

Mechanism for the frozen photoconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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In the model proposed here, the density of hole carriers which are responsible for the electrical conductivity of the compound increases upon exposure to light as the result of a localization of electrons at oxygen vacancies of symmetry D_{2h} . During electron transitions, the positions of the atoms near the vacancies change, giving rise to an energy barrier. This barrier can be overcome through zero-point and thermal vibrations of the lattice. Numerical estimates of the barrier height and of the relaxation time agree with experimental data.

A “frozen conductivity” has recently been observed¹ in a study of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. At an oxygen deficiency $\delta \approx 0.5$, the conductivity of the crystal increased upon exposure to green light from an argon laser. After the light was turned off, the excess conductivity $\Delta\sigma$ retained a value $\Delta\sigma/\sigma \approx 0.3$ for an indefinitely long time at a crystal temperature $T = 100$ K. At $T = 295$ K, $\Delta\sigma$ decreased by a factor of 2 over a time scale $\tau_1 = 20$ h. This relaxation was not exponential. At $T = 320$ K the relaxation time was $\tau_2 = 4$ h. The oxygen deficiency δ was achieved through vacuum annealing of the original crystal, with a value $\delta < 0.1$.

We know² that a reduction of the oxygen content in the compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ signifies an oxygen (O) vacancy in so-called Cu1–O1 “chains.” The O1 position has the point symmetry of the crystal, which belongs to the orthorhombic point group D_{2h} . Figure 1 shows the nearest neighbors of the O1 atom and the coordinate system, centered at the position of the O1 vacancy, with x axis running along the lattice axis with $a = 3.820$ Å, with y axis running along the direction with $b = 3.885$ Å, and with z axis along the direction with $c = 11.68$ Å (Ref. 3). The z coordinate of the Ba atoms is $z = 2.15$ Å, and that of the O4 oxygen atoms is $z = 1.85$ Å. Above and below the Ba–O4 layer there are layers of an O2–Cu2–O3 network, followed by a layer of yttrium, Y. It may be that an O1 vacancy, which arises upon annealing, creates a local level, which

is filled by either an electron, e^- , or two e^- 's during exposure to light.

It is known from general considerations (Ref. 4, for example) that a local perturbation V of the potential energy of an electron at a site in an ideal crystal with a band width Δ , under the condition $|V| > \Delta$, gives rise to a local level above the top of the band (if $V > 0$) or below the bottom of the band (if $V < 0$). The distance from the edge of the band is on the order of $\epsilon_0 = \sqrt{\Delta^2 + V^2} - \Delta$. A cell with an O1 vacancy in a $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystal is equivalent to a cell in an ideal $\text{YBa}_2\text{Cu}_3\text{O}_6$ crystal, in which the $\text{Y}(d^1s^2)$, $2\text{Ba}(s^2)$, $\text{Cu1}(s^1)$, and $2\text{Cu2}(d^1s^1)$ atoms supply 12 e^- 's with the atomic orbitals given in parentheses and completely saturate the valence bonds of the oxygen, $6 \times \text{O}(p^2)$. The compound $\text{YBa}_2\text{Cu}_3\text{O}_6$ is therefore an insulator at $T = 0$. The additional O1 atom fills its $2p^4$ shell with a $3d$ electron of Cu1 and one delocalized valence-band electron. The conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is of the p type and is mediated by carriers near the top of the valence band.² An O1 vacancy means a positive perturbation, $V > 0$, and gives to a local level $\epsilon_0 \sim 1$ eV if we assume, in agreement with the calculations of Ref. 2, that the width of the band is $\Delta \sim 2$ eV and that V is on the same order of magnitude, according to data on the electron affinity. Since there is no magnetic moment at O1 centers, we should assume that the ϵ_0 level is filled by two electrons on a singlet spin state. Their electrostatic repulsion is screened to a large extent by the mobile carriers. For the calculated density of states at the Fermi level μ , which is on the order of $N_\mu \simeq 1$ eV⁻¹ per cell,² the Debye screening length $r = (4\pi e^2 N_\mu)^{-1/2}$ is $r \sim 0.5 \text{ \AA} \ll a$.

The frozen-conductivity effect is associated with a deformation of the lattice near a defect upon a change in its electronic state.^{5,6} We denote by ν the occupation number of level ϵ_0 . We denote displacements of the atoms with respect to their equilibrium positions in the case $\nu = 0$ by vectors \vec{u}_j , where j specifies equivalent positions whose type is specified by the symbol of the atom in parentheses. We assign the Cartesian components indices $\beta = x, y, z$. We consider the complex of nearest neighbors of an O1 atom, which consists of 11 atoms. We introduce the normal coordinates $q_i = \sum_j \vec{s}_{ij} \vec{u}_j$, where $1 \leq i \leq 27$ and where we are using the coefficients $s_{ij\beta} = 0, \pm 1$. The small value of $u_{j\beta} \ll a$ means that we can expand the electron Hamiltonian in powers of q_i :

$$\hat{H} = \hat{H}_0 + \sum_i \frac{\partial \hat{H}}{\partial q_i} q_i + \sum_i \frac{\partial^2 \hat{H}}{\partial q_i^2} q_i^2. \quad (1)$$

In first-order perturbation theory, the energy of the electron term of a localized state plus the elastic energy of the lattice deformation is

$$E_1 = \epsilon_0 + \sum_i (w_i q_i + k_i q_i^2 / 2), \quad (2)$$

where the matrix elements $w_i = \langle 0 | \partial \hat{H} / \partial q_i | 0 \rangle$ are determined by the unperturbed functions of the state ϵ_0 , and the elastic coefficients $k_i = \text{const}$. With $\nu = 0$ we have $w_i \simeq 0$ for all w_i by virtue of the local nature of the potential perturbation. For $\nu \neq 0$, we have $w_i = 0$ in most cases by virtue of the symmetry of the problem. The group D_{2h} has only one-dimensional irreducible representations Γ_a . The electron levels are

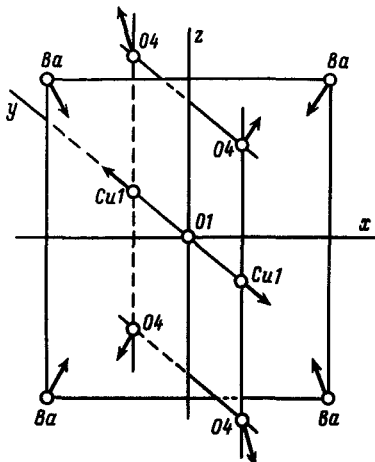


FIG. 1. Normal vibrations of the nearest neighbors of an O1 oxygen vacancy with a complete symmetry D_{2h} .

therefore nondegenerate, the direct product $\Gamma_a \times \Gamma_a = A_g$ is the unique representation, and we have $w_i \neq 0$ for only those values of q_i which correspond to completely symmetric normal vibrations. The complete vibrational representation Γ for an O1 complex can be expanded in terms of irreducible components as follows:

$$\Gamma = 5A_g + 2A_u + 2B_{1g} + 5B_{1u} + 2B_{2g} + 4B_{2u} + 3B_{3g} + 4B_{3u}.$$

Let us specify the meaning of the five variables q_i corresponding to representations A_g : q_1 corresponds to u_{jz} (Ba), q_2 to u_{jx} (Ba), q_3 to u_{jz} (O4), and q_4 to u_{jy} (O4) with $j = 1-4$, and q_5 corresponds to i_{jy} (Cu1) with $j = 1, 2$. Here we have specified the $u_{i\beta}$ which correspond to $s_{i\beta} \neq 0$, whose signs are determined by the directions of the vectors shown in Fig. 1.

It is difficult to calculate the vibron coupling coefficients w_i . To find a rough estimate, we introduce displacements $Q_i = -w_i = k_i$, and we assume that the corresponding values of $u_{j\beta}$ upon the switch from $\nu = 0$ to $\nu = 2$ are the same in order of magnitude as the displacements of the equilibrium positions of the atoms upon the conversion from the tetragonal cell of $\text{YBa}_2\text{Cu}_3\text{O}_6$ to the orthorhombic cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$. This approach is justified by the following comparison. The tabulated values of the atomic radii are⁷ $R(\text{O}) = 0.66 \text{ \AA}$, $R(\text{Cu}) = 1.28 \text{ \AA}$, $R(\text{Y}) = 1.81 \text{ \AA}$, and $R(\text{Ba}) = 2.21 \text{ \AA}$. We thus have $a \approx b = 2[R(\text{O}) + R(\text{Cu})]$ and a constant $c \approx 2R(\text{Y}) + 4R(\text{Ba})$. These results indicate that we can use a model of hard spheres in which the O1 oxygen atom freely fills the cavity shown in Fig. 2. On the other hand, the ion radius $R(\text{O}^-) = 1.40 \text{ \AA}$ indicates a significant role for a change in the state of the oxygen valence shell. These relations are evidence of a fairly close packing of the lattice. The coefficients k_i can be determined from the frequencies of normal vibrations, w_i , by using the Raman-scattering data of Ref. 8. From measurements of the interatomic distances³ we can calculate the elastic energies $u_i = k_i Q_i^2/2$. We find the following estimates (in electron volts): $u_1 \approx 0.4$, $u_2 \approx 0.003$, $u_3 \approx 0.07$, $u_4 \approx 0.008$, and $u_5 \approx 0.003$.

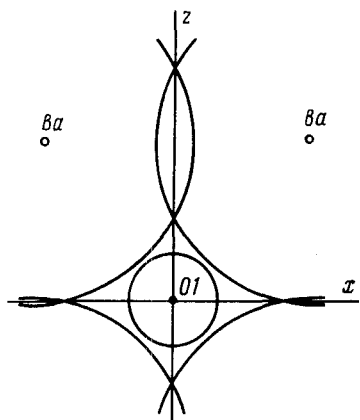


FIG. 2. Configuration of an O1 vacancy in the $y = 0$ plane. The radii of the circles correspond to the atomic radii of the elements.

We are thus left with only the terms with q_1 in (2). We rewrite this expression as $E_1 = \epsilon_0 + k_1(q_1 - Q_1)^2/2 - k_1Q_1^2/2$.

In the ground state we have $\tilde{E}_1 = \epsilon_0 - k_1Q_1^2/2 + \hbar\omega_1/2$. The term of a delocalized electron is $E_0 = -\mu + k_1q_1^2/2$. The term crossing $E_0 = E_1$ at $q_1 = \tilde{q} = (\epsilon_0 + \mu)/k_1Q_1$, which occurs in the adiabatic approximation, is shown in Fig. 3 for the case $k_1Q_1^2 \gg \epsilon_0 + \mu$. The radiationless transitions $\tilde{E}_1 \rightarrow E_0$ are caused by lattice vibrations with an activation energy

$$\tilde{u} = \frac{(\epsilon_0 + \mu - k_1Q_1^2)^2}{2k_1Q_1^2}.$$

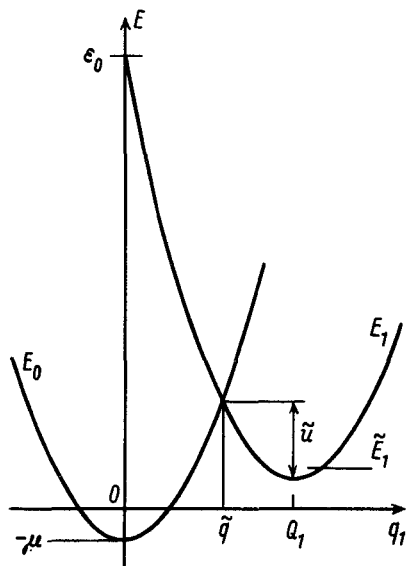


FIG. 3. Crossing of the delocalized term E_0 and the localized term E_1 . The origin for the energy scale is the top of the valence band.

It is clear from these estimates that we have $\tilde{u} \approx 1$ eV.

The temperature dependence of the photoconductivity relaxation time τ is given approximately by⁵

$$\tau = \tau_e \exp\left[\frac{2\tilde{u}}{\hbar\omega_1} \tanh\left(\frac{\hbar\omega_1}{2k_B T}\right)\right] \quad (3)$$

for constant τ_e . Using the experimental data of Ref. 8, we find $\hbar\omega_1 = 0.014$ eV. At $T \gg \hbar\omega_1/k_B \approx 170$ K, expression (3) becomes $\tau = \tau_e \exp(\tilde{u}/k_B T)$. Working from the experimental values of τ_1 and τ_2 from Ref. 1, we find $\tilde{u} = 0.52$ eV. The coefficient of the exponential function in (3) is on the order of the electron-transition time, $\tau_e \approx 10^{-8}$ s. At $T < 80$ K, at which we can assume $\tanh[\hbar\omega_1/(2k_B T)] \approx 1$ in (3), we find $\tau > 10^8$ s. If we assume a smaller vibron coupling $k_1 Q_1^2 < (\epsilon_0 + \mu)$, so that we have $\tilde{q} > Q_1$, and the point at which the parabolas intersect in Fig. 3 lies to the right of the E_1 minimum, then the transition $\tilde{E}_1 \rightarrow E_0$ can occur at a constant q_1 , accompanied by the emission of a photon. In this situation we cannot achieve a value $\tau > 1$ s, even under the most favorable conditions. Because of the dependence of u on μ , i.e., on the free-carrier density, the constant τ increases upon the restoration of the unilluminated state. This result explains the nonexponential nature of the observed relaxation of the photoconductivity.

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