Calculation of the thermal conductivity of single-crystal $La_2CuO_{4+\Delta}$

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A theoretical study is given of the thermal conductivity of $La_2CuO_{4+\Delta}$. The umklapp-process quasiconservation of wave vector is taken into consideration. The expression used for the umklapp-process relaxation time differs from those used in earlier work. The effect of magnon-phonon interaction is reasonably well accounted for along the direction perpendicular to the Cu-O planes. The results agree quantitatively with recent measurements.

Recently considerable effort and speculation have been devoted in studying the thermal[1-6] and magnetic[7-12] properties of $La_2CuO_{4+\Delta}$. Such studies have yielded valuable information concerning high-temperature superconductors, in spite of the fact that $La_2CuO_{4+\Delta}$ itself is not a superconducting material. Measurements of the thermal conductivity and specific heat of a single crystal of $La_2CuO_{4+\Delta}$ have been reported in Morelli *et al.*[6] in the temperature range $T=10-300$ K. These measurements show that the thermal conductivity $\kappa(T)$ of $La_2CuO_{4+\Delta}$ is highly anisotropic. However, along all crystalline directions $\kappa(T)$ has a phononlike peak. Also, no significant changes in the results for $\kappa(T)$ have been observed when a magnetic field of about 2 T was applied. Moreover, the specific-heat measurements display a behavior which is similar to that of the Debye model, with a T^3 dependence at low temperatures. These observations strongly suggest that the heat current is dominantly transported by phonons in $La_2CuO_{4+\Delta}$. On the other hand, the measurements of thermal conductivity exhibit anomalous minima at temperatures and functional forms that differ significantly from one direction to the other. In the Cu-O planes (along the [110] direction), the minimum in $\kappa(T)$ is broad and occurs between 130 and 200 K while in the perpendicular direction [001] the minimum is sharp and occurs at the Néel temperature ($T_N=250$ K). The unusual rise in the thermal conductivity along the direction [001] for $T>T_N$ may be attributed to a magnon effect. For the direction [110] as well as [221] this is not the case, and it is not clear *a priori* what mechanism causes such a large anomaly.

According to Morelli *et al.*[6] the thermal conductivity at the Debye temperature is approximately half the value which they had estimated by using the model of Roufosse and Klemens.[13] However, in the work of Roufosse and Klemens,[13] the effect of the quasiconservation of wave vector in the umklapp process was not taken into account. It is known (Simons,[14] Srivastava,[15] Mikhail,[16] and Mikhail and Madkour[17]) that the umklapp wave-vector quasiconservation reduces the thermal conductivity by about 50%. It seems, therefore, that the effect of magnon-phonon interactions for temperatures in the vicinity of Θ_D might be considerably smaller than that predicted by Morelli *et al.*[6] In the present work the expression for phonon thermal conductivity given by Mikhail[16] will be utilized. Thus, we take

$$\kappa=\kappa_c-\gamma T^3\left[\frac{a^2}{I_3\delta}\right], \tag{1}$$

where

$$\kappa_c=\gamma T^3[I_1+(I_2^2/I_3)], \tag{2}$$

and where

$$a=I_2I_4+I_3I_5, \tag{3}$$

$$\delta=I_4^2+\tfrac{1}{3}I_3(I_6+I_7), \tag{4}$$

$$\gamma=\frac{k_B}{2\pi^2 v}\left[\frac{k_B}{\hbar}\right]^3. \tag{5}$$

Here κ_c stands for the Callaway expression for thermal conductivity[18] and the second term of Eq. (1) represents the effect of the umklapp-process quasiconservation of wave vector. v is the average phonon Debye velocity and I_i, $i=1,2,\ldots,7$ are integrals which depend on Θ_D and the relaxation times τ_n, τ_u, τ_s of normal, umklapp, and other resistive phonon processes. According to Böni *et al.*[19] and Morelli *et al.*,[6] v can be adequately taken to be equal to 4×10^3 m/sec, which corresponds to $\Theta_D=500$ K. However, in earlier work, on sintered samples (Nunez-Regueiro *et al.*[5]) Θ_D was taken to be equal to 300 K. Thus, we took $\Theta_D=400$ K in agreement with the average value given in Fischer *et al.*[20] Regarding the relaxation times of the normal and umklapp processes, they are usually taken as (Berman[21])

$$\tau_n^{-1}=\beta_n x T^4, \tag{6}$$

and

$$\tau_u^{-1}=\beta_u x^2 T^4\exp(-b/T), \tag{7}$$

where $x=\hbar v k/k_BT$ and k is the phonon wave vector. These forms were consistently used in most of the earlier work on phonon thermal conductivity.[21] They lead to the familiar behavior of κ at high temperatures in which umklapp interactions are the dominant process and accordingly κ decays as T increases, regardless of the values of β_n, β_u, and b. It is shown by Mikhail and Simons[22] that if the limits of the integral over the phonon wave vector, which is involved in the calculation of τ_u, are more accurately treated, then Eq. (7) for τ_u^{-1} takes the form

$$\tau_u^{-1} = \beta_u x^3 T^2 \exp(-b/T) . \quad (8)$$

This equation was derived for small values of k and for transverse acoustic phonons which are expected to carry most of the heat current. The effect of optical phonons was also entirely neglected. In spite of these approximations Eq. (8) has the advantage that it allows umklapp processes to dominate only in an intermediate temperature interval which can be adjusted by choosing the values of the parameters β_n, β_u, and b. For higher temperatures, normal processes become stronger and outweigh umklapp processes. The thermal conductivity will then start to increase as T increases, since, in Eq. (1), all phonons are assumed to have the same group velocity and accordingly normal processes do not contribute to the thermal resistivity.[21] At temperatures much higher than Θ_D, Eq. (8) for τ_u is invalid and umklapp processes dominate again, causing the final decay of the thermal conductivity. This limit is outside the temperature range in which the experiment by Morelli *et al.*[6] was performed. It is felt that such an idea may give a good explanation for the thermal conductivity measurements of Morelli *et al.*[6] and may thus deserve serious consideration. This is the prime motivation of the present work.

To carry out the calculation, the scattering processes in the low-temperature range ($T \leq 20$ K) have to be specified. The mean free path in this temperature range is found to be 4 orders of magnitude less than the dimensions of the crystal, and accordingly the effect of the crystal boundaries need not be included. Also, in a single crystal, grain boundaries have a minor effect. This is confirmed from the measurements of Morelli *et al.*[6] which show a T^2 rather than a T^3 dependence. Assuming that most of the heat current is transported by phonons, then the T^2 dependence observed for κ may be due to dislocation scattering. We may consequently take (Berman[21])

$$\tau_s^{-1} = \tau_d^{-1} = \epsilon x T , \quad (9)$$

where ϵ is a parameter which is related to the density of dislocations. It should be emphasized, however, that the T^2 dependence has been observed in some sintered and single-crystal samples of high-temperature superconductors[5,20,23] and was attributed to low-energy two-level systems (glasslike tunneling systems). However, in these materials the T^2 dependence is restricted to the range $T \leq 1$ K with a plateau occurring above $T \sim 10$ K. This is not the case for the measurements of Morelli *et al.*[6] Besides, these features are usually associated with a specific heat containing a dominant linear term for $T \leq 1$ K. The specific-heat measurements of Morelli *et al.*[6] were not taken to such a low temperature and thus the existence of a low-temperature linear term cannot be examined.

Now, using Eq. (1) for the thermal conductivity together with Eqs. (6), (8), and (9) for relaxation times, good quantitative agreement with the experimental measurements has been obtained for the two directions [110] and [221]. The results are shown in Fig. 1. The values of the parameters β_n, β_u, b, and ϵ are given in the figure caption. In view of the observed anisotropy, a different set of values has been used for each direction. The small

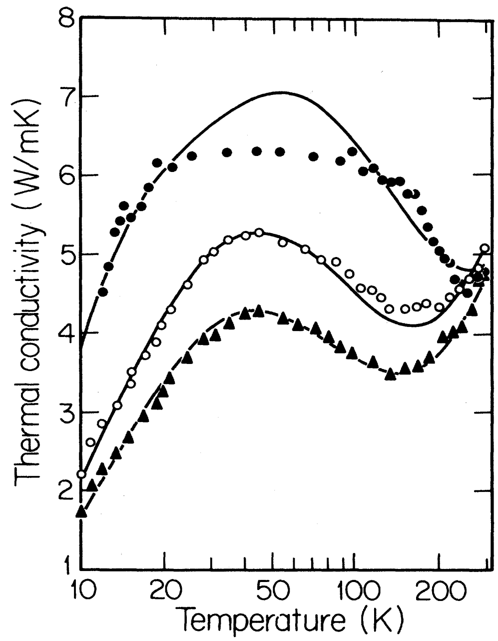

FIG. 1. Graph of thermal conductivity against temperature for single-crystal $La_2CuO_{4+\Delta}$. The solid curves refer to the theoretical results while ▲, ○, and ● refer to the experimental data (Ref. 6) along the directions [110], [221], and [001]. Along these directions the values of the parameters $(\beta_n, \beta_u, \epsilon)$ are $(2.6\times10^{-3}, 6.7, 130)$, $(1.7\times10^{-3}, 6.3, 98)$, $(0.5\times10^{-3}, 8, 48)$, respectively, the relaxation times are given in units of μsec. The parameter b is equal to 53, throughout.

discrepancies between the theoretical and experimental results may be due to the entire neglect of optical phonons or due to the other approximations assumed in deriving Eq. (8). They may also be due to a very weak magnon-phonon interaction. It can, however, be concluded that magnon-phonon interactions may not play an essential role along these two directions, in particular, along the [110] direction. This is expected since the velocity of magnons is ten times larger than the velocity of phonons in the Cu-O planes.[8,9]

The best fit along the [001] direction is also shown in Fig. 1. The agreement with our model is not so convincing in the regions of the broad maximum and sharp minimum. Regarding the latter, the effect of the magnon-phonon interaction must be included, as was expected. According to Shirane *et al.*[8] and Endoh *et al.*[9] $La_2CuO_{4+\Delta}$ exhibits two-dimensional antiferromagnetic behavior in the Cu-O planes above T_N. Phonons will thus be scattered in this temperature range by disordered spins along the perpendicular direction [001]. Also, following Slack[24] and Morelli *et al.*[6] such scattering processes can be represented by a constant relaxation time τ_{m0} (independent of temperature and phonon wave vector). Below T_N the fraction of disordered spin varies as $[1-\sigma(T)]$, where $\sigma(T)$ is the magnetic order parameter along the [001] direction. The rate by which disordered spins scatter phonons will thus be decreased by the same factor and accordingly we may take

$$\tau_m^{-1}(T)=\tau_{m0}^{-1}[1-\sigma(T)] \ . \qquad (10)$$

The relaxation time τ_s will now be defined as

$$\tau_s^{-1}=\tau_d^{-1}+\tau_m^{-1}=\epsilon x T+\tau_{m0}^{-1}[1-\sigma(T)] \ . \qquad (11)$$

To determine the magnetic order parameter $\sigma(T)$ we have applied the molecular-field theory with $S=\frac{1}{2}$ and $T_N=250$ K. Also, τ_{m0} has been treated as a fitting parameter. The results are displayed in Fig. 2. In this figure, curve *a* has been obtained by using the same set of values for β_n, β_u, *b*, and ϵ as that used in Fig. 1, while curve *b* gives the best fit to the data at low and high temperatures. Curve *c* represents an attempt to fit the broad maximum. In this connection, some success has also been achieved by interpreting the broad maximum as two maxima, the first being due to the effect of normal and umklapp processes, while the second is attributed to normal and magnon-phonon interactions. Unfortunately, in such a case the agreement with the experimental results in the low- and high-temperature ranges appears to be quantitatively unreasonable.

In general, the values of the parameters β_n, β_u, and ϵ are higher than the values used for normal insulator materials by 2 orders of magnitude, which should be expected since the thermal conductivity is less by the same order. This, in turn, indicates that the values of the third-order elastic constants as well as the Grüneisen constant for $La_2CuO_{4+\Delta}$ must be an order of magnitude larger than their values for normal insulators to justify that the majority of heat current is transported by phonons.

In our opinion, the main source of error in the calculations along the [001] direction is the use of molecular-field theory. For $La_2CuO_{4+\Delta}$ the effect of quantum fluctuations is found to be very large (Huse[25] and Chakravarty *et al.*[11,12]) and this may considerably affect the simple form of τ_m^{-1} given in Eq. (10). Also, more sophisticated expressions (Dixon[26]) for the magnon-phonon interaction might be necessary. However, severe approximations have to be made to simplify these expressions. In addition, the number of unknown parameters will be substantially increased. Finally we point out that the broad flat maximum in $\kappa(T)$ for heat flow in the [001] direction may be due to an electron-phonon interaction along the [001] direction or may be the onset of a plateau in a tunneling system. The former is unlikely to occur since electrons are expected to have a very minor effect on κ for $La_2CuO_{4+\Delta}$. Also, the other features of a tunneling system have not been observed and this might exclude the second hypothesis.

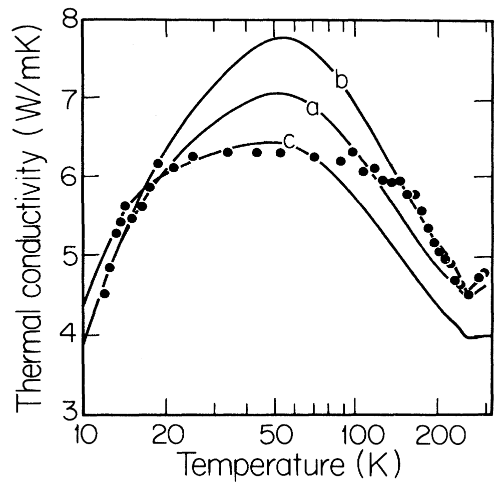

FIG. 2. A plot of κ vs T, along the direction [001], with the magnon-phonon interaction taken into account. The solid circles (●) refer to the experimental results. $\tau_{m0}=12.5$, 4.75, and 12.5 psec, for curves *a*, *b*, and *c*, respectively. For curve *a*, the values of the other parameters are identical with those used in Fig. 1. The values of $(\beta_n,\beta_u,\epsilon)$ are equal to $(0.45\times10^{-3},7,50)$ for curve *b* and to $(0.45\times10^{-3},10,40)$ for curve *c*. These values give the relaxation times in units of μsec. For both curves the parameter $b=53$.

In conclusion, we have performed a theoretical calculation for the thermal conductivity of single-crystal $La_2CuO_{4+\Delta}$. Along the two directions, [110] and [221], the calculations have been entirely carried out by using phonon scattering mechanisms, while along the [001] direction, the effect of magnon-phonon interactions has been explored. The results show a good quantitative agreement with the experimental data of Morelli *et al.*[6]

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[1] N. E. Phillips, R. A. Fisher, S. E. Lacy, C. Marcenat, J. A. Olsen, W. K. Ham, and A. M. Stacy, Jpn. J. Appl. Phys. **26**, 1115 (1987); in Proceedings of the 18th International Conference on Low Temperature Physics, Kyoto, 1987 [Jpn. J. Appl. Phys. **26**, Suppl. 26-3 (1987)].

[2] P. Gutsmiedl, K. Andres, E. Amberger, and H. Rietschel, Jpn. J. Appl. Phys. **26**, 1117 (1987); in Proceedings of the 18th International Conference on Low Temperature Physics, Kyoto, 1987 [Jpn. J. Appl. Phys. **26**, Suppl. 26-3 (1987)].

[3] S. W. Cheong, Z. Fisk, J. O. Willis, S. E. Brown, J. D. Thompson, J. P. Remeika, A. S. Cooper, R. M. Aikin, D. Schiferl, and G. Gruner, Solid State Commun. **65**, 111 (1987).

[4]K. Kumagai, Y. Nakamichi, I. Watanabe, Y. Nakamura, H. Nakajima, N. Wada, and P. Lederer, Phys. Rev. Lett. **60**, 724 (1988).
[5]M. Nunez-Regueiro, D. Castello, M. Izbizky, D. Esparza, and C. D'Ovidio, Phys. Rev. B **36**, 8813 (1987).
[6]D. T. Morelli, J. Heremans, G. L. Doll, P. J. Picone, H. P. Jenssen, and M. S. Dresselhaus, Phys. Rev. B **39**, 804 (1989).
[7]D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).
[8]G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).
[9]Y. Endoh, K. Yamada, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. R. Thurston, J. M. Tranquada, G. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami, Phys. Rev. B **37**, 7443 (1988).
[10]M. A. Kastner, R. J. Birgeneau, T. R. Thurston, P. J. Picone, H. P. Jenssen, D. R. Gabbe, M. Sato, K. Fukuda, S. Shamoto, Y. Endoh, K. Yamada, and G. Shirane, Phys. Rev. B **38**, 6636 (1988).
[11]S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988).
[12]S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. B **39**, 2344 (1989).
[13]M. Roufosse and P. G. Klemens, Phys. Rev. B **7**, 5379 (1973).
[14]S. Simons, J. Phys. C **8**, 1147 (1975).
[15]G. P. Srivastava, Philos. Mag. **34**, 795 (1976).
[16]I. F. I. Mikhail, J. Phys. C **13**, 335 (1980).
[17]I. F. I. Mikhail and S. S. R. Madkour, J. Phys. C **18**, 3427 (1985).
[18]J. Callaway, Phys. Rev. **113**, 1046 (1959).
[19]P. Böni, J. D. Axe, G. Shirane, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, and T. R. Thurston, Phys. Rev. B **38**, 185 (1988).
[20]H. E. Fischer, S. K. Watson, and D. G. Cahill, Comments Mod. Phys. B **14**, 65 (1988).
[21]R. Berman, *Thermal Conduction in Solids* (Clarendon, Oxford, 1976).
[22]I. F. I. Mikhail and S. Simons, J. Phys. C **8**, 3068 (1975).
[23]J. E. Graebner, L. F. Schneemeyer, R. J. Cava, J. V. Waszczak, E. A. Rietman, in *High-Temperature Superconductors,* edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1987), Vol. 99, p. 745.
[24]G. A. Slack, Phys. Rev. **122**, 1451 (1961).
[25]D. A. Huse, Phys. Rev. B **37**, 2380 (1988).
[26]G. S. Dixon, Phys. Rev. B **21**, 2851 (1980).