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Anomalous thermal conductivity of $La_{2-x}Sr_xCuO_4$: Possibility of a polaronic glass

M. Núñez Regueiro, D. Castello, M. A. Izbizky, D. Esparza, and C. D'Ovidio
Centro Atomico Bariloche, Comision Nacional de Energia Atomica, 8400 Bariloche, Argentina

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We present measurements of the thermal conductivity of La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$. The results on the pure sample show that lattice conduction is predominant with a $T^{1.8}$ dependence at low temperatures and a strong T-independent scattering above 30 K. We observe a similar behavior for the superconductor but with a $T^{1.4}$ law at low temperature and a small electronic contribution in the normal state. These results together with the behavior of the specific heat and sound attenuation are consistent with the existence of a two-level tunneling system for an amorphous state.

The recent discovery of high-temperature superconductivity[1] has triggered huge theoretical and experimental efforts to understand its possible origin. Different theories have been suggested involving new mechanisms for the attractive interaction between electrons.[2-4] A common feature is that there is an insulating ground state supporting charge-density waves (CDW), itinerant antiferromagnetism [spin-density wave (SDW)], or a resonant-valence-bond state (RVB) in La_2CuO_4. Doping it with an alkaline earth metallizes the compound while maintaining the strong electron interaction responsible for high-temperature superconductivity. There are now two known order phases in La_2CuO_4, i.e., the orthorhombic one at 570 K involving a tilting of the oxygen octahedra and the itinerant commensurate antiferromagnetic phase that develops at 240 K.[5] However, the passage from an insulating state to a superconducting one does not occur, as is usual in strong-coupling systems in which the same portion of the Fermi surface is affected by a CDW or superconductivity. For example, in $NbSe_3$ (Ref. 6) bulk superconductivity appears only when the CDW transition temperature goes to zero. On the contrary, in $La_{2-x}Sr_xCuO_4$ the onset of superconductivity does not coincide with the disappearance of the SDW or of the orthorhombic phase.[4] This can mean that neither of the ground states are caused by the interaction responsible for high-temperature superconductivity and that another phase, (e.g., related to an oxygen breathing mode[2]) might be present in La_2CuO_4. Alternatively, inhomogeneities in the sample could allow the coexistence of semiconducting and superconducting regions. In this paper we present measurements of the thermal conductivity in $La_{2-x}Sr_xCuO_4$ that furnish strong evidence for a disordered phase even in pure La_2CuO_4. The combined behavior of the thermal conductivity, specific heat,[7] internal friction,[8] and ultrasound attenuation[9] strongly suggests that there are two-level tunneling systems (TS) characteristic of an amorphous state in the $La_{2-x}Sr_xCuO_4$ system. We propose the existence of a polaronic glass, probably stabilized by oxygen vacancies.

Measurements of thermal conductivity are suitable tools to study structural transitions as long-wavelength phonons, which play the predominant role in lattice conductivity, are sensitive to specific translational anharmonicities.[10] They have also furnished key information for the comprehension of amorphous systems.[11] As to our knowledge, there are no existing data on high-temperature superconductors, we have undertaken the study of the thermal conductivity of the $La_{2-x}Sr_xCuO_4$ system and in this work we report measurements on two concentrations: La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$.

The samples were prepared following the method described by Cava, van Dover, Batlogg, and Rietman[12] and then oxygen-annealed for 2 h at 1100 °C. They are 80% ceramics of typical grain size 100μm and were characterized by x-ray, resistivity, and magnetization measurements. The pure sample was in an orthorhombic phase and showed, in the resistivity and susceptibility curves, the SDW transition at 150 K. The doped sample had a sharp superconducting transition over 2 K with a midpoint at 35.5 K and full Meissner effect. Both were cut to typical dimensions $20\times4\times0.5$ mm^3 and mounted on a temperature-regulated copper block with an epoxy resin. A thermal gradient measured by an AuFe-Chromel thermocouple was imposed on the sample with a known heat flux furnished by an attached heater. The temperature was determined by a calibrated germanium resistor and stabilized to within 0.2%. The measured gradients were less than 3% of the absolute temperature for low temperatures and within 1 K at high temperatures.

La_2CuO_4 has a rather low thermal conductivity compared to similar perovskite insulators.[13] It can be attributed entirely to phonons, as the electronic contribution calculated through the Wiedemann-Franz relation from the electrical resistivity is two orders of magnitude smaller. It shows a $T^{1.8}$ dependence (Fig. 1) at low temperatures that gradually flattens to a very slowly increasing behavior near 100 K. $La_{1.85}Sr_{0.15}CuO_4$ has an even smaller thermal conductivity that follows a $T^{1.4}$ law below 10 K and then behaves similarly to the pure sample up to the superconducting transition temperature. At higher temperatures the electronic thermal conduction, which is about 10% of the lattice conduction, starts contributing in an appreciable manner and is probably responsible for the slope, which is steeper than in La_2CuO_4. Within the precision of the measurement, no sharp effect on the lattice

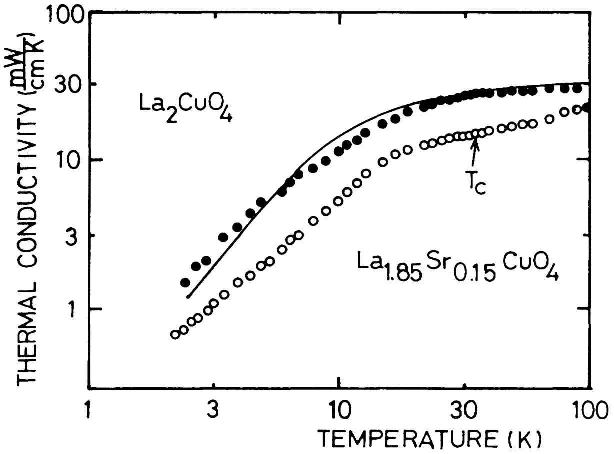

FIG. 1. Thermal conductivity of La_2CuO_4 (full circles) and of $La_{1.85}Sr_{0.15}CuO_4$ (open circles). The solid line is a fit considering that phonons scatter against two-level tunneling systems, as in an amorphous system.

conductivity due to the condensation of the electrons and hence of the disappearance of phonon-electron scattering is apparent near the transition temperature, implying that it is another mechanism that limits lattice conduction. Different samples from the same button show the same value and behavior at temperatures smaller than 20 K but have different parallel values for the flat region around the superconducting transition and at higher temperatures.

As our samples are ceramics we must be careful to separate the effects due to their granular nature from those intrinsic to the compound. The longest mean free path circulated from specific-heat[7] and sound-velocity measurements from the internal friction[8] at 5 K is 50μm, while the average grain size is 100 μm implying that intragrain scattering is predominant throughout the measured temperature range. The absence of the grain-boundary scattering T^3 dependence[14] agrees with this assumption, suggesting that the measured behavior is due to intrinsic processes.

Reviewing the mechanisms that can yield the anomalous lattice condition, we must consider the bidimensionality of the system. Though it can yield a square power law, it would do so in a very small temperature range (5 K for pyrolitic graphite[15]). On the other hand, T^2 laws have been measured in CDW compounds[16] and though they can be attributed to discommensurations their real origin is far from clear. Conduction of heat by ferromagnetic magnons can give a $T^{1.5}$ dependence,[17] but all indications point towards antiferromagnetic behavior in La_2CuO_4.

To gain insight into the problem we can analyze other phonon properties. The specific heat of La_2CuO_4 (Ref. 7) shows an anomalous linear term at low temperatures that cannot be attributed to electrons in this semiconducting material. It is, however, of the same order of magnitude as those found in amorphous ferroelectrics[13] and for which TS typical of amorphous systems are held responsible. On the other hand, internal friction[8] and ultrasonic attenuation[9] measurements show anomalous plateau similar to those found in amorphous systems, where it is due to the relaxation absorption of phonons by TS. Thus, we have fitted our La_2CuO_4 data with the usual expression for the thermal conductivity in the manner similar to that done in amorphous solids:[11]

$$K = 3k_B \frac{N}{\Omega} v_S^2 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx ,$$

where N is the number of atoms in a unit cell of volume Ω, $x = \hbar\omega / k_B T$, and the total relaxation time is that of the scattering of phonons against TS $\tau(x) = A\omega^{-1}$ for $\omega < \omega_0$ and a constant $\tau(x) = B$ for $\omega > \omega_0$, Θ_D is the Debye temperature, and v_S is the sound velocity. The fit in Fig. 1 with $\Theta_D = 300$ K (Ref. 7), $v_S = 4 \times 10^5$ cm/sec (Ref. 8), $A = 850$, $\omega_0 = 6.17 \times 10^{12}$ Hz, and $B = 1.38 \times 10^{-13}$ sec shows the good agreement of the data in terms of a TS interpretation. We can quantitatively compare our data with sound-attenuation[8] and specific-heat[7] measurements. Using standard TS theory we obtain a value of $P = 2.3 \times 10^{35}$ erg^{-1}cm^3 for the density of tunneling systems. In a similar way a value of $P = 10^{35}$ erg^{-1}cm^{-3} (Ref. 8) is extracted from internal friction measurements and $P = 10^{34}$ erg^{-1}cm^{-3} is extracted from the linear term of the specific heat. This order-of-magnitude accord shows the soundness of our interpretation of the data. On the other hand, the fact that the linear term in the specific heat and the thermal resistivity is smaller in the pure sample which has less oxygen vacancies than in the superconducting one suggests that oxygen vacancies play a significant role in the formation of TS.

In view of the absence of a complete microscopic description of oxygen defects in this system, we can only tentatively advance a simple picture of the disordered state. In the CDW compound 2H-$TaSe_2$ (Ref. 10) polarons exist at high temperatures in a disordered but dynamical state. At the CDW transition temperature they order themselves into a long-range distorted phase. Electron irradiation which creates point defects causes the order-disorder transition to disappear.[18] A short-range-order incoherent state is left over which can be viewed as polaronic or CDW glass. We propose that such a polaronic (or bipolaronic) glass exists in the $La_{2-x}Sr_xCuO_4$ system due to oxygen vacancies. The random distribution of oxygen vacancies and associated polarons creates a static disorder which is responsible for the constant mean free path at high temperatures. This constant scattering rate probably overwhelms other mechanisms, such as phonon-phonon scattering, which normally dominate lattice conductivity in crystalline systems. The same random vacancy distribution is also at the origin of the frustration that causes TS, which relaxationally scatters phonons at low temperatures with a ω^{-1} dependence. Such a oxygen-vacancy-induced disordered polaronic state must have a number of sites without polarons. As the Sr concentration is increased the number of normal sites would increase, until the concentration would be enough to sustain superconducitivity. This is the reason why the critical concentration for the appearance of superconductivity does not coincide with that of a phase transition. Furthermore, as superconductivity will exist in a percolative network around polaronic glass clusters, the superconductive glass state of Müller, Takashige, and Bednorz[19] is in this way naturally understood.

Finally, we can conclude that the picture that emerges from the analysis of thermal properties of $La_{2-x}Sr_xCuO_4$ is that of an amorphous state with a certain kind of TS. We suggest a polaronic glass state caused by oxygen vacancies. Though the nature of the polarons (one of the already known existing phases or possibly a third one[20]) cannot be yet determined, it is clear that strong oxygenation partially destroys the polaronic glass allowing the development of superconductivity.[21]

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