Evidence for the shift of the transition temperature in $R\mathrm{Ba_2Cu_4O_8}$ by thermal-conductivity measurements

A. Jeżowski and J. Klamut

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław 2, P.O. Box 937, Poland

B. Dabrowski

Department of Physics, Northern Illinois University, DeKalb, Illinois 60115

We have measured the thermal conductivity (K) of polycrystalline specimens of $R\mathrm{Ba_2Cu_4O_8}$ ($R=$Dy, Gd, and Eu) within the temperature range 4.2–300 K during both cooling and heating. The results show hysteresis between 70 and 230 K and the change of temperature at which a strong enhancement of $K(T)$ below T_c is observed—the difference between T_c^c cooling and T_c^h heating. We propose the conclusion that these anomalous properties are due to the anharmonic unstable sublattice of the apical oxygen atoms.

The thermal conductivity in the high-T_c superconductors (HTS) is an important property which offers information on transport mechanisms in both the normal and superconducting states. Thus, measurements of thermal conductivity are very convenient in studying the phonon-charge carrier interactions and the scattering of phonons and carriers against lattice imperfections. Heat transport have therefore been extensively studied in HTS (see Refs. 1 and 2) for most materials, particularly for $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (Y 1:2:3).

In this paper we report our investigation of the thermal conductivity of $R\mathrm{Ba_2Cu_4O_8}$ (Dy 1:2:4, Eu 1:2:4, and Gd 1:2:4). The crystal structures of 1:2:3 and 1:2:4 type superconductors are similar, differing mostly by the presence of a second chain in the latter compound. There are, however, significant differences between the two compounds. While 1:2:3 is very unstable with respect to its oxygen stoichiometry with a related orthorhombic-to-tetragonal phase transition at high temperatures, the other, 1:2:4, has excellent thermal stability regarding both its oxygen stoichiometry and structural properties. Also, good samples without twinning are available in the latter case.

Although 1:2:4 superconductors are appealing for their properties, there is, according to our best knowledge, only one report on their thermal conductivity, for $\mathrm{YBa_2Cu_4O_8}$ (Y 1:2:4).[3] The lack of works comes, undoubtedly, from difficulty in producing this material.

Several theories and experiments have shown the existence of structural instabilities and anomalies in the lattice of the HTS. These instabilities are related to a highly nonlinear interaction between the carriers charge and phonons. Also, the phonon spectrum and phonon relaxation may change due to the changes in structure. This should be reflected in the heat transport phenomena. Given the great sensitivity of the thermal conductivity to oxygen content[1] it is possible to detect atomic size disorder within the oxygen system. This behavior was observed earlier by us in the Y 1:2:3 (Ref. 4) and Tl 2:2:2:3 (Ref. 5) where we have noticed differences between the heating and cooling curves over a broad temperature range of 80–240 K. Since this anomalous behavior was not seen in the electrical resistance and since the electron component of the thermal conductivity was comparatively

small, we concluded that the hysteresis was not due to the electron component and was, instead, the result of an instability of the phonon subsystem. Better oxygen stability of R 1:2:4 and possibly intrinsic differences in the scattering properties have driven our interest into extending these measurements to the studies of lattice instability effects on the thermal conductivity of 1:2:4 compounds.

Polycrystalline samples of $R\mathrm{Ba_2Cu_4O_8}$ were synthesized from stoichiometric mixtures of oxides of R ($R=$Dy, Gd, and Eu) and Cu, and barium carbonate. Powder samples were fired several times in air at 900 °C with frequent intermediate grinding until no trace of barium carbonate could be detected in the x-ray diffraction pattern. A subsequent high-pressure synthesis was done using a large capacity hot isostatic press system. Samples were pressed into pellets and fired three times for 12 h in 20% O_2 in argon at a total pressure of 3 kbar at 1050 °C followed by slow cooling (1.5 deg/min) down to room temperature. The specimens for thermal conductivity and electrical resistivity measurements were cut from pellets to dimensions of $12\times2\times2$ mm^3. X-ray analysis indicated good structural quality of the material.

Precise thermal conductivity measurements during heating and cooling cycles were performed over the temperature range 4.2–300 K using the steady-state method. The absolute temperature as well as the temperature gradient along the sample (about 0.2 K) was determined with a calibrated manganin-konstantan thermocouple, with a wire diameter of 50 μm. Particular care was taken to avoid heat transfer between the sample and the environment. The systematic maximum experimental error was below 4% (mainly connected with geometrical uncertainties of the sample dimensions); however, the rms statistical scatter of points for both cycles (during the heating and cooling processes) did not exceed 0.3%. Thus, the measured T dependence of K in both cycles is much more accurate than the absolute values of K for different samples.

The thermal conductivity of $\mathrm{DyBa_2Cu_4O_8}$, $\mathrm{GdBa_2Cu_4O_8}$, and $\mathrm{EuBa_2Cu_4O_8}$ is shown in Fig. 1. No earlier data were presented for these compounds in the literature. We can compare our results only with the data from the investigation of $K(T)$ of $\mathrm{YBa_2Cu_4O_8}$ by Andersson *et al.*[3] Although the au-
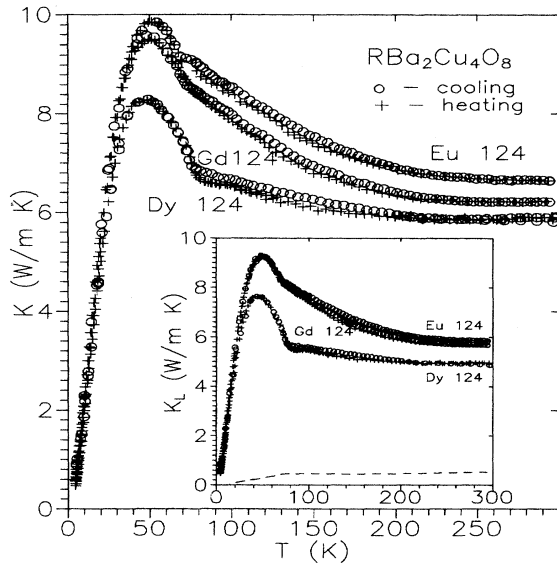
FIG. 1. Thermal conductivity K versus temperature for RBa$_2$Cu$_4$O$_8$ (R=Dy, Gd, and Eu). The inset shows lattice thermal conductivity K_l of R 1:2:4 versus temperature. The solid line shows electronic component $K_e(T)$ of GdBa$_2$Cu$_4$O$_8$ (see text for details).

FIG. 2. High-temperature lattice thermal conductivity for Dy 1:2:4 versus temperature. The values A have been obtained during heating, and values B during cooling. Temperatures T_1 and T_2 denote the beginning and the end of the hysteresis loop, respectively.

thors of Ref. 3 note that the T dependence for Y 1:2:4 is very different from that for Y 1:2:3, we did not find significant differences between other high-T_c superconductors and our samples when we measured K in one cycle. The magnitude of thermal conductivity of R 1:2:4 is comparable to those of other high-T_c ceramics, where the K falls typically between 1 and 10 W m^{-1} K^{-1}. The slightly lower value for R 1:2:4 than for Y 1:2:4 may be connected with differences in porosity of their structures. However, measurements of sintered samples of R 1:2:3 show a higher thermal conductivity of parent material (YBa$_2$Cu$_3$O$_{7-\delta}$) than substituted 1:2:3 compounds.[6] The most notable feature in the data is the strong temperature dependence of K in normal state for R 1:2:4 similar to what was observed for Y 1:2:4. Such temperature dependence was observed only for mixed phase polycrystals of Y 1:2:3,[7] single crystals, and liquid phase processed specimens of Y 1:2:3 (see, for example, Ref. 8). The characteristic behavior of new superconductors, i.e., sharp increase of $K(T)$ at $T \approx T_c$ and peak in $K(T)$ is also observable for our samples, whereas for Y 1:2:4 only a small change in dK/dT was detected. Several explanations exist in connection with electronic versus phononic scenarios for this anomaly. The most obvious interpretation is that this behavior arises from an increase in the phonon mean-free path due to reduced scattering of phonons by charge carriers after superconducting transition. The height of the peak varies strongly among cuprates, presumably reflecting differences in sample purity, and is sensitive to oxygen defects.[9] The maximum value of K at the peak occurs at temperatures: 48 K for Dy 1:2:4, T_c=76.3 K; 50 K for Gd 1:2:4, T_c=73.1 K; and 52 K for Eu 1:2:4, T_c=68 K (T_c was determined as midpoint from resistivity measurements). It is an interesting fact since usually the temperature of the peak was observable at about $\frac{1}{2}T_c$. Our results clearly show that positions of the
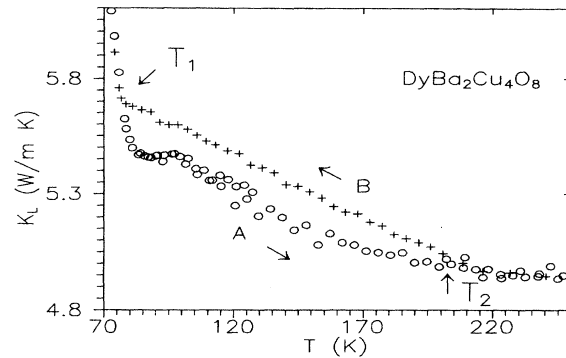
peaks are shifted toward upper temperatures as a function of the rare-earth atom mass. We note also that the magnitude of $K(T)$ varies with the R mass.

The total thermal conductivity can be seen as a sum of lattice and carrier components. From the electrical resistivity ρ, using the Wiedemann-Franz law, we estimate the upper limit for the electronic component K_e of thermal conductivity above T_c. The estimated maximum electronic part $K_e \leqslant 10\%$ is weakly independent of T as shown by the solid line in the inset of Fig. 1 [for clarity of the figure, only $K_e(T)$ for Gd 1:2:4 has been shown]. Below T_c, K_e is found by extrapolating the normal-state values linearly, employing correction factors given by Geilikman, Dushenat, and Chehetkin,[10] assuming that phonons are the dominant electron scatters. The lattice conductivity, $K_l=K-K_e$ versus temperature, where K_e is determined as above, is plotted in the inset of Fig. 1. We attribute the strong temperature dependence of K_l in normal state to phonon-phonon scattering because other sources of phonon scattering (phonon-carrier and phonon-defect) yield a nearly temperature-independent lattice thermal conductivity. Otherwise, for R 1:2:4, K_l increases by 16% (Dy 1:2:4), 43% (Gd 1:2:4), and 50% (Eu 1:2:4) upon cooling from 300 to 90 K.

Andersson and Sunqvist,[3] using standard models to fit their data for Y 1:2:4, found that K_l (change in K_l ~50%) is limited mainly by phonon-phonon interactions, in contrast to point-defect scattering which dominates K in 1:2:3 superconductors.

We now analyze the data for the normal state (Figs. 2 and 3). There are two prominent features of the data: hysteresis in the thermal conductivity between the cooling and heating cycles, and shift of the temperature in which the abrupt change of $K(T)$ at $T=T_c$ is observed for both cycles. Although in the absolute sense the hysteresis is not large (at most a 1.6–3% effect), the data points within the hysteresis region are stable, reproducible, and do not depend on the rate of cooling or heating. The hysteresis loop for investigated samples lies in similar broad intervals $T_1 < T < T_2$. The limits are: $T_1 \leqslant 76.2$–202 K for Dy 1:2:4, $\leqslant 73.2$–210 K for Gd 1:2:4, and $\leqslant 68.1$–218 K for Eu 1:2:4.

Earlier we found the hysteresis in $K(T)$ for superconducting and nonsuperconducting Y 1:2:3 (Ref. 4) and Tl 2:2:2:3.[5]

We connected that effect with instability of oxygen stoichiometry in these compounds and strong phonon-defect scattering.

The formulation of a plausible explanation for $K(T)$ hysteresis seems now to be much more feasible because point defect scattering is much weaker in 1:2:4 than in 1:2:3 due to stable oxygen stoichiometry of 1:2:4. Besides, there is an appearance of new experimental facts which could justify new interpretation of the hysteresis occurring in HTS. Measurements of the mean square displacement of atoms at the O(4) sites in the Y 1:2:3 by extended x-ray-absorption fine structure (EXAFS)[11] and the Y sites by Mössbauer spectroscopy[12] have revealed large amplitude anharmonic oscillations. On the contrary, neutron diffraction gives normal harmonic oscillations at such sites.[13] A possible explanation of the disagreement could be that the latter experi-
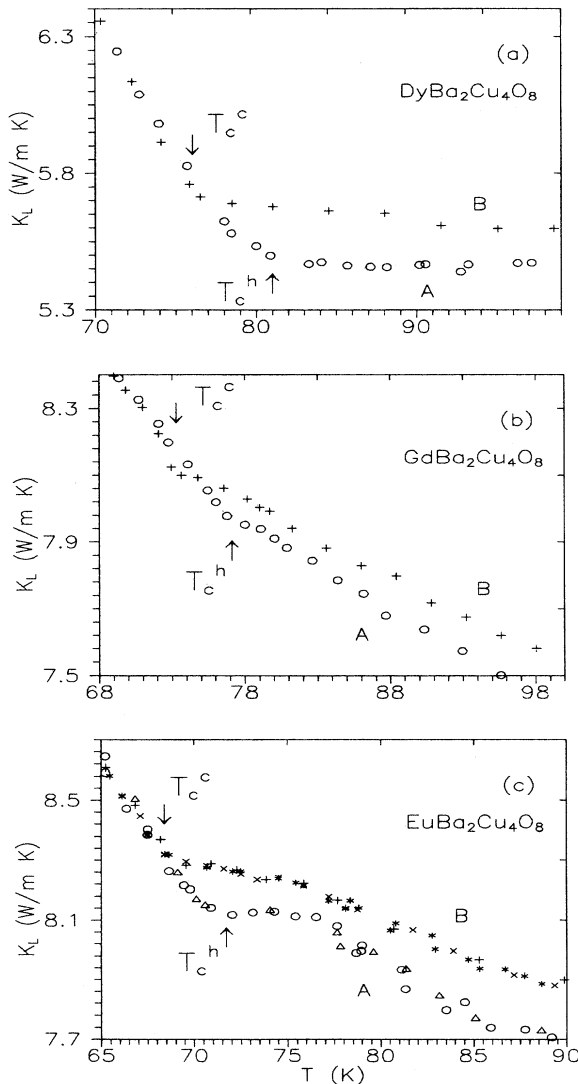

FIG. 3. Lattice thermal conductivity in the vicinity of T_c versus temperature for R 1:2:4 [(a) Dy 1:2:4, (b) Gd 1:2:4, (c) Eu 1:2:4]. The vertical arrows indicate the temperature at an abrupt change in the value of dK/dT:T_c^h upon heating, T_c^c upon cooling (symbols A and B have the same meaning as in Fig. 2).

mental technique is a nonlocal one.[14] Also, from investigation of the IR-excited Raman-scattering spectra of Y 1:2:3,[15] results show that the isotope shift of the apex oxygen phonon is consistent with a highly anharmonic potential for this atom. It was recently shown[16] that the bistable behavior of the sublattice of O(4) apical oxygen atoms gives possibility to offer a theoretical explanation for the hysteresis in the thermal conductivity of Y 1:2:3. Taking into account similarities in structure between 1:2:3 and 1:2:4, the same explanation may be tried. The explanation is based on the hypothesis that apical oxygen atoms in the known class high-T_c superconductors are mobile and can find themselves in two nonequivalent positions—in an asymmetric double-well potential—along the crystallographic c axis. As the temperature is changed, a competition between the anharmonic contributions to the potential well would have the result that metastable states of the O(4) atoms could become stable and vice versa; i.e., abrupt transitions would occur from one state to another. This effect would be accompanied by hysteresis. Taking into account the interaction of the metastable states of the apical oxygen sublattice with both the host lattice and the electron subsystem, it is possible to explain the temperature hysteresis of thermal conductivity. The hysteresis curves of the thermal conductivity changes shape, depending on the shape of the potential in which the O(4) atom is moving.

During cooling, when the T_1 point is reached from the right side (Fig. 2), a jump of K to the final value A takes place, whereas upon heating, when the T_2 point is reached from the left side, K tends to B. At points T_1 and T_2 a discontinuity takes place in the average displacement of O(4) atoms from its equilibrium position along the c axis.

It should be noted that a bistable behavior is characteristic for the thermodynamic parameters of the HTS. Hysteresis in acoustic, thermal, optical, and transport parameters has been observed as a function of temperature by various groups (see, for example, Refs. 17–19). Recently, we found a great hysteresis of $K(T)$ in a single crystal of CaNdAlO$_4$ in measurements along the c-axis direction.[20] This hysteresis is probably connected with oxygen movement along the c axis in this compound, belonging to the group of perovskite-like crystals.

Returning to Fig. 2 we now examine the shift of T_c for hysteretic cycles which is evident for all of the investigated compounds. The value of critical temperature is determined by the manner of approach to the critical point: $T_c = T_c^c$ upon cooling, and $T_c = T_c^h$ upon heating, with $T_c^c < T_c^h$. Experiments give the following values for $\Delta T_c = T_c^h - T_c^c = 5.0$ K for Dy 1:2:4, 3.8 K for Gd 1:2:4, and 3.3 K for Eu 1:2:4.

We can describe the transition temperature by the standard formula[21]

$$k_B T_c = 0.26\Omega(e^{2/\lambda} - 1)^{-1/2}, \quad \lambda = \eta/m\Omega, \qquad (1)$$

where Ω is the "one-particle" frequency renormalized by the anharmonic interactions, λ is the effective electron phonon constant, and η is the Hopfield parameter. The vibration frequency Ω of the O(4) atom should change with jumps at temperatures T_1 and T_2. It is clear from Eq. (1) that changes in T_c are determined by the bistable behavior of Ω. Thus, formally, T_c will be multiple-valued function, which is confirmed by our measurements. Experiments on the determina-

tion of ΔT_c are not known up to now. However, there were some experimental facts that point out to the existence of the ΔT_c evidenced by the thermal-conductivity measurements of Y 1:2:3 (Ref. 4) and resistivity measurements.[22]

Phenomena observed by us: the hysteresis of thermal conductivity and the concomitant shift in T_c indicate that anharmonic oxygen phonon modes may be present in the investigated compound. The question of the presence of large amplitude anharmonic vibrations in cuprates is very important, as the answer would establish whether the oxygen ion oscillations do or do not play an essential role in electron pairing.

The similarity of heat transfer features in various HTS compounds reveals the identical nature of the electron-phonon interaction and the relevance of the role played by apex oxygen atoms. These results suggest that the high-superconducting transition temperature can be explained within the framework of a conventional electron-phonon in-

teraction for the electron pairing involving the anharmonically bistable sublattice mode formed by the apical oxygen atoms.

In summary, we have performed measurements of the thermal conductivity of R 1:2:4 compounds. Our measurements during cooling and heating show hysteresis that occurs between 70 and 220 K, which we explained in terms of bistable behavior of the sublattice of O(4) apical oxygen atoms. The confirmation of our interpretation is in detection of the fact that the value of the critical temperature is determined by the manner of the approach to the critical point upon cooling or heating.

These results reveal that the mechanism which will be able to explain the high-superconducting transition temperature must be based on a thorough understanding of the normal state. A more detailed work with the theoretical explanation of the temperature hysteresis and analysis for ΔT_c and also the influence of hydrogenation on thermal conductivity hysteresis will be published later.

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