

## Mechanism for Electric Field Effects Observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Films

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(Received 15 January 1993)

The chain oxygen dynamics of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  have been investigated using a Monte Carlo simulation of the asymmetric next-nearest-neighbor Ising model for the oxygen atoms in the basal plane. The effect of an electric field is to change the basal plane coordination of Cu ions, resulting in a change in the carrier doping of the  $\text{CuO}_2$  planes. The ratio of magnitudes of the changes in the doping under potentials of +10 V and -10 V is in good agreement in magnitude and sign with that observed in field effect experiments, as are also the time constants for the resistance changes.

PACS numbers: 74.72.Bk, 74.76.Bz

Early and recent work demonstrating the effect of applied electric fields on the properties of superconducting films has been interpreted as resulting from changes in the charge-carrier density in a film, without altering its chemical structure [1-3]. Considerable interest exists in three terminal devices exploiting this phenomenon [4]. In point contact spectroscopy, relaxation effects attributable to oxygen motion have been observed by Rybal'chenko *et al.* [5]. Investigations of oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  single crystals, in which increases of the transition temperature by as much as 30 K were observed by room temperature aging [6-8], demonstrate significant oxygen mobility even at room temperature. This ordering may be involved in the interpretation of the effect of applied electric fields on resistance and of other phenomena observed in high- $T_c$  materials such as the enhanced and persistent conductivity upon photoexcitation by red light [9,10].

In this Letter we report the results of a Monte Carlo study of the effect of applied electric fields on the dynam-

ics of chain oxygen in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . We find that considerable rearrangement of chain oxygen takes place, causing a change in the doping of the  $\text{CuO}_2$  planes. As a result, the carrier concentration, which is related to the ordering of oxygen vacancies, is altered. Experiments on oxygen-deficient single crystals [6,7] have established that the relevant parameter governing the doping of the  $\text{CuO}_2$  planes is not their oxygen content, but the nature and extent of oxygen order in the basal plane. An activation energy of  $0.97 \pm 0.03$  eV has been measured for oxygen by tracer diffusion [11]. Despite this apparently high activation energy, it has been demonstrated [6-9] that significant oxygen rearrangement and ordering can occur even at room temperature.

We use the asymmetric next-nearest-neighbor Ising (ASYNNNI) model, first proposed by de Fontaine, Willie, and Moss [12], to study the thermodynamics of oxygen ordering in this system. The Hamiltonian of the ASYNNNI model,

$$H = \sum_{i,j}^{\text{NN}} V_1 \sigma_i \sigma_j + \sum_{i,j}^{\text{NNN}(\text{Cu})} V_2 \sigma_i \sigma_j + \sum_{i,j}^{\text{NNN}} V_3 \sigma_i \sigma_j - \epsilon \cdot \sum_i \frac{1}{2} (1 + \sigma_i) \mathbf{p}_i, \quad (1)$$

allows the calculation of the energy of a given collection of oxygen atoms and vacancies in the basal plane. Here the  $\sigma$ 's denote the pseudospin variables (oxygen=+1, vacancy=-1) and  $i$  is the site index. The presence of an external electric field adds the term  $\epsilon \cdot \mathbf{p}_i$  to the Hamiltonian, where  $\epsilon$  is the local field and  $\mathbf{p}_i$  is the site-specific electric dipole moment of the oxygen. This term is present only when the site is occupied by oxygen. The averaged values of the dipole moments  $\mathbf{p}_i$  are taken to be nonzero. There exists a large body of experimental evidence [13-20] showing that permanent electric dipole moments are present in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and similar materials. The coexistence of local permanent electric moments and superconductivity is not new; it occurs, e.g., in doped  $\text{SrTiO}_3$ . This model regards the "chain" plane as a two-dimensional Ising model with repulsive first-neighbor effective pair interactions, denoted  $V_1$ , and second-neighbor interactions, which take on different values depending upon whether the interaction is mediated by an

intervening Cu ion or not, denoted by  $V_2$  and  $V_3$ , respectively.

The ground states of order were determined rigorously [21] for all possible ratios  $V_2/V_1$ ,  $V_3/V_1$  ( $V_1 > 0$ ) and were later rederived analytically [22]. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  the effective interactions had to obey the following inequalities:

$$V_2 < 0 < V_3 < V_1, \quad (2)$$

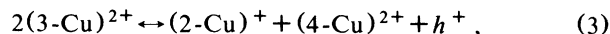
since  $V_2$  is mediated by an intervening Cu ion, and hence is attractive. Values of 0.094, -0.032, and 0.015 eV were given by Sterne and Willie [23] for  $V_1$ ,  $V_2$ , and  $V_3$ , respectively. The ASYNNNI model is sufficiently robust against changes in the  $V$ 's provided that (2) is satisfied.

In the following, we consider  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  at a single oxygen concentration,  $x = 0.25$ . Thus there are 6.75 oxygen atoms per unit cell. This stoichiometry was chosen based on the consideration that it is easily attained in thin film work, and oxygen contents around this value have

been reported in the thin film literature. The substoichiometry is accommodated, as is well known, by oxygen vacancies in the basal plane. The electric dipole moments for this particular stoichiometry have been determined from a shell model calculation given in Ref. [24]. We need be concerned only with the dipole moments on the oxygen atoms. The shell model calculation yields a dipole moment of  $0.003e \text{ \AA}$  at the  $O1$  site and  $0.013e \text{ \AA}$  at the  $O5$  site [25] at this concentration.

Typical values of potential differences that have been used in field effect experiments range from 3 to 10 V for films that are typically a unit cell to  $100 \text{ \AA}$  in thickness. We use the Lorentz relation to obtain the local electric field from the macroscopic field. Testardi *et al.* and others [13,16] report a value of  $\sim 400$  for the dielectric constant at 100 K. Since film thicknesses are smaller than the Debye screening length, the local field seen by the oxygen ions will be large, of the order of 130 times the macroscopic field. The ASYNNNI Hamiltonian at zero applied field yields typical site energies of about 0.4 eV for the chain oxygen. The electric field contribution to the energy may be readily estimated with the value of the dielectric constant above. This turns out to be about 0.16 eV at the macroscopic field corresponding to a potential drop of 10 V over a  $100 \text{ \AA}$  film, clearly a significant contribution.

The central idea behind this Monte Carlo study is to follow the evolution of the arrangement of oxygen atoms in the basal plane from some specified initial state. The positions of the basal plane oxygen atoms are treated as a two-dimensional array, with oxygen chains consisting of alternating  $O1$  and  $O5$  sites. The Cu ions in the basal plane are either twofold, threefold, or fourfold coordinated by oxygen. Since the apical oxygen sites are always occupied, these coordinations correspond to V-Cu-V, V-Cu-O, and O-Cu-O chain segments, respectively. In studies of single crystal aging [8], the threefold coordinated Cu were found to exhibit very interesting dynamics. Chains grew, with a reduction in the number of threefold coordinated Cu ions thereby increasing doping to the  $\text{CuO}_2$  planes, according to the reaction



since threefold coordinated Cu ions are in the  $2+$  state and a configuration of higher energy [26] in comparison to the square planar coordination (twofold or fourfold Cu). Here  $h^+$  denotes a hole. The reverse reaction will cause a reduction in the doping of the  $\text{CuO}_2$  planes, by consumption of a hole.

Monte Carlo simulations in the canonical ensemble were performed using a  $64 \times 64$  lattice (4096 sites) with periodic (toroidal) boundary conditions. This lattice size has been demonstrated to be large enough to avoid finite size effects [8]. A standard Metropolis algorithm was used. The simulations are neither technically difficult nor demanding in terms of computer time. In the simula-

tions, initial conditions were taken corresponding to equilibrium concentrations of local Cu coordinations. A field corresponding to a potential drop of  $+10$  and  $-10$  V over a  $100 \text{ \AA}$  film thickness was then applied. Since these are very thin films with low carrier concentration (typically an order of magnitude lower than that in a metal), we expect the Debye length to be larger than the film thickness. This clearly obviates the screening of the external field by the movement of charge. The time evolution of the Cu coordinations was tracked for 100 Monte Carlo steps (MCS) per site, since the local Cu environments give an indication of the ordering dynamics and the doping. In practice, Cu environments with more than two basal plane oxygen atoms were not observed in the simulations due to the highly repulsive nearest-neighbor interaction  $V_1$ . The time evolution of the fraction of twofold, threefold, and fourfold coordinated Cu ions for positive and negative biases at 100 K are shown in Fig. 1 on a linear scale and in Fig. 2 on a log scale. This figure shows that at a positive bias the twofold and fourfold coordinated Cu fractions decrease, while the threefold coordinated Cu fraction increases. The change in fractional coordinations is most pronounced during the first few MCS of the simulation, which is the reason for tracking these only for 100 MCS.

At the negative bias, also at 100 K, the twofold and fourfold coordinated Cu fractions increase at the cost of the threefold coordinated, as seen in Figs. 1 and 2 on linear and log scales, respectively. Their sum always equals unity, as it should. At a negative bias, the number of holes available to the  $\text{CuO}_2$  planes increases, while the opposite effect is observed at the positive bias. The physics is that of chain formation in the first case and reduction in the number of chains (healing) [8] in the second. In studies of single crystal aging, no significant changes in the fraction of threefold coordinated Cu were observed for high oxygen contents, which could be attributed to the lack of sufficient driving force for the ordering induced doping. In this case, however, the driving force is provid-

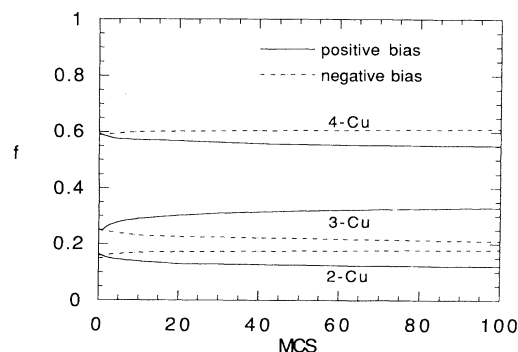


FIG. 1. Fraction  $f$  of Cu atoms in a given coordination geometry as a function of simulation time at positive and negative biases as explained in the text. Note the asymmetry of the results.

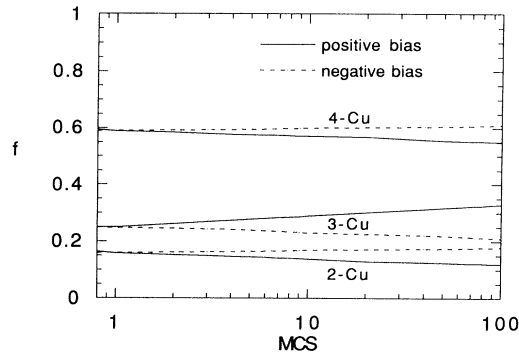


FIG. 2. As in Fig. 1 but on a log scale.

ed by the external electric field. The asymmetry of the effect (in that the changes in the threefold coordinated Cu are not of the same magnitude for positive and negative biases) is worth noting, and will be discussed further below.

It is useful to obtain a relation between real time and Monte Carlo time since the temporal dynamics of the model and experiment can then be compared. Ceder, McCormack, and de Fontaine [7] make the assignment of  $1 \text{ MCS} \approx 1 \text{ min}$ , at room temperature, by comparing results from several Monte Carlo runs to the  $a$ - $b$  plane diffusion constant for oxygen [21]. Since the attempt rate is only weakly temperature and field dependent in comparison with the activated form of the transition probability, and, furthermore, the field and the temperature dependence have opposite effects, we make the reasonable assumption that the assignment is still correct in order of magnitude, which is all we require.

Experimental data have been obtained by Mannhart *et al.* [2] on the resistive transition in the presence of an electric field. The data clearly depict an asymmetry of the effect with respect to the sign of the electric field. In order to eliminate unknown parameters in comparing the model with experiment, we study the ratio of the changes in the resistance at 100 K which follow from a change in the sign of the bias voltage. The ratio of the magnitudes of the change in resistance at  $+10 \text{ V}$  to that at  $-10 \text{ V}$  in the experiment is 1.75. Our results from the model (Figs. 1 and 2) yield, using Eq. (3), a value of 2, in good agreement with the observations. This estimate assumes that the conductance is proportional to the number of holes. The sign of the change is also in agreement with the model. The input parameters for the model are all obtained from independent considerations not involving fitting, with the results depending exponentially on these input parameters.

We consider now the characteristic times. The behavior of the resistance after the abrupt application of a bias of  $-10 \text{ V}$  is reported by Mannhart [27]. The time period for a resistance change of  $2 \Omega$  following such a pulse is of the order of several seconds. Since the temperature at which these data were taken is  $82 \text{ K}$  there is again re-

markable agreement with our results which predict characteristic times of the order of minutes, with the most noticeable changes occurring in the first few MCS. From the values of the resistance and capacitance for the device studied by Mannhart [27] we obtain an  $RC$  time constant of about  $150 \mu\text{s}$  for his experiment. A careful examination of Fig. 4 in Ref. [3] (Xi *et al.*) leads to an interpretation of the data as exhibiting a time constant of the order of ms, in contrast with an  $RC$  time constant of  $10 \mu\text{s}$  for the structure. Clearly for both experiments the observed longer temporal responses are inconsistent with a field effect interpretation. Response times for semiconductor field effect devices are usually set by the  $RC$  time constant [28].

Aspects of the observed persistent photoconductivity [9,10] can also be treated. From the site energies, an estimate can also be made of the photon energy required to displace an oxygen atom in the basal plane so as to effect a change in the Cu coordination and consequently the doping. Oxygen diffusion or motion in these materials clearly occurs by a vacancy mechanism. The activation barrier for the process, given the existence of an adjacent vacant site, is to a first approximation the difference in the site energies. We estimate this activation barrier to be about  $650 \text{ meV}$ . In the absence of a vacant site, the energy would be correspondingly higher. Photoexcitation studies indicate that a one photon process is the relevant mode [9,10] and that the conductivity is enhanced upon irradiation by red laser light ( $1.9 \text{ eV}$ ), which is compatible with the activation barrier estimated above. The site energies at zero bias are of such magnitude as to favor the hopping of oxygen in a manner which would reduce the number of threefold coordinated Cu ions. This ensures that the photoexcitation enhances the conductivity. Further, the enhanced conductivity is reported to persist for several hours at  $270 \text{ K}$  [9,10]. An elementary evaluation of the decay time of our model at the energy barriers and temperatures involved yields a decay time of  $5 \text{ h}$  at  $270 \text{ K}$  and several tens of days at lower temperatures of  $50$  to  $100 \text{ K}$ . These results are consistent with experimental observations.

In conclusion, we have demonstrated that chain oxygen dynamics in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  under applied electric fields and photoexcitation may explain features of experimental observations attributed to the field effect and observations of persistent photoconductivity. As a consequence of the motion of oxygen atoms rather than only the transfer of charge, devices exploiting this phenomenon would of necessity be slow, as existing experimental data demonstrate. The dynamics of chain oxygen may be of importance in the interpretation of pion contact spectroscopy data, in both the normal and superconducting states, since the fields are of comparable magnitude, and relaxation effects have been observed.

One of us (N.C.) acknowledges invaluable discussions with Dr. Roger Baetzold and Ryan P. McCormack. This research was supported in part by the Materials Research

Group program of the National Science Foundation under Grant No. NSF/DMR-8908094 and by the Air Force Office of Scientific Research under Grant. No. F49620-93-1-0076.

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