Nearly large-radius polarons and transport properties of La_2CuO_{4+y}

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Experimental data on the conductivity and the Hall effect in La_2CuO_4 are interpreted as evidence that the carriers are of a polaron nature. The anisotropy of the conductivity activation energy is explained. A theory of nearly large-radius polarons is derived.

Determining the structure of the current carriers in the high-T_c superconducting cuprates[1] is important for reaching an understanding of this superconductivity. In particular, it would be worthwhile to determine whether the carriers acquire the polaron "clothing" which plays a fundamental role in certain theories (see, for example, Ref. 2). Apparently the simplest way to answer this question is to study nonsuperconducting crystals with a low carrier density, in which the interaction of carriers with each other can be ignored. In the present letter we show that the unusual temperature dependence of the conductivity of insulating $LaCuO_{4+y}$ (Ref. 3) can be explained in a natural way on the basis of a polaron model.

The first systematic studies[4] of lightly doped La_2CuO_4 revealed a hopping conductivity, which can be described over a wide temperature range by the Mott law.

$$\sigma_{\parallel,\perp}^{(M)}(T) \approx B_{\parallel,\perp}^{(M)} \exp\{-(T_0/T)^{1/4}\}. \tag{1}$$

The power of 1/4 and the agreement of the values of $T_0(\sim 10^6\text{K})$ for the conductivity along ($\sigma_\parallel$) and perpendicular to ($\sigma_\perp$) the layers point to a three-dimensional nature of the hops. The relatively slight anisotropy of the coefficient of the exponential function, $B_\parallel^{(M)}/B_\perp^{(M)} \lesssim 10$ does not depend on T. It reflects an anisotropy of the effective radii of the localized states, which is due to an anisotropy of the hopping tunneling integrals $t_\parallel$ and $t_\perp$. We have previously presented arguments[5,6] in favor of the assertion that the localization of carriers at impurities should be accompanied by a polaron distortion. This idea would, in particular, help explain experiments on the magnetoresistance in the hopping region.[7,8]

Recent experiments[3] have shown that in pure crystals at sufficiently high temperatures ($T > T^*$) Mott's law (1) gives way to a simple activation dependence

$$\sigma_{\parallel,\perp}^{(A)}(T) \approx B_{\parallel,\perp}^{(A)} \exp(-E_{\parallel,\perp}/T). \tag{2}$$

The quantity T^* decreases with decreasing amount of excess oxygen (y); in typical crystals with $y \sim 0.01$ it would be $T^* \sim 50$ K. The anisotropy of the conductivity, $\gamma = \sigma_\parallel/\sigma_\perp$, increases with increasing T, from values $\gamma \sim 10$ at $T \lesssim T^*$ to $\gamma \sim 500$ at $T \sim 200$ K. The most surprising result is that the activation energy is anisotropic, and in such a way that a relatively large activation energy corresponds to a relatively high

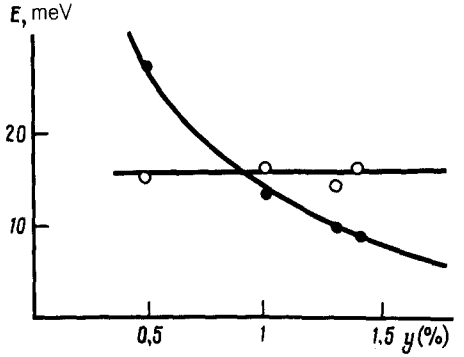

FIG. 1. Activation energy versus the concentration of excess oxygen, y (according to the data of Ref. 3). ●—$E_\perp$; ○—$W_\parallel = E_\parallel - E_\perp$.

conductivity: $E_\parallel > E_\perp$. The temperature dependence found for the Hall coefficient in Ref. 3 (for $\mathbf{H} \perp CuO_2$ layers) is also of an activation nature, with an activation energy E_H close to $E_\parallel$. The Hall conductivity is $\mu_\parallel \sim 1$ cm/(V·s). Such a low mobility was explained in Refs. 3 and 9 in terms of a scattering of carriers (with a moderate effective mass $m^* \sim 2m_e$) by spin fluctuations. It was assumed that the corresponding relaxation time was $\tau \sim \hbar/J \sim 10^{-14}$s, where $J \sim 10^3$ K is the characteristic energy of the magnons in the system. With these values of m^* and τ one can also explain the frequency dependence of the conductivity.[9] Magnons with such large energies could not participate in a scattering, however, and the value of τ^{-1} should at most be less than $\hbar/T$. On the other hand, similar mobility values were linked in Refs. 10 and 11 with a large mass $m^* \sim (10^2 - 10^3)m_e$ due to a polaron effect. The anisotropy of the activation energy[3] cannot, in our view, be explained under the assumption that the activation occurs in a band of free carriers or at the mobility edge. One-dimensional localization effects associated with a disorder between planes might lead to an anisotropy, but its sign would be the opposite of that observed experimentally ($E_\perp > E_\parallel$). We would like to call attention to the circumstance that the difference $E_\parallel - E_\perp$ calculated from the data of Ref. 3 is essentially the same from sample to sample, i.e., is independent of y (Fig. 1).

We offer the following picture to explain the transport properties of La_2CuO_4 (in particular, the anisotropy of the activation energy). Most of the carriers are localized at impurities, forming bound polarons.[5,6] The Fermi level ϵ_F lies in a regfion of localized states, and at low T it dominates the hopping conductivity. At $T > T^*$, the conductivity of carriers activated into a band of free polarons is predominant; their number satisfies $N \propto \exp(-E_0/T)$. The activation energy E_0 is the distance from ϵ_F to the bottom of the polaron band. With increasing y, the system approaches an insulator–metal transition, ϵ_F rises, and E_0 therefore falls. In transitions from site to site, a polaron must overcome a potential barrier.[12] The probability for overcoming the barrier is

$$w \propto \exp(-S), \qquad S \approx \begin{cases} cW/\omega & (T < T_c) \\ W/T & (T > T_c) \end{cases}, \tag{3}$$

where W is the barrier height, ω is the oscillation frequency near the minimum, and $c = 4$–6 is a number which depends on the shape of the barrier.[12,13] The upper line in (3) corresponds to a tunneling through the barrier, and the lower line to a surmounting of the barrier by an activation mechanism. The temperature at which one mechanism gives way to the other is $T_c \approx \omega/s$. We assume that the barriers are overcome by an activated process in the case of transitions in a CuO_2 plane, while in transitions from plane to plane there is instead a tunneling

$$T_{c\parallel} < T < T_{c\perp}. \tag{4}$$

Then

$$\sigma_\perp^{(A)} \propto N w_\perp \propto \exp(-E_0/T) \exp(-c_\perp W_\perp/\omega_\perp), \tag{5}$$

$$\sigma_\parallel^{(A)} \propto N w_\parallel \propto \exp(-E_0/T) \exp(-W_\parallel/T). \tag{6}$$

Identifying E_0 with $E_\perp(y)$, identifying $W_\parallel$ with $E_\parallel - E_\perp \approx 150$ K, and assigning the second factor in (5) to $B_\perp^{(A)}$, we find (2) with a difference $E_\parallel - E_\perp > 0$, which depends on only the structure of the polaron, not the quality of the crystal. The anisotropy of the polaron barrier is responsible for the T-dependent anisotropy of the conductivity: $\gamma \propto \exp(c_\perp W_\perp/\omega_\perp - W_\parallel/T)$.

The most significant aspect of the picture sketched above is the requirement that inequality (4) hold over the entire temperature interval from T^* to ~ 200 K; this requirement could be met only under the condition $T_{c\parallel} \ll T_{c\perp}$. We will show below that the latter inequality arises in a natural way in the model of a "nearly large-radius polaron." The barrier height W in (3) depends strongly on the polaron radius r. For a small-radius polaron we would have $W \sim W_p$, where the right side is the polaron shift, whose typical values are $W_p \sim 0.5$ eV (Ref. 12). With increasing r, the barrier becomes lower, $W \ll W_p$. In the continuum limit we find $W = 0$. The small value $W_\parallel \approx 150$ K suggests that a "nearly large-radius polaron," with $r_\parallel > a_0$ (a_0 is the lattice constant), is realized in the plane. We would thus have $W_\parallel \ll W_p$ but still $W_\parallel > T, \omega_\parallel$. An important point is that as r increases, there is also a decrease in ω in (3). In the continuum limit, the spatial-translation group becomes continuous, and zero modes corresponding to a displacement of a polaron as a whole arise in the system. At large but finite values of r, the translational modes correspond to small but nonzero frequencies. On the other hand, it is clear that specifically these displacement modes are responsible for the transport of a polaron from site to site, and ω in (3) will be the frequency of soft displacement modes. For a small-radius polaron we would have $\omega \sim \omega_0$, where the right side is the frequency of the phonons which form the polaron.

A polaron in the CuO_2 plane thus has a large radius; transitions along the plane are adiabatic; the corresponding barrier height is small, $W_\parallel \ll W_p$; the corresponding frequency is small, $\omega_\parallel \ll \omega_0$; and the barrier is overcome in an activation process at $T > T_c \sim \omega_\parallel/c \ll \omega_0$. As we will show below, a nearly large-radius polaron may be thought of as a "rigid" particle which adiabatically carries its clothing in a weakly modulated periodic potential. When a polaron of this type overcomes a barrier, it is "undressed" essentially not at all, in contrast with a small-radius polaron. In this

situation we would expect a long lifetime τ, so all polarons with energies $E > W_{\|}$ would make the standard contribution to the Hall effect [$1/(nec)$, where $n \sim \exp(-E_{\|}/T)$]. The Hall activation energy would then be $E_H \equiv E_{\|}$, in contrast with that for small-radius polarons, for which we would have $E_H > E_{\|}$ [in the simplest model, $E_H = E_0 + (4/3)W_{\|}$; Ref. 12]. With regard to transitions between different planes, we would expect that they would not be adiabatic, because of the small value of $t_{\perp}$, that the transverse radius of the polaron would be small, and that we would have $W_{\perp} \sim W_p, \omega_{\perp} \sim \omega_0$, and $T_{c\perp} \gg T_{c\|}$.

An independent test of the polaron effect might be a study of the thermal emf in a CuO_2 plane. According to the standard theory,[12] we would have $S = E_s/eT + \text{const}$; if the difference between $E_{\|}$ and $E_{\perp}$ were indeed due to a polaron effect, then E_s would be the same as $E_0 = E_{\perp}$, not $E_{\|}$.

To illustrate the qualitative conclusions presented above, we consider the very simple model of a particle with a quasi-one-dimensional dispersion law in a contact interaction with one branch of dispersion-free optical phonons (Holstein's[14] set of one-dimensional chains, for hops between the hopping integral, satisfies $t_{\perp} \ll t_{\|}$, where the right side is the hopping integral along the chains). In the adiabatic approximation, the Lagrangian of a single chain with an electron is

$$L = (M/2)\sum_n \dot{Q}_n^2 - U\{Q\},$$
$$U\{Q\} = (M\omega_0^2/2)\sum_n Q_n^2 + \min_{\psi} \sum_n \{t_{\|} |\psi_{n+1} - \psi_n|^2 - VQ_n |\psi_n|^2\}, \tag{7}$$

where n is the index of the site in the chain, Q_n are nuclear displacements, U is an adiabatic potential, and ψ_n is the normalized electron wave function. If $\Lambda = 4tM\omega_0^2/V^2 \gg 1$, the polaron radius satisfies $r_{\|} = \Lambda a_0 \gg a_0$, and the minimum of $U\{Q\}$ corresponds to $Q_n = Q(x)_{x=na_0}$, where $Q(x)$ is the solution of the problem in the continuum approximation. We introduce the collective coordinate x_0 (the center of a polaron), which corresponds to a displacement mode. Its energy, $U(x_0)$, reckoned from the minimum of U, is $W_p = t/3\Lambda^2$ and is a periodic function of x_0 with a period of a_0. In other words, we have $U(x_0) = \sum_{e=1}^{\infty} U_e(1 - \cos 2\pi l x_0)$. Since $Q(x)$ is smooth, the coefficients U_l fall off as $\exp(-\pi^2 \Lambda l)$, and at large Λ we need retain only the first harmonic. As a result, we find from (8) an effective Lagrangian for the collective coordinate x_0:

$$L_0 = M^* \dot{x}_0^2/2 - W_{\|} \sin^2(\pi x_0/a_0), \tag{8}$$

where $M^* = M\int dx (dQ/dx)^2 a_0$ is the mass of a continuum polaron. This mass is large in comparison with the mass of a "bare" electron, $m \sim 1/t_{\|} a_0^2$, by a factor proportional to the adiabatic parameter $(W_p/\omega_0)^2$. The barrier height for polaron hops along a chain is exponentially small, $W_{\|} \propto W_p \exp(-\pi^2\Lambda) \ll W_p$. The transition probability for single-mode system (8) is given by (3) with $W = W_{\|}$, $c = c_{\|} = 8$, and an exponentially low frequency of the displacement mode, $\omega = \omega_{\|} = \pi/a_0\sqrt{2W_{\|}/M^*} \propto \omega_0 \times \exp(-\pi^2\Lambda/2)$. Transitions between chains at a small value or $t_{\perp}$ are not adiabatic, and the relation $r_{\perp} < a_0$ holds. In these transitions, the polaron clothing should

undergo a complete restructuring, so the corresponding barrier would be $W_\perp \sim W_p$, and we would have $T_{c\perp} \sim \omega_\perp \sim \omega_0$. In this model we would thus have $T_{c\parallel}/T_{c\perp} \propto \exp(-\pi^2\Lambda/2) \ll 1$, and there would be a wide temperature range, (4), in which the motion of a polaron along chains would be of an activation nature, while that perpendicular to the chains would be a tunneling.
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The quasi-one-dimensional model, which can be solved exactly in the continuum limit, was considered above as an illustration. We believe that real quasi-two-dimensional polarons in La_2CuO_4 will have similar properties. We will examine the structure of the latter polarons in a separate paper.

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