

Thermal conductivity of insulating $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ and superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$: Failure of the phonon-gas picture

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The ab -plane thermal conductivity $\kappa(T)$ of insulating $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ and superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is measured from $T=10$ to 300 K on single-crystal samples. Metallic $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has a significantly higher κ than $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$; the difference $\Delta\kappa$ agrees well in magnitude with a Wiedemann-Franz estimate of the electronic contribution to κ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The shape of $\kappa(T)$ in insulating $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ differs from normal insulators described by the Peierls-Boltzmann theory. Assuming that atomic vibrations are the main heat carrier, and noting that κ is more similar to that of silica glass than to a normal insulating crystal like CuO , we suggest that the "phonon" mean free path is sufficiently short that the Peierls-Boltzmann theory is not applicable. This is consistent with evidence from neutron scattering that phonons are poorly defined. Our data support the idea that the peak in $\kappa(T)$ observed below T_c in superconducting samples originates from electronic rather than vibrational heat currents.

I. INTRODUCTION

Although $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is one of the most widely studied high- T_c materials, its insulating antiferromagnetic analog, $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ has received comparatively little attention. Here we report a study of the ab -plane thermal conductivity $\kappa(T)$ of single crystals of both $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$. The results are consistent with the idea that lattice vibrations carry heat equally in both materials, and an extra electronic contribution, quantitatively close to Wiedemann-Franz law expectations, occurs in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. However, the lattice contribution is anomalous, not following the expectations of conventional Peierls-Boltzmann theory.¹

Thermal conductivity of high- T_c materials has been reviewed by Uher.² There are several previous measurements of thermal conductivity on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ single crystals.^{3,4} Our measurements agree reasonably well with Ref. 3. In Ref. 4 the point was made that the low- T κ of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ resembles the behavior of glassy materials. Here we note that the high- T κ of both $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, and more reliably $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ (because the absence of conduction electrons simplifies things) also bears a strong resemblance to the behavior of glassy materials, and we interpret this resemblance in light of information available from neutron and Raman spectroscopy as evidence for very strong damping of phonons. Simultaneous with our study, Inyushkin *et al.*⁵ measured $\kappa(T)$ of both $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ single crystals. Our measurements agree quite closely with theirs.

II. EXPERIMENT

Single crystals of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ were grown from a copper-oxide-rich melt as described in detail elsewhere.⁶

Thin, shiny sheets of single crystals were cleaved from the bulk. The sheets were then cut into rectangular shape of typical dimensions $2 \times 1 \times 0.01$ mm, with the shortest dimension lying along the c axis. The orientation within the ab plane was not determined. First resistivity was measured, using a four-probe method, and then the same samples were used for measurements of thermal conductivity.

A modified steady-state comparative method was used in measuring the thermal conductivity. Figure 1 shows a diagram of the experimental setup. Two Constantan wires of diameter 0.075 mm were attached to each end of the sample serving as calibrated heat links. The assembly was then mounted across two chip resistors. The resistors were used as heaters to generate heat flows. Three differential thermocouples were used to measure the temperature gradient across the two heat links and the sample.

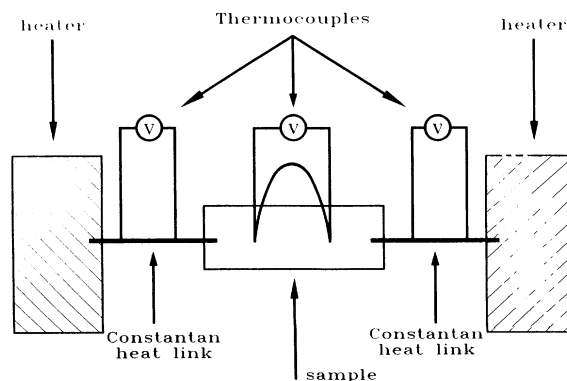


FIG. 1. Experimental setup of the thermal conductivity measurement.

The thermocouple of the sample was made of Chromel and Constantan wires of diameter $12.5 \mu\text{m}$, and was glued with insulating epoxy on top of the voltage leads used in resistivity measurements. The thermocouples for the heat links were made by spot welding $12.5 \mu\text{m}$ diameter Chromel wires directly on to the thick Constantan wires.

The measurement of the thermal conductivity was done with one of the two heaters activated, and it was repeated using the other heater to check symmetry and reproducibility. A typical temperature difference across the sample was $\approx 1 \text{ K}$. The heat leak becomes important when the temperature is high—in our setup it is about 30% at 200 K. But the symmetry of the setup allows easy correction for the heat loss. The procedure is mathematically analogous to the calculation of the resistance of an electrical circuit. In this circuit there are several resistors representing the heat leak, and by solving this circuit the effect of the heat loss is corrected. To make sure that this experimental setup works properly, κ of a thin piece of mica was measured. The data agree with a previous measurement by Gray and Uher.⁷

III. RESULTS FOR METALLIC $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

Figure 2 shows our results for $\rho(T)$ and $\kappa(T)$. Our results are close to those of Crommie and Zettl³ and Inyushkin *et al.*⁵ Our κ is $\approx 10\%$ higher than Ref. 3, and this difference can be completely attributed to a higher electrical conductivity σ of our sample. Below T_c a characteristic peak in $\kappa(T)$ occurs in the range 60–70 K in all three experiments. In conventional superconductors the electronic thermal conductivity diminishes rapidly below T_c , causing the total κ also to diminish in clean samples where electrons usually dominate. However, in

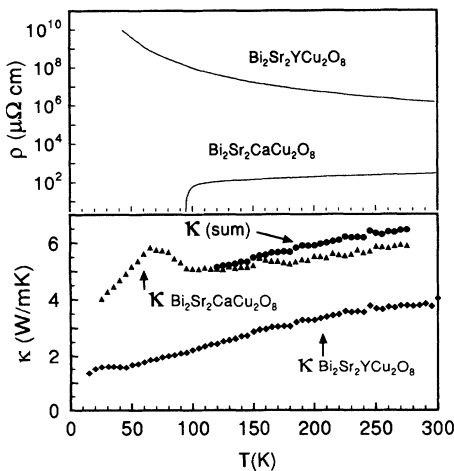


FIG. 2. (a) *ab*-plane electrical resistivity of superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and insulating $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$. (b) Thermal conductivity of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and the $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ samples. The curve labeled “sum” is the sum of the measured κ of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ plus the calculated electronic contribution using the Wiedemann-Franz law and the resistivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ from part (a).

dirty samples vibrations can dominate, and other behavior can occur. A factor of 2 enhancement was seen below T_c in $\kappa(T)$ in Pb/Bi alloy by Olsen.⁸ There is little doubt that this reflects the enhanced mean free path of the heat-carrying long-wavelength phonons when the electrons condense into the superconducting state and are no longer available to scatter phonons of energy less than $2\Delta(T)$. Phonons of shorter wavelength are less likely to have their mean free paths affected much by electrons because they are strongly damped by the alloy disorder, but long-wavelength phonons are more immune to this effect.

Unlike ordinary superconductors, in high- T_c materials, a high ratio of vibrational to electronic degrees of freedom can permit vibrations to dominate κ even in pure samples. A factor of 2 enhancement in κ was seen in detwinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ (1:2:3) by Yu *et al.*⁹ Most commonly it has been argued that this enhancement is caused by lengthened vibrational mean free paths in the superconducting state, as in Pb/Bi alloys, but Yu *et al.* argue that the electronic heat current is enhanced in an unconventional way. Our experiment gives only a 15% enhancement (comparing the peak value of κ to the value at 100 K) in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, consistent with the results of Ref. 3 (13%) and Ref. 5 (20%). We suspect that our samples are sufficiently perfect that this represents the intrinsic effect in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, so the model for the low- T peak in κ should account for a smaller effect in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ than in 1:2:3.

IV. RESULTS FOR INSULATING $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$

It is logical to believe that the lattice part of κ should be very similar in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. A careful study of changes in phonon density of states was done by Renker *et al.*,¹⁰ who found only a very small softening of the spectrum of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ relative to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, consistent with the heavier mass of Y relative to Ca. Since $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is a metal, the phonons have an additional interaction with the metallic electrons which could soften the spectrum, but the effect is seen¹⁰ to be small. This interaction will also shorten the phonon mean free path and thus reduce the lattice part of κ . That this is also a small effect can be seen in two ways. Crommie and Zettl³ estimated the lattice thermal conductivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ by subtracting the Wiedemann-Franz estimate of the electronic contribution. Their answer agrees closely with our measured κ of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ except for having a smaller temperature derivative. Alternatively, in Fig. 2 we show an estimate of $\kappa_{\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8}$ obtained by adding $L_0 T / \rho_{\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8}$ to $\kappa_{\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8}$, where $L_0 = \pi^2 k_B^2 / 3e^2$ is the Sommerfeld-Lorenz number. The near agreement implies the near equality of lattice contributions in both materials. Another way of seeing that electronic decay of phonons is not large in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is to study the change in phonon linewidth caused by superconductivity. Mook *et al.*,¹¹ insofar as they were able to find any phonons in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, observed electronic changes in linewidth caused by su-

perconductivity to be smaller than other sources of linewidth. Therefore we believe it is appropriate to consider $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ as a model for the lattice effects which occur in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, with the simplification of having no electronic effects to sort out. Elsewhere¹² we have exploited this belief to deduce more completely the T dependence of the Lorenz ratio in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and find discrepancies between experiment and the theoretical prediction based on inelastic scattering of electrons by phonons. The focus of the present paper is to interpret the peculiar shape of the temperature dependence of κ in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$.

V. DISCUSSION

A. Magnetic effects

We see no evidence for magnetic effects in $\kappa(T)$ for either material. Nevertheless, magnetism surely contributes to $\kappa(T)$ in two ways: (i) spins serve as an additional carrier of heat, and (ii) they provide an extra scattering mechanism for the other carriers. In a study of insulating La_2CuO_4 (2:1:4) Morelli *et al.*¹³ reported a “sharp kink in the heat conductivity near 250 K ... correlated ... with changes in the magnetic structure.” In Fig. 3, these data are replotted with a linear rather than logarithmic temperature scale. The “sharp kink” is now only a shallow broad minimum. The data of Nakamura *et al.*¹⁴ for the same system are also shown. Neither experiment shows convincing evidence for magnetic effects. An instructive comparison is the study of antiferromagnetic and nonmagnetic fluorides by Slack.¹⁵ While antiferromagnetic MnF_2 is qualitatively similar to nonmagnetic ZnF_2 , showing only a weak anomaly near the Néel temperature, antiferromagnetic CoF_2 , with a lower Néel

temperature of 38 K shows a pronounced dip in $\kappa(T)$. Although the collapse of long-range magnetic order surely influences κ , this experiment shows that the magnitude of the effect can be small, appearing unambiguously only for a low Néel temperature where κ is dominated by long-wavelength modes which are especially sensitive to small effects. This may explain the absence of any obvious magnetic effects in $\kappa(T)$ in high- T_c materials with high magnetic temperatures.

B. Comparison with glasses

Figure 3 shows our data for $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ compared with various other insulating systems, including the 2:1:4 data mentioned above, data for glassy SiO_2 ,¹⁶ and data for insulating polycrystalline CuO .¹⁷ It is interesting that $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ behaves more like a glass than a crystal, while 2:1:4 is intermediate. Similar behavior was seen by Hagen *et al.*¹⁸ in insulating, oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_7$ (1:2:3). However, such behavior is not “universal” in insulating analogs of high- T_c materials. Figure 4 shows that the “electron-doped” material Nd_2CuO_4 (lightly doped with Ce but still insulating) (Ref. 19) has a very conventional behavior of $\kappa(T)$, with a low- T peak and a roughly $1/T$ trend at higher T . Inyushkin *et al.*⁵ found similar conventional behavior in isostructural Pr_2CuO_4 . This is characteristic of heat carried by phonons with a mean free path limited by ordinary anharmonic decay (often called “umklapp” scattering because the current cannot decay by this mechanism alone without participation of k -nonconserving umklapp events to relax the momentum.) Also shown in Fig. 4 are data for other layer-structure insulators muscovite,⁷ graphite,²⁰ and BN.²¹

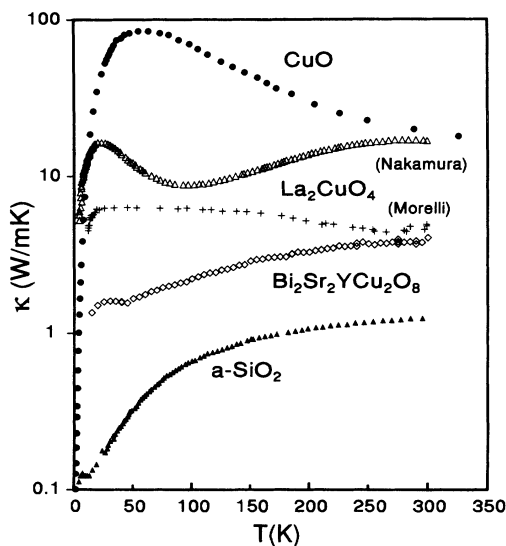


FIG. 3. Thermal conductivity (log scale) vs temperature (linear scale) for a simple crystal [CuO (Ref. 17)], a glass [SiO (Ref. 16)], 2:1:4 (Refs. 13 and 14), and $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ (present work.)

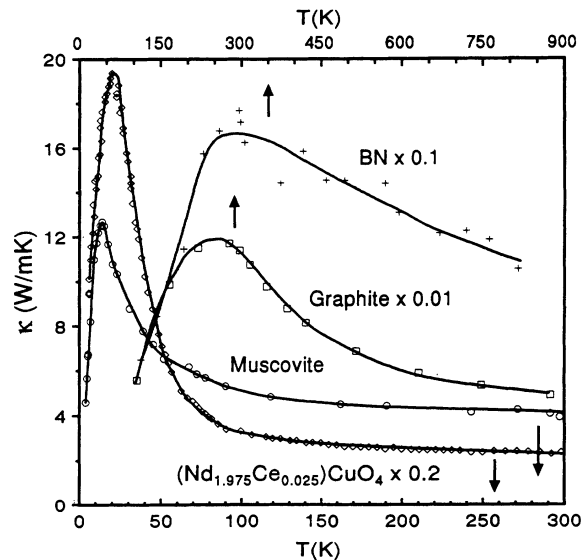


FIG. 4. Thermal conductivity vs temperature for layered insulators showing normal behavior. Muscovite (Ref. 7) and Nd_2CuO_4 (Ref. 19) are plotted with the lower temperature scale, graphite (Ref. 20) and BN (Ref. 21) are plotted with the upper scale.

This shows that conventional behavior is in fact common in layered insulators. Therefore it is surprising that clean single crystals of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ have such unconventional $\kappa(T)$.

Crystalline behavior can be expected to evolve into amorphous behavior when unit cells become so complicated that periodicity is locally absent. Examples are YB_{68} as emphasized by Cahill *et al.*²² and “plastic” crystals and “inclusion” compounds as reviewed by Ross.²³ However, especially in the *ab* plane which should be relevant for κ_{ab} , $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ has a much simpler crystal structure than these materials.

C. Do phonons exist?

It was originally pointed out by Kittel²⁴ that a simple heuristic picture for understanding $\kappa(T)$ at higher temperatures in glasses is to use the standard qualitative result of Peierls-Boltzmann phonon gas theory,¹ $\kappa = \frac{1}{3}Cv\ell$, with C the (temperature-dependent) lattice specific heat, v a characteristic sound velocity, and with the mean free path ℓ replaced by a typical interatomic distance a . This replacement has no specific justification; it stretches the condition for the applicability of the phonon gas model, namely that the phonons should live for a long enough time between collision events that the collisions do not overlap and the frequency of a quasi-independent oscillator can be defined ($\omega\tau \gg 1$). A microscopic investigation of the foundations of Peierls-Boltzmann theory²⁵ shows that a somewhat more stringent condition is required, namely $\Delta\omega\tau \gg 1$, where $\Delta\omega$ is the level spacing between adjacent phonon eigenvalues at a fixed wave vector \mathbf{k} . When this condition is violated, it is no longer possible to neglect the nondiagonal parts of the oscillator density matrix $\rho_{ij} = \text{tr}\rho a_i^\dagger a_j$. Here i and j represent different oscillator states belonging to the same wavevector. The diagonal term ρ_{ii} is the phonon occupation function, the sole object of interest in gas theory. The heat current operator has off-diagonal matrix elements, which contribute significant amounts when $\Delta\omega\tau \approx 1$, and this effect requires an enlarged and much more complicated theory involving $\rho_{i \neq j}$. Such a computation has been carried out in harmonic approximation for amorphous Si,²⁶ and accounts for the measured thermal conductivity at $T > 30$ K. Because the shape of $\kappa(T)$ in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ is similar to that in amorphous Si, we believe that the criterion $\Delta\omega\tau \gg 1$ is violated also in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$, and that interband effects give important contributions to $\kappa(T)$.

If we ask what it means for a “phonon to exist,” it turns out that the same condition, $\Delta\omega\tau \gg 1$, is needed. First the definition of a phonon must be fixed. The operational answer is that it is a reasonably clean peak in the neutron cross section $S(\mathbf{Q}, \omega)$ provided that elementary counting and continuity rules are obeyed (there should be $3n$ peaks *modulo* symmetry-induced degeneracies, the peak positions varying smoothly with \mathbf{Q}). The theoretical definition²⁷ is a reasonably clean peak in the imaginary part of the phonon Green’s function, obeying the same rules. Since the Green’s function is the displacement-displacement correlation function, and $S(\mathbf{Q}, \omega)$ is the

density-density correlation function, the two definitions are intimately related and essentially the same. Macroscopic elastic response guarantees the existence of long-wavelength propagating sound modes. When $\Delta\omega\tau \approx 1$ or < 1 for nearly all other phonons, then phonons can be said “not to exist.” Liquids and amorphous materials are of this type, but most simple crystals and many crystalline disordered alloys do have phonons according to this definition. When phonons “do not exist,” the source of the line broadening can be either static disorder or anharmonic interactions. Rare gas solids and simple ionic materials are cases where anharmonic interactions almost destroy the phonons at high temperatures. In the case of neon²⁸ at 22 K and argon²⁹ at 81 K (close to melting), phonons near the zone boundaries are often hard to pick out from the broad background, while in NaCl (Ref. 30) at 600 K (half of melting temperature) the phonon spectral functions depart from simple Lorentzians and have widths typically greater than 0.15ω .

A very dramatic and simple example is CuCl, which has a rich Raman spectrum³¹ which evolves from somewhat phononlike at low T to completely not phononlike at high T . Neutron scattering³² shows that this behavior is generic throughout the Brillouin zone. The mechanism is not completely clear, but is possibly^{31,33} caused by a temperature-dependent random Cu atom displacement. Interestingly, this mechanism for destroying phonons can be simultaneously classified both as a static defect and as an anharmonic effect.

D. Minimum thermal conductivity

Slack³⁴ has made a systematic study of how the thermal conductivity of simple insulators deviates from the usual $1/T$ law at higher T when the phonon mean free path becomes small. He uses the same heuristic notion of minimum mean free path that was used for glasses by Kittel. Cahill and Pohl³⁵ have pointed out that Einstein³⁶ attempted a theory of thermal conductivity based on a heuristic argument which supports the minimum mean free path idea. We reformulate the argument as follows. The thermal diffusivity D is defined as $D(T) = \kappa/C(T)$. In gas theory, $D = \frac{1}{3}v\ell$. For lattice vibrations it is undesirable to define the minimum diffusivity D_{\min} by replacement of ℓ with a , because this still leaves v in the formula, and the sound velocity has no special significance, especially in a material with a complicated unit cell. A more meaningful heuristic formula is

$$D_{\min} = \frac{1}{3}\omega_{\text{rms}}a^2. \quad (1)$$

The interpretation is that the heat is undergoing a random walk consisting of jumps by a distance a which occur with frequency ω_{rms} . In common with Einstein, we are assuming that energy is transmitted incoherently with each atomic excursion. To have an explicit model applicable to any material, we choose a^3 to be the volume per atom. The mean square vibrational frequency has an interpretation as the average diagonal restoring force constant. Finally, we define

$$\kappa_{\min} = C(T)D_{\min}, \quad (2)$$

where $C(T)$ should be the measured specific heat, but can be taken as a computed harmonic specific heat with little loss of phenomenological integrity.

Figure 5 shows ratios of measured $\kappa(T)$ to calculated κ_{\min} for $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ and three reference materials. $C(T)$ and ω_{rms} are obtained from experimental information in various ways. For $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$, the generalized phonon density of states $G(\omega)$ measured by neutrons¹⁰ was used. For CuO, a density of states fitted to measured dispersion curves³⁷ was used. For α -Si, the neutron measurement of $G(\omega)$ (Ref. 38) was used. For CuCl, the density of states fitted by Prevot *et al.*³² to their dispersion curves was used. For amorphous Si, $\kappa(T)$ was measured in Refs. 39 and 40. For CuCl, $\kappa(T)$ was measured at various pressures by Slack and Andersson.⁴¹

We interpret Fig. 5 as follows. Consistent with its conventional shape of $\kappa(T)$, CuO remains safely in the regime $\kappa > \kappa_{\min}$. The other three materials are all close to or below κ_{\min} by 100 K. There is direct evidence for the nonexistence of phonons in amorphous Si and in CuCl at $T > 100$ K. We take Fig. 5 as indirect evidence for either the nonexistence or the poorly defined quality of phonons in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$. In the next section we confront the direct evidence.

E. Neutron and Raman spectra

In spite of the extreme difficulty of inelastic neutron scattering in high- T_c superconductors, a lot of good phonon spectroscopy has been done.⁴² Recently the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been studied by Mook *et al.*¹¹ with particular attention to the question of line shapes, concerning which they say: "Because of the large number of closely spaced phonon modes, it is, in general,

almost impossible to isolate individual phonon modes to study." There are two interpretations one could assign to this statement. (1) Perhaps with enough effort in sample preparation and improvement in neutron flux, the difficulty could be surmounted. (2) Perhaps the difficulty is intrinsic. We believe that the latter interpretation is supported by the thermal conductivity data. It may be difficult to "isolate" phonons by neutron measurements because in fact the spectral response $S(\mathbf{Q}, \omega)$ does not contain very many separable peaks. This would be equivalent to saying that many of the phonons "do not exist."

Figure 6 shows how certain measured "phonon" line shapes evolve with temperature in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Ref. 11) and in CuCl.³² These particular phonons are chosen simply because they are almost the only available published "raw" data. In the case of CuCl, the phonon shown is mentioned as typical, whereas in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, it is one of the rare phonons that has been resolved at all. The only phonons (away from $\mathbf{Q}=0$) which have been observed¹¹ are a longitudinal acoustic mode with $\omega \approx 5$ meV, which is broad but well defined up to 300 K, and the two highest-energy oxygen vibrations ($\omega=62$ and 76 meV). The higher of these, shown in Fig. 6, disappears into the background at $T > 120$ K, similar to the behavior in CuCl. Other high- T_c materials apparently support phonons well enough that dispersion curves can be measured. Even these should be treated with skepticism. When 21 branches (as in 2:1:4) occur, identifying peaks and plotting their evolution in \mathbf{k} space is a perilous enterprise subject to revision as theoretical models converge in different ways onto incomplete data. Thus it has happened that "dots" on dispersion curves have migrated as interpretation "improves."⁴³ We believe that inspection of the thermal conductivity of 2:1:4 (Fig. 3) encourages the view that phonons are intrinsically imperfectly defined. In this situation, the real physics is in the response function (ideally in the raw data) and probably we should not accept dispersion curves as an adequate portrait of physical reality.

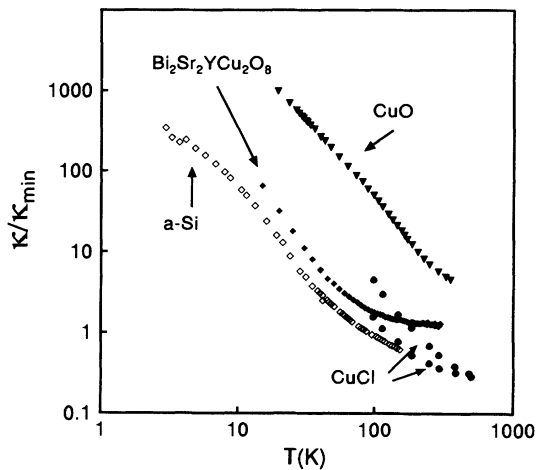


FIG. 5. log-log plot of the ratio of measured thermal conductivity to calculated minimum thermal conductivity, as explained in the text. Measured κ for CuO is the same as in Fig. 3; amorphous silicon from Refs. 39 and 40; CuCl from Ref. 41. The upper data set for CuCl is at low pressure and the lower data set is at 2.5 GPa.

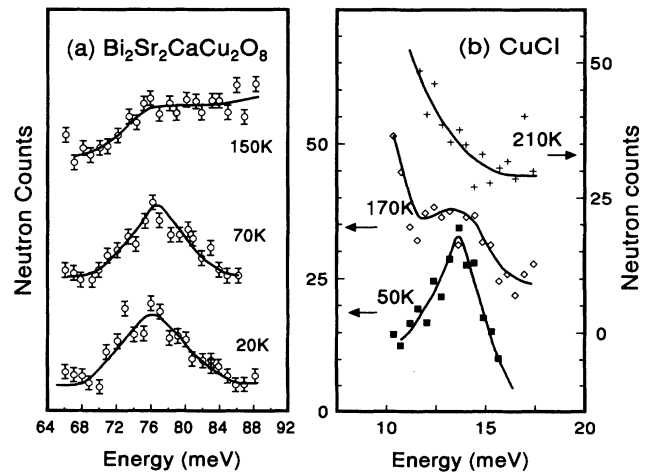


FIG. 6. Line shapes of a particularly well-resolved phonon in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Ref. 11) and of a typical phonon in CuCl (Ref. 32). Arbitrary vertical displacements have been made to separate the data.

Raman scattering can also be used to judge whether phonons exist or not. A good example is the Raman study of pressure amorphization of SiO_2 by Kingma *et al.*⁴⁴ Raman data for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Refs. 45 and 46) are much sharper than amorphous SiO_2 and seem at first sight to demonstrate that phonons do exist. In Ref. 46, a rich Raman spectrum is reported which contains more peaks than simple symmetry arguments predict. Many of these are tentatively assigned to breaking of tetragonal symmetry by incommensurately ordered oxygen interstitials. The lifetime broadening of the $\mathbf{Q}=0$ phonons is directly seen. For example, the intense 463 cm^{-1} feature has a half width at half maximum of 18 cm^{-1} (reading from Fig. 1 of Refs. 45 and 46). This width is sufficiently small compared to the spacing of adjacent Raman active modes that we can assert that phonons of A_{1g} symmetry exist. However, the condition $\Delta\omega\tau \gg 1$ is violated when we use the mean spacing between levels of arbitrary symmetry ($700\text{ cm}^{-1}/45 = 15\text{ cm}^{-1}$) rather than just of A_{1g} symmetry. This means that at a generic point of the Brillouin zone with no special symmetry, we cannot expect to distinguish the different modes because their lifetime broadenings overlap. Thus phonons “do not exist” except when permitted by special symmetry.

A characteristic property of insulating glasses at very low temperature⁴⁷ is a T^2 power law for $\kappa(T)$, which is usually attributed to resonant scattering of phonons from “two-level systems,” the nature of which is still speculative. It is very interesting that T^2 behavior has been seen in superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ⁴. To avoiding the complication of possible electronic contributions, the study of the low- T limit of κ in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ and other insulating analogs of high- T_c materials would be particularly helpful.

F. Electronic or vibrational superconducting peak?

It can be seen from Fig. 5 that as T decreases below 100 K, the vibrations responsible for heat conduction in $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ start to acquire coherent diffusivity. In metallic $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ we should expect the same thing, except that because of the additional electronic damping, the onset of coherent diffusivity should be somewhat slower. But when electrons condense into the superconducting state, the coherence of vibrations in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ should catch up with $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$.

This picture for an enhanced κ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ below T_c can only give a peak which lies close to the $\kappa(T)$ curve of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$. The fact that the peak lies well above the corresponding κ of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$ indicates that the excess conductivity is probably an electronic rather than vibrational effect. A less quantitative version of this argument was already made by Yu *et al.*⁹ for the case of 1:2:3. The reason why it is a smaller effect in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ than in 1:2:3 is unclear. Since both materials have of order 50% of κ assigned to electronic currents, a greater similarity could be expected. Perhaps our samples of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ have greater damping of electronic heat currents by impurities or static disorder than the best 1:2:3 samples. Further careful studies of κ in reduced oxygen and insulating variants of 1:2:3 would help clarify this.

VI. COMMENTS

To summarize, $\kappa(T)$ in insulating CuO-based layer compounds seems to show a range of behaviors from normal (Nd_2CuO_4) to almost glassy ($\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$) with La_2CuO_4 intermediate. Neutron scattering confirms that at a relatively low- T phonons are hard to isolate in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, a close relative of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_8$. Given that such behavior is not well documented in many materials, one could argue that such a unique effect must have something to do with enhancing T_c . However, there is no convincing theory of how anharmonicity could cause a giant enhancement of T_c . On the other hand, the absence of well-defined phonons still allows the electron-phonon mechanism to work, as is clear from the fairly high T_c 's found in metals like amorphous Bi. Our guess is that the absence of phonons in these materials is not a unique effect, but may occur commonly in complex ionic crystals with many atom unit cells, requiring moderate disorder or moderately large anharmonicity.

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