, a small resistive tail remains and the resistance becomes undetectable only at 90–91 K.

It is well known that hot pressing promotes alignment of the crystallites during the processing by favoring faster growth in the directions that help to relieve internal stress.[13] The resulting structural anisotropy is reflected in the transport phenomena and our resistivity data on samples B and C show this effect. While the T_c's are the same, both the magnitude and the temperature dependence of the resistivity differ significantly between the perpendicular (sample B) and parallel (sample C) sample orientations. The anisotropy ratio, R_C/R_B, is equal to 4.2 at room temperature and the resistivity in the parallel direction has a slightly activated character. Both hot-pressed samples have a significantly higher resistivity than sample A. A similar trend has been observed recently by Murayama *et al.*[13] Only after prolonged annealing in air did the normal-state resistance of their hot-pressed samples fall below those of sintered materials.

Investigations of the thermal conductivity were carried

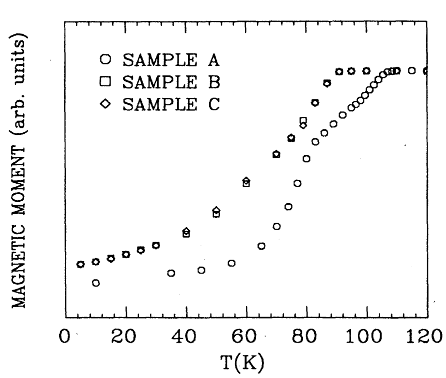

FIG. 1. Field-cooled magnetization (Meissner effect) for Bi-Sr-Ca-Cu-O superconductors. Measurement field is 150 Oe.

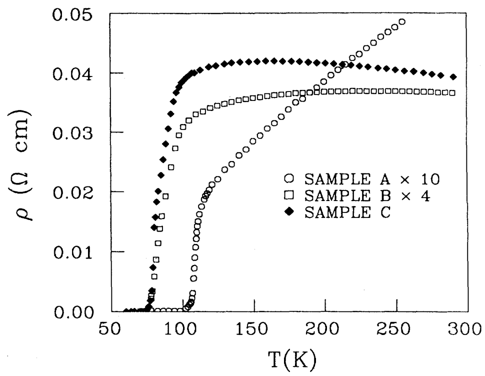

FIG. 2. Temperature dependence of the resistivity of Bi-Sr-Ca-Cu-O samples determined by a four-probe technique. Note different scales for the samples and large anisotropy for the hot-pressed material.

out by a steady-state technique and cooling was provided by a dilution refrigerator. As temperature sensors, we used Ge thermometers with calibrations traceable to NBS standards, and stability checked against superconducting fixed-point devices. The heater is a small metal-film resistor attached on the free end of the sample. All electrical leads are made of very thin and long cupro-nickel-clad Nb-Ti superconducting wires in order to limit any stray heat to or from the sample. We stress that the thermal conductivity of all high-T_c oxides is rather low, at subkelvin temperatures more than 2 orders of magnitude below that of typical metal alloys, such as steel, and care must be exercised to minimize heat losses. Measurements on sample A were extended to room temperature in a separate helium 4 cryostat where a differential Au(Fe)/Chromel P thermocouple was employed to determine the temperature gradient.

The high-temperature data for sample A are shown in Fig. 3. The thermal conductivity gradually decreases until near 110 K one observes a clear upturn that continues and peaks around 75 K, followed by a rapid decrease of the conductivity as the temperature falls. This behavior, specifically the proximity of the upturn to the superconducting transition temperature, is reminiscent of the situation of $YBa_2Cu_3O_7$. We[14] and others[15–18] have associated this sudden increase in thermal conductivity with an enhancement in the phonon mean free path (mfp), which arises as the carrier system undergoes condensation. This feature is a signature of the phonon-carrier coupling in the system. An attempt[19] to quantify this interaction by fitting the thermal conductivity in the neighborhood of the peak to the Bardeen-Rickayzen-Tewordt theory yielded a magnitude of the BCS-type energy gap in fair agreement with other experimental data. It should be noted, however, that the calculation was done under rather simplified assumptions that included the use of a free-electron model, a physical picture that is likely to be inappropriate for the carriers in the high-T_c oxides.

We estimate the maximum contribution that the carriers provide to the heat transport as no more than 13% of the phonon thermal conductivity. We arrive at this upper bound on the carrier thermal conductivity by using the

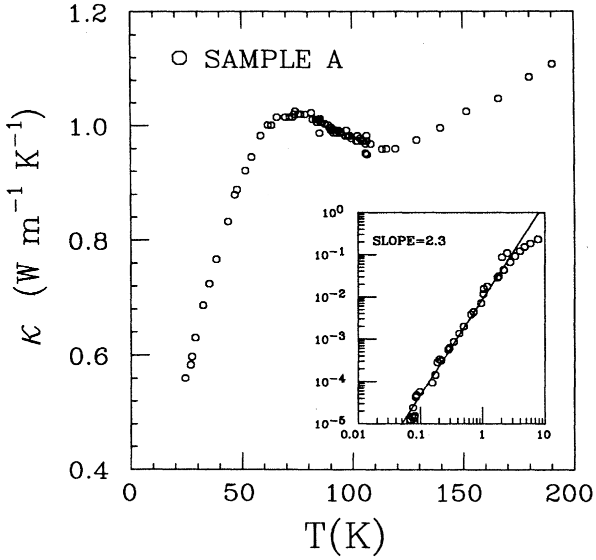

FIG. 3. Temperature dependence of the thermal conductivity for sample A. The inset shows the data at very low temperatures and the line through the data points has a slope of 2.3.

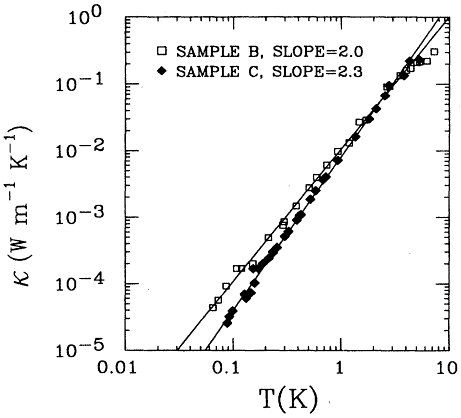

FIG. 4. Thermal conductivity for the hot-pressed samples of Bi-Sr-Ca-Cu-O at very low temperatures. Lines of best fit and their slopes are indicated.

resistivity data of sample A in Fig. 2 and invoking the Sommerfeld value of the Wiedemann-Franz law. Again, this fraction is comparable to the one observed on the 1:2:3 compounds.

Since there is evidence (see Figs. 1 and 2) for two superconducting phases coexisting in sample A, one might expect an additional upturn on the κ vs T plot corresponding to the lengthening of the phonon mfp as the remaining normal carriers (those associated with the lower-T_c phase) condense. We have looked for such a feature but no effect was detected. Of course, it is more difficult to resolve an upturn on an already rising thermal conductivity, but it is also possible that the additional enhancement in the phonon mfp is small due to a smaller number of the remaining normal carriers or their weaker coupling to the phonon system.

Low-temperature data for sample A are shown in the inset of Fig. 3 and those for samples B and C are presented in Fig. 4. We note that below about 3 K a straight line on a log-log plot is a very good description of the thermal conductivity of all the specimens. In this whole temperature range the power-law variation is close to T^2 and even at temperatures as low as 70 mK, we do not detect any sign that might indicate a crossover to a T-linear dependence. This behavior contrasts sharply with the situation in the 1:2:3 and La-based high-T_c ceramics and it represents the key experimental observation of this paper. Assessing all the low-temperature thermal conductivity data on the high-T_c sintered oxides, we arrive at a correlation between the occurrence of the linear term in the specific heat and the presence of a limiting T-linear behavior of the thermal conductivity. Just as the presence of the linear specific heat is not a universal feature of the high-T_c oxides, so the T-dependence of the thermal conductivity is not an intrinsic feature of these materials. Furthermore, the correspondence between the specific-heat and thermal conductivity anomalies suggests that whatever causes the nonzero γ term is not simply a static structural feature but has a dynamical character that is reflected in the transport process. An obvious candidate appears to be a minute amount of a normal phase dispersed in the high-T_c matrix that yields an electronic specific-heat term as well as a small free carrier density that dominates heat transport at subkelvin temperatures. The data suggest that Bi-Sr-Ca-Cu-O does not contain any such phase and one can only speculate whether perhaps among Ba- or La-containing compounds there exists a phase that affects both the La-Sr-Cu-O and Y-Ba-Cu-O materials. Additional evidence in support of the impurity phase comes from measurements on $YBa_2Cu_3O_7$ single crystals[20] where an approximately quadratic temperature dependence of the thermal conductivity, similar to the data of Fig. 3, is observed. Presumably, high-quality single crystals would not contain a significant amount of the impurity phase and the T^2 variation might then be interpreted as arising from phonon scattering on the tunneling states of the system, much like the situation in glasses but without the typical plateau.

We also note that in spite of the large processing-induced anisotropy in the normal-state electrical resistivity of the hot-pressed samples, their phonon systems appear much less affected. Around 4.2 K samples B and C have comparable thermal conductivities and at lower temperatures sample C gradually becomes a less efficient heat carrier than sample B. Including sample A whose normal-state resistivity is a factor of 2 lower than that of sample B and an order of magnitude below sample C, the impression one gets from Figs. 3 and 4 is that the lattice and electron transports do not correlate well. This was also apparent[21] in the thermal conductivity data on hot-pressed 1:2:3 where the conductivity of "parallel"-oriented samples below 10 K actually exceeded the conductivity of the sample cut from the same ingot but perpendicular to the pressing direction. Clearly, the electronic properties are much more sensitive to the orientation of the grains than the phonon transport. While estimates of anisotropy in the electrical resistivity of single crystals of high-T_c oxides are known, anisotropy of heat transport must await the availability of larger crystals more amenable to measurements along the c-axis direction.

In conclusion, we have shown that the missing γ term in the specific heat of Bi-Sr-Ca-Cu-O high-T_c ceramics has its direct counterpart in the missing T-linear limiting thermal conductivity behavior. Combined with the consistent presence of T-linear terms in the data for specific heat and thermal conductivity of both the 1:2:3 and La-Sr-Cu-O materials, we suggest that the 1:2:3 and La-Sr-Cu-O oxides contain a trace impurity phase that contributes a small number of carriers that do not participate in superconductivity. Bi-based high-T_c superconductors do not show this feature possibly because no Ba compounds are used in their synthesis. To test this latter hypothesis ultrapure starting chemicals should be used to synthesize 1:2:3 compounds to determine their specific heat and low-temperature thermal conductivity.

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