Atomic disorder and the transition temperature of cuprate superconductors

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Particle-induced shifts in the transition temperature T_c of cuprate superconductors are much larger than expected for the number of defects expected to be produced, and suggest that oxygen displacements in CuO_2 planes are about an order of magnitude more effective in reducing T_c than oxygen displacements in the intercalating layers.

The transition temperature T_c of the cuprate superconductors depends closely on the structure, composition, and morphology of the material. Supercurrent is known to be carried in CuO_2 planes that are intercalated in different materials with layers of BaO, BiO, CuO, LaO, PbO, or TlO. One model which provides a link between atomic structure and T_c is the charge-transfer model, in which the intercalated layers act as charge reservoirs to control the electron density in the planes, thereby determining the charge valence state of the copper atoms and hence, to some degree, the transition temperature.[1] As atomic disorder in the reservoir increases, typically in the form of vacancies and interstitials in the oxygen sublattice,[2,3] the electron density in the planes shifts from its optimum value and decreases T_c. Various techniques for producing controlled amounts of disorder include thermal quenching, desorption techniques, and substitution.[2–6] These techniques have been employed in examining the complex relationship between T_c and structural disorder. Desorption experiments on $YBa_2Cu_3O_{7-\delta}$ (YBCO), for instance, indicate that increasing the fraction of oxygen vacancies in the reservoirs promotes migration of oxygen atoms to normally vacant sites, decreases T_c, and eventually leads to an orthorhombic-to-tetragonal phase transition and a nonsuperconducting state.

Structural disorder can also be introduced into the lattice by particle irradiation. In high-quality quasiepitaxial films and single crystals, particle irradiation causes the transition temperature to shift downward with little broadening. It has been shown previously for YBCO that the rate of shift of the onset T_c with fluence Φ, $dT_c/d\Phi$, is directly proportional to the nonionizing energy loss (NIEL) of the incident particle over a wide range of particles and energies.[7] NIEL is a measure of the average number of atoms displaced by particle irradiation. It is calculated from a product of the cross section for interaction and the average energy of the recoiling atom, suitably corrected for ionization losses (Lindhard partitioning).[8] The proportionality of $dT_c/d\Phi$ with NIEL holds for particles ranging from 2-MeV electrons to high-energy protons and heavy ions. This result shows conclusively that the particle-induced depression of T_c is due to atomic displacements over the range of energies considered. Recent results indicate that atomic displacements, and hence shifts in T_c, can also be produced by ionization during irradiation with very high-energy heavy ions.[9,10] Other results also demonstrating very large T_c shifts at high fluences have been associated with phase transitions.[11] However, these effects, which complicate the relationship between T_c shifts and NIEL, occur outside the range of particle energies and fluences considered here.

Recently, radiation measurements have been extended to Tl- and Bi-based cuprate superconductors, and corresponding NIEL calculations have been made.[12–16] Figure 1 shows the unexpected result that the same proportionality found for YBCO relates $dT_c/d\Phi$ and NIEL for

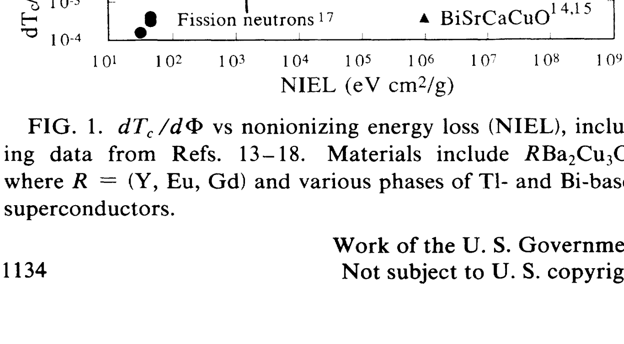

FIG. 1. $dT_c/d\Phi$ vs nonionizing energy loss (NIEL), including data from Refs. 13–18. Materials include $RBa_2Cu_3O_7$, where R = (Y, Eu, Gd) and various phases of Tl- and Bi-based superconductors.

these materials also. Furthermore, the calculations have now been extended to include fission neutrons incident on YBCO, for which the total NIEL is calculated to be 1.42 keV cm^2/g,[12] and again the experimentally determined value[17,18] for $dT_c/d\Phi$ falls close to the other data. Figure 1 shows therefore that for all the currently available cuprate superconductors, there is a general universal curve that relates $dT_c/d\Phi$ and NIEL, which extends over eight orders of magnitude of displacement-damage energy. The existence of the universal curve implies that the particle-induced shift in T_c is determined by the average number of point defects initially formed during irradiation, even if the damage occurs in large cascades, as is the case for fission neutrons. In this paper, the implications of the universal curve of NIEL vs $dT_c/d\Phi$ are explored. In particular, it will become apparent that oxygen displacements in the CuO_2 planes are much more effective in depressing T_c than generally thought. This observation provides an important criterion for prospective theories describing the mechanism of high-temperature superconductivity.

The functional form of the universal curve (Fig. 1) is

$$\frac{dT_c}{d\Phi} \approx cS^m , \tag{1}$$

c and m being constants and S being the total NIEL. The experimental data plotted in Fig. 1 show that the value of m is close to unity and that $c \approx 5\times 10^{-21}$ g K/eV. The value of S is calculated by summing the individual NIEL contributions S_i of each atomic species in the superconductor, i.e., $S=\sum S_i$. For the purpose of a later discussion, a NIEL partition fraction p_i is defined which describes the probability that initial displacement occurs in atomic sublattice i, such that $p_i S = S_i$. For interactions within the scope of Fig. 1, the parameters involved in calculating S and p_i are atomic mass, interaction cross sections including atomic energy thresholds for effective displacements E_{di}, and recoil energies. There is evidence that the displacement energy threshold for oxygen is anisotropic for atoms in the CuO chains of YBCO and also that some oxygen displacements may change T_c very little. This tends to complicate an exact definition of the effective displacement energy. However, exact values of E_{di} are not essential in determining S_i for the data of Fig. 1, since it has been demonstrated that little error is involved in taking $E_{di}=E_d=20$ eV.[8,9] Experimental determination of the displacement energy threshold for oxygen atoms in YBCO (Ref. 19) is consistent with the value of E_d used for the remainder of this text (20 eV). Exact values for recoil energies associated with inelastic collisions are also uncertain, but for high-energy-proton interactions are only important for proton energies greater than about 60 MeV. Only a few measurements of $dT_c/d\Phi$ have been made for these particles.

The fact that Eq. (1) fits all the known cuprate superconductors implies that there is a common link between the transition temperature and radiation-induced disorder. In this regard it is instructive to combine a theoretical expression for NIEL with one for $dT_c/d\Phi$ and then to compare the result with Eq. (1) and to other experimental results, such as from gettering. A first step is to relate NIEL to the number of stable defects per incident particle per unit length via the commonly used Kinchin-Pease approach.[7,8] If α_i is the fraction of initially formed defects of atomic type i that remain unrecovered and n is the atomic mass density of the entire crystal, then the number of displacements per incident particle per unit length, N_i, for atoms of type i is given by

$$N_i = \alpha_i n S_i / \beta E_{di} , \tag{2}$$

where β is a constant of value ≈ 2. One may consider as an alternative to N_i the number of displaced atoms of type i per incident particle per unit cell, δ_i. If the incident particle direction is along the c axis of the superconductor, for example, then $\delta_i = L_c N_i$, where L_c is the c-axis length.

Assuming that the observed shift in T_c is a combination of T_c shifts due to displacements in each of the sublattices (so long as the fluence is low enough to preclude a phase transformation), then, for YBCO, $T_c = T_c(\delta_i) = T_c(\delta_Y, \delta_{Ba}, \delta_{Cu}, \delta_O)$. More generally, $dT_c/d\Phi$ can be expanded by use of the chain rule into the form

$$\frac{dT_c}{d\Phi} = \sum \frac{\partial T_c}{\partial \delta_i} \frac{\partial \delta_i}{\partial \Phi} , \tag{3}$$

with the summation over the various atomic sublattices of the superconductor.

With the usual assumption that the defect-production rate is directly proportional to the fraction of undisplaced atoms, one obtains

$$\frac{\partial \delta_i}{\partial \Phi} = V_c N_i \exp(-N_i \Phi / n_i) , \tag{4}$$

where V_c is the unit-cell volume and n_i is the preirradiation density of ith component atoms ($n=\sum n_i$).

Combining Eqs. (2)–(4) yields an expression for $dT_c/d\Phi$ in terms of known variables and $\partial T_c/\partial \delta_i$. It is

$$\frac{dT_c}{d\Phi} = C'S , \tag{5}$$

where

$$C' = \frac{n V_c}{\beta} \sum_i \frac{\partial T_c}{\partial \delta_i} \frac{\alpha_i p_i}{E_{di}} \exp\left[\frac{-\alpha_i n S_i \Phi}{\beta E_{di} n_i}\right] . \tag{6}$$

For sufficiently low fluences, where the exponential in Eq. (6) can be approximated by unity, Eq. (5) takes the same form as Eq. (1). Thus the existence of the universal curve can be explained by accounting for defect accumulation and T_c shifts due to displacements of various types of atoms. For increasing NIEL, Eqs. (5) and (6) predict that $dT_c/d\Phi$ should become more negative than predicted by the universal curve, gradually falling more and more below the curve until T_c goes to zero. This is not observed in the case of YBCO,[2,11] because the onset of the nonsuperconducting tetragonal phase at high defect concentration leads, under high-Φ conditions, to an invalidation of the assumption preceding Eq. (3).

It is interesting to explore some other features implied by the above equations in the low-Φ limit. For simplicity, we consider first the "worst-case" limit in which no defect recovery occurs ($\alpha_i = 1$). Then equating Eqs. (1) and (5) and taking $E_{di} = E_d$ gives

$$\frac{E_d \beta c}{n V_c} \approx \sum p_i \frac{\partial T_c}{\partial \delta_i} . \quad (7)$$

For YBCO the numerical value of the left-hand side of Eq. (7) is about 180 K. Since values of p_i can be calculated fairly readily, Eq. (7) provides a way to estimate values of $\partial T_c / \partial \delta_i$.

Consider an irradiation experiment in which only oxygen displacements occur, as would be the case for incident electrons with energy less than about 450 keV.[8,19] In such an experiment, all oxygen atoms share a similar probability of being displaced. Then, according to an extrapolation of the universal curve, the decrease in T_c per oxygen displacement per unit cell is $\partial T_c / \partial \delta_0 \sim 200$ K/defect. However, the results of oxygen gettering and desorption experiments indicate that for orthorhombic YBCO the rate of decrease of T_c is between about 5 and about 17 K/defect.[2,20,21] X-ray experiments on YBCO show that the defects in gettering experiments consist of both vacancies and interstitials created from displaced oxygen atoms in CuO chains. Thus radiation-induced displacements appear to be between 12 and 40 times more effective in reducing T_c than are displacements caused by removing oxygen atoms from chains in the intercalating layers. Two possible explanations for the order-of-magnitude disagreement between the two values of $\partial T_c / \partial \delta_0$ suggest themselves. These are (1) that the universal curve is not valid for low-energy electron irradiation or (2) that the type of defects created by irradiation and gettering are different. These possibilities are discussed sequentially in the following two paragraphs.

It may be argued that if oxygen displacements were to play a minor role in determining shifts in T_c for irradiated superconductors, then extrapolating the universal curve to very low electron energies, where only oxygen displacements occur, could result in an overestimation of $\partial T_c / \partial \delta_0$. The magnitude of the potential overestimation can be examined by comparing values of $dT_c / d\Phi$ for 2-MeV-electron- and 2-MeV-proton-irradiated YBCO. Both values fall on the universal curve, indicating similar values of C', but the NIEL partition fractions differ. For (Y,Ba,Cu,O), one has[7,8] $p_i = (0.08, 0.20, 0.26, 0.46)$ and (0.13,0.33,0.29,0.25) for the electrons and protons, respectively. Substituting each set of p_i's into Eq. (7) and equating the results shows that

$$\frac{\partial T_c}{\partial \delta_{\mathrm{O}}} = 0.14 \frac{\partial T_c}{\partial \delta_{\mathrm{Cu}}} + 0.62 \frac{\partial T_c}{\partial \delta_{\mathrm{Ba}}} + 0.24 \frac{\partial T_c}{\partial \delta_{\mathrm{Y}}} . \quad (8)$$

Published chemical-substitution results in which, for example, Cu is partially replaced by Ni or Fe can be used to estimate that $(\partial T_c / \partial \delta_i)/(\partial T_c / \partial \delta_0) \sim 2.8$ for Cu, ~ 0.7 for Ba, and ~ 0.2 for Y.[4-6] These numbers satisfy Eq. (8) quite well and show that oxygen displacements could contribute as little as 20% to the total shift in T_c. In other words, the assumption that the universal curve can be extrapolated to include electrons with energy less than about 450 keV might result in an overestimation of $\partial T_c / \partial \delta_0$ by a factor of about 5. The disagreement between values of $\partial T_c / \partial \delta_0$ for irradiation and oxygen gettering would then decrease to a factor of 2.4–8, which would be marginally reasonable if it were not for the fact that atoms displaced during the cascade have been assumed to remain frozen in their displaced positions. In actuality, some recombination always occurs, and so the number of stable defects will be less than estimated here. The T_c shift per remaining radiation-induced defect will be greater than estimated. Thus recombination tends to restore the order-of-magnitude discrepancy.

A more likely explanation for the large disagreement between values of $\partial T_c / \partial \delta_0$ determined from radiation and gettering experiments is that oxygen atoms in the CuO_2 planes are more important to the superconducting state than oxygen atoms in the reservoir. Then radiation, which displaces atoms in the planes, will lead to larger values of $\partial T_c / \partial \delta_0$ than will gettering and desorption, which do not.[2,20] It can then be estimated from comparison of the above values of $\partial T_c / \partial \delta_0$ that a displaced oxygen atom in a CuO_2 plane has at least 10 times the detrimental effect on T_c as does a displaced oxygen atom in an intercalating layer. Furthermore, the striking fact that all cuprate superconductors obey the universal curve becomes more comprehensible if it is recognized that displacements in the CuO_2 planes dominate radiation-induced T_c shifts because then displacements in the dissimilar intercalating layers contribute only a relatively minor amount to the total shift in T_c. A recent set of experiments involving Cu substitutions specific to either planes or chains in YBCO has produced an analogous result, namely, that superconductivity depends much more strongly on the integrity of Cu in the CuO_2 planes than on the integrity of Cu in the CuO chains.[22]

The results presented here indicate that the perfection of the CuO_2 perovskite layer is critical to the large values of T_c in cuprate superconductors.

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