Radiation-Induced T_c Reduction and Pair Breaking in High-T_c Superconductors

E. M. Jackson,[1] B. D. Weaver,[2] G. P. Summers,[2,3] P. Shapiro,[1] and E. A. Burke[1]
[1]SFA, Inc., Landover, Maryland 20875
[2]Naval Research Laboratory, Washington, D.C. 20375-5345
[3]University of Maryland, Baltimore County, Baltimore, Maryland 21228
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The radiation-induced reduction of the transition temperature in several high-T_c superconductors is quantitatively compared to the predictions of pair breaking theory for magnetic defects in isotropic superconductors and nonmagnetic defects in anisotropic superconductors. In all cases the reduction in T_c is consistent with theory if Cu and O vacancies in the CuO_2 planes are pair breaking. Copper plane site vacancies appear to scatter charge carriers twice as effectively as O site vacancies. Scattering potentials are found to be comparable to magnetic scattering potentials in conventional superconductors.

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The transition temperature T_c in particle-irradiated cuprate superconductors exhibits two very interesting traits. First, T_c is more than an order of magnitude more sensitive to the presence of radiation-induced disorder than is the transition temperature in the low-T_c superconductors [1]. Second, the rate of change of T_c with particle fluence, $dT_c/d\Phi$, is directly proportional to the average amount of displacement damage caused by an incident particle and is roughly independent of sample composition, irradiation temperature (between 20 and 300 K), incident particle mass and energy (provided that nuclear tracks are not formed), onset T_c, and other parameters. The numerous theories of high-T_c superconductivity provide few qualitative explanations for these traits, because it is difficult for the theories to survive the class-wide generality of the effects. However, one explanation for the rapid decrease of T_c by displacement damage which can explain its commonality is strong depairing.

The concept of depairing has been previously invoked to explain the rapid decrease of T_c in irradiated $YBa_2CU_3O_{7-x}$ (YBCO) but has been applied quantitatively only for the case of magnetic oxygen vacancies [2]. It is now known that Cu defects depress T_c as well as O defects [3]. Also, although magnetic moments have been observed in irradiated YBCO, the origin of these magnetic defects is still controversial since many impurity phases have magnetic moments [4,5]. Therefore, it is important to consider nonmagnetic depairing mechanisms as well.

In the following discussion we summarize the results of Abrikosov and Gor'kov depairing theory as they apply to depairing interactions (magnetic, anisotropic s-wave, or d-wave) in any superconductor [6,7]. We then discuss the significance of the defect concentration in determining the scattering or the depairing time, and calculate the density of radiation-induced defects for numerous irradiated cuprates. Next, data from an electron irradiation experiment are fitted by the model to determine values of the scattering potentials. Finally, a quantitative comparison is made between the predictions of the fixed parameter model and a large collection of experimental results [1,3,8]. In every case, we find that pair breaking theory is sufficient to explain the observed radiation-induced variations in T_c.

Anderson has shown that nonmagnetic defects in homogeneous, isotropic BCS superconductors have little effect on T_c [9]. Disorder modifies the wave functions of the normal state charge carriers without changing the nature of the pairing interaction between them. In this case the most significant effect of the disorder is to cause averaging over the Fermi surface, which can change the density of states at the Fermi energy and other normal state properties. These in turn can change T_c, but the effect is generally quite small compared to the effect of magnetic impurities. Magnetic impurities cause a very large degradation in T_c at a concentration of only a few atomic percent because the magnetic scattering interaction lacks the time reversal symmetry of the Cooper pairs. Thus magnetic scattering dissolves paired carriers and inhibits pair formation.

Even nonmagnetic impurities cause depairing effects similar to those of magnetic impurities in superconductors with large anisotropy [6,7,10]. The most commonly cited example is that of isotropic scatterers in a d-wave superconductor. In this case, the scattering causes averaging over parts of the order parameter (Δ) which are out of phase by a factor of π. The resulting interference rapidly reduces Δ and T_c to zero. In anisotropic s-wave superconductors, depairing also occurs because the scattering causes averaging over regions of k space where pairing is less energetically favorable (i.e., where Δ is smaller or zero). However, in the case of anisotropic s-wave pairing, the order parameter usually has an isotropic component, so although depairing reduces Δ and T_c they remain nonzero [11]. In all of these cases, T_c is given by

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \chi\left[\Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{\alpha}{2\pi k_B T_c}\right)\right], \quad (1)$$

where Ψ is the digamma function, k_B is Boltzmann's constant, χ is a measure of the anisotropy, and T_{c0} is the transition temperature in the absence of pair breaking.

In Eq. (1), the parameter α represents the pair breaking strength of the scattering. For magnetic impurity scatterers, the well-known definition is $\alpha \equiv \hbar/\tau$, where τ is the electron scattering time, and, for nonmagnetic scatterers, $\alpha = \hbar/2\tau$. At low defect concentrations, τ is always inversely proportional to the concentration of scattering impurities n (see below), so that α is directly proportional to n.

For samples containing magnetic defects one defines the parameter χ to be 1. Otherwise, χ is a measure of the anisotropy of the energy gap [6]. In ideal, isotropic superconductors with nonmagnetic defects, $\chi = 0$, which means that nonmagnetic defects have no depairing effect and do not affect T_c. In zinc, $\chi \approx 0.05$, which means that disorder-induced variations of T_c are small [12]. For s-wave superconductors in general, $\chi < 1$, but in superconductors whose order parameter averages to zero over the Fermi contour, such as in d-wave superconductors, one has $\chi = 1$. Both magnetic and nonmagnetic scatterers can have $\chi = 1$.

We wish to consider small impurity concentrations ($\delta T_c \ll T_{c0}$), where Eq. (1) has the form

$$\delta T_c \equiv T_{c0} - T_c = [2]\,\frac{\chi h}{16 k_B \tau}\,. \qquad (2)$$

The factor of 2 in square brackets in Eq. (2) applies only in the magnetic scattering case. In order to obtain Eq. (2) we have used the definitions of α.

The standard definition of the normal state impurity scattering time for nonmagnetic impurities is

$$\frac{1}{\tau} = \frac{4\pi}{h}\,\frac{\pi N(0) n v^2}{1 + [\pi N(0) v]^2} \equiv \frac{4n}{hN(0)}\,\frac{z^2}{1 + z^2}\,, \qquad (3)$$

where $N(0)$ is the density of states at the Fermi energy and v is the scattering potential energy [7]. Because Eq. (3) is valid for both soft- and hard-sphere scattering, we are not limited to special scattering cases, such as the Born limit. Also, given the appropriate potential, Eq. (3) is valid for magnetic scatterers.

Combining Eqs. (2) and (3) gives a final relation for T_c shifts at small defect concentrations. It is

$$\delta T_c = [2]\frac{\chi n}{4 k_B N(0)}\,\frac{z^2}{1 + z^2}\,. \qquad (4)$$

We now discuss each of the parameters involved in Eq. (4).

In examining Eq. (1), one finds that as the defect concentration increases the ratio T_c/T_{c0} tends to asymptotically approach a nonzero value unless χ is close to unity. Experiments on irradiated nongranular cuprate superconductors show that T_c does indeed go to zero (or at least becomes unmeasurably small) at large particle fluences [13]. Furthermore, the rate of decrease of T_c with fluence often increases at large fluences. The only way that this behavior can be explained by depairing theory is if the value of χ is near unity for the high-T_c cuprates. We therefore make the assumption that the value of χ is approximately 1. This implies either the presence of magnetic defects, an order parameter which has a vary small average value, or a very special relationship between the scattering symmetry and the symmetry of the order parameter [11].

The density of states can be obtained from band-structure calculations. In YBCO, four bands cross the Fermi energy. Two of these correspond to the planes and two correspond to the chains [14]. It is likely that defects cause primarily intraband scattering because the bands are spatially separated. Indirectly, the near universal magnitude of the depairing effect also supports the idea that intraband scattering is dominant since the total density of states of the high-T_c superconductors varies by a factor of 3 and would produce comparable variations in the radiation sensitivity. The density of states of the plane band is more consistent with the behavior of the T_c shifts since it is about the same in all the high-T_c superconductors except $La_{2-x}Sr_xCuO_4$ (LSCO). Therefore, we assume that the density of states required in Eq. (4) is the density of states associated with one plane band, which is about 1.1 states/eV cell volume (4.0×10^{40} states/J cm^3) [14]. As shown below, the values of v determined under this assumption are reasonable.

The number of defects used in Eq. (4) should include only those that are pair breaking since other defects do not affect T_c. Since all the high-T_c superconductors exhibit similar radiation-induced T_c shifts for a given damage energy, it is likely that the defects responsible for the T_c shifts are common to them all [1]. The natural candidates for such defects are Cu and O vacancies in the planes, since the Cu-O planes are the major structural constant. Also, conduction in the high-T_c superconductors is primarily localized in the planes so defects elsewhere cannot directly cause scattering. Therefore, we expect only vacancies in the Cu-O planes to be pair breaking. Considerable circumstantial evidence supports this conclusion. A study of low energy electron radiation damage in YBCO found that both Cu and O defects suppress T_c, but did not observe any effect from Ba and Y displacements [3]. Comparison of substitution data with irradiation data suggests that defects in the planes are much more effective in reducing T_c than are defects in the chains [1]. Also, magnetic defects in the chains seem to have little effect on T_c [15]. Finally, recent resistance measurements on untwinned, single crystals provide direct evidence that defects on the planes rather than defects in the chains cause the T_c reductions observed [5]. Accordingly, we define the number of depairing scattering centers in YBCO to be $2n_{Cu}/3 + 4n_O/7$ where n_{Cu} and n_O are the total number of Cu and O vacancies computed, respectively. Similarly, in the other cuprate superconductors Cu and O vacancies in the planes are assumed to be produced in proportion to the stoichiometric fraction of Cu and O plane sites.

The initial number of defects created during irradiation is determined by the displacement scattering cross sections [$\sigma(E)$], which are well known, and by the displacement threshold energies (E_d) of the various atoms. Given E_d and $\sigma(E)$, the number of radiation-induced defects can be estimated with Monte Carlo programs such as TRIM [16] or by analytical calculations of the nonionizing energy loss (NIEL) [17] coupled with a model of defect production. TRIM was used to determine the number of defects produced by positive ion irradiations of YBCO. Analytical NIEL calculations with the Kinchen-Pease model were used to determine the number of defects produced in other irradiation experiments, and, in particular, for electron irradiation experiments.

Values of E_d for Cu and O are taken to be 15 and 10 eV, respectively [3], and $E_d = 20$ eV for the other atoms. The choice of Cu and O displacement energies is a bit unconventional, since most sources report $E_d \approx 20$ eV (or larger) for all atoms [3,18,19], but was made in order to facilitate comparison with the results of Legris *et al.*, whose data are reanalyzed in a later section of this text. However, displacement energies play only a small role in the present study because the defect number calculations are ultimately applied to experiments with incident MeV protons and other nuclei. The average recoil energy of primary knockon atoms that are generated by these particles is typically well above the displacement energy threshold, and exact values of E_d are not needed.

Some fraction of the vacancies initially produced is expected to immediately recombine with interstitials. This fraction is unknown, as there is very little data on recombination in materials as complex as the high-T_c superconductors. Therefore, we have not attempted to correct the number of defects for possible recombination. If some recombination is included in the calculation, the value of the scattering potentials determined below would increase.

Only the scattering potential remains to be determined. This can be done by comparing Eq. (4) to a set of data. Analysis of data from low-temperature (20 K) electron irradiations shows that the T_c shift produced in YBCO by a defect density of 1 Cu vacancy per cubic centimeter in the planes is 16×10^{-20} K [3]. Similarly, the T_c shift produced by a defect density of 1 O vacancy per cubic centimeter in the planes is about 6.5×10^{-20} K. The T_c shifts computed using both these values and our estimates of the numbers of defects produced are plotted against incident electron energy in Fig. 1 as a solid line. The measured T_c shifts are shown as data points. Comparing these values with Eqs. (2) and (3) we obtain

$$[2] \times 7 = 1 + 1/z_{\mathrm{O}}^2 \tag{5}$$

and

$$[2] \times 2.8 = 1 + 1/z_{\mathrm{Cu}}^2 , \tag{6}$$

where $z_{\mathrm{O(Cu)}} = \pi N(0) v_{\mathrm{O(Cu)}}$, as defined in Eq. (3), and where the factor [2] again applies only in the case of magnetic scattering. For the magnetic scattering case we find that $v_{\mathrm{O}} = 0.08$ eV cell volume and $v_{\mathrm{Cu}} = 0.13$ eV cell volume. For an anisotropic d-wave superconductor, we find $v_{\mathrm{O}} = 0.12$ eV cell volume and $v_{\mathrm{Cu}} = 0.22$ eV cell volume. In either case, the scattering potentials are comparable to typical magnetic scattering potentials in conventional superconductors, which are on the order of 0.2 eV cell volume [20]. The lower scattering potential of O defects compared to Cu defects is consistent with the fact that v is an integral over the scattering potential weighted by the k-space, electronic state occupation probabilities, and that O is twofold coordinated whereas Cu is fourfold coordinated in the planes [21].

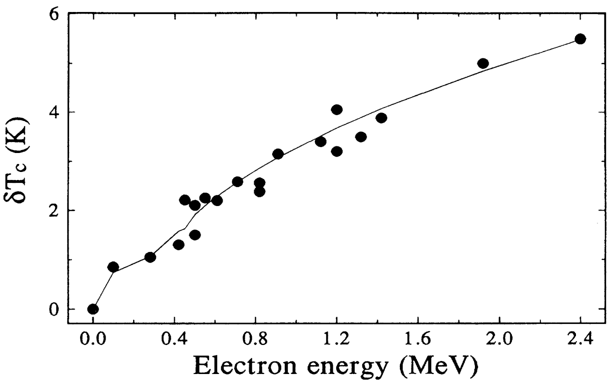

FIG. 1. The decrease in transition temperature produced by irradiation to a fluence of 10^{18} electrons/cm^2 vs electron energy. The solid line is calculated as discussed in the text. The points are data taken from Ref. [3].

The general applicability of the above results and Eq. (4) can now be tested by examining how well radiation-induced T_c shifts can be predicted for other experiments and incident particles. Experimentally determined values of $dT_c/d\Phi$ [$\equiv \delta T_c(\Phi)/\Phi$] are plotted in Fig. 2 versus computed values of $dT_c/d\Phi$ for electron and heavier ion irradiations of YBCO. From this figure it is clear that using the independently derived scattering potentials provides a good description of the damage produced by heavier ions despite much greater damage rates and supposedly dissimilar defect distributions produced by the heavier ions. The data include particles ranging from 2 to 100 MeV protons and heavier ions up to 12 MeV Si^{n+}. Fast neutrons have been excluded from consideration because irradiations typically take place at elevated temperatures (>300 °C) and often result in extended defects. Particles that cause nuclear tracks have also been excluded because the mechanism of atom displacement remains unknown.

Some of the data in Fig. 2 are taken from irradiations at room temperature since we have observed little correlation between the T_c shifts and irradiation temperatures below 300 K. Also shown in Fig. 2 are $dT_c/d\Phi$ values for LSCO, $\mathrm{Tl_2Ba_2CaCu_2O_8}$, and $\mathrm{Tl_2Ba_2Ca_2Cu_3O_{10}}$. The calculated values of δT_c were computed from Eqs. (2) and (3) using the appropriate partial density of states of a

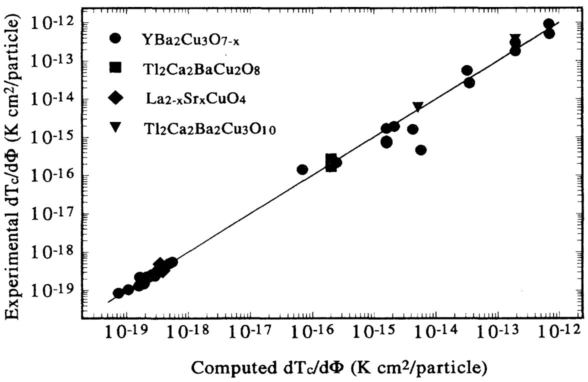

FIG. 2. Experimental vs computed values of $dT_c/d\Phi$ for a wide range of incident particles on YBCO and other high-T_c superconductors. Values of the scattering potentials are those deduced from electron irradiation data (Ref. [3]), and no new fitting parameters are used. The solid line is $dT_c/d\Phi$(expt.) = $dT_c/d\Phi$(theory).

plane for each material and the same scattering potentials (corrected for differing unit cell sizes) as determined for YBCO. It is seen that the scattering potential is roughly the same in all of these superconductors, as is expected of potentials determined by the local Cu-O plane structure. Within this context it is interesting to note that Vichery *et al.* find that $YBa_2Cu_3O_{7-x}$ becomes increasingly sensitive to displacement damage with increasing x [22]. This increased sensitivity of $YBa_2Cu_3O_{7-x}$ to radiation damage with increasing oxygen deficiency may be due to the fact that it is approaching a structural phase transition driven by the chain oxygen deficiency.

In summary, the radiation-induced reduction in T_c in the cuprates is quantitatively consistent with the standard pair breaking theory if all the vacancies formed in the Cu-O planes by particle irradiation are pair breaking scatterers and Cu vacancies are about twice as effective as O vacancies. This occurs regardless of whether the depairing originates from magnetic scattering or nonmagnetic scattering in highly anisotropic potentials. The strength of the scattering potential is about the same in all of the optimally doped cuprates and comparable to magnetic scattering potentials in conventional superconductors.

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