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A model of knock-out of oxygen by charged particle irradiation of Bi-2212

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Abstract. A model of knock-out of oxygen by charged particle (α and proton) irradiation of $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) is proposed on the basis of Monte Carlo TRIM calculations. In Bi-2212, the loosely bound excess oxygen is vulnerable to be displaced by particle irradiation. Binding energy and hence, displacement energy of this loosely bound excess oxygen is less compared to that of stoichiometric lattice bound oxygen and other atoms. The displaced or knocked out oxygen goes to pores or intergranular region and generates large pressure inside the sample. Because of porosity of the material, this displaced oxygen diffuses out and there is a net reduction of oxygen content of the sample. The irradiation induced oxygen knock-out is dominant in the bulk where nonionizing energy loss is maximum.

Keywords. Oxygen knock-out; Bi-2212; particle irradiation.

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1. Introduction

High energy charged particles interact with solids by elastic and inelastic processes [1,2]. Elastic or nuclear energy loss causes displacement of atoms. Inelastic or electronic energy loss manifests in ionization and excitation of atoms. In superconductors, it is the nonionizing energy loss (causing displacement of atoms) that plays a significant role in controlling physical properties like critical temperature, resistivity, etc. In conventional superconductors, point defects generated by radiation induced atomic displacements changes the density of states around Fermi surface, thereby causing depression of T_c [3,4]. In high T_c superconductors also, atomic displacements caused by nonionizing energy loss of incident particle control the change of T_c as a function of fluence [5,6]. For all cuprate superconductors, there is a universal relationship between rate of shift of T_c with fluence ϕ, i.e. $dT_c/d\phi$, and nonionizing energy loss (NIEL) of the incident particle over a wide range of energies [5–12]. The NIEL and hence atomic displacements can be ascertained by Monte Carlo simulation program TRIM (TRansport of Ions in Matter) developed by Biersack *et al* [13]. This program takes into account relative cross-sections for elastic and inelastic processes.

In multiatomic system, the total NIEL is given as $S = \Sigma f_i S_i$, where S_i is the NIEL for each atom and f_i its atomic weight fraction given as

$$f_i = x_i A_i / \Sigma x_i A_i,$$

where x_i is the stoichiometric number for the ith element, e.g. 8 for oxygen in $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) [6]. Hence, it is expected that in Bi-2212, NIEL and hence, displacement of oxygen induced by light charged particle irradiation will be significant.

Oxygen plays a significant role in controlling various physical properties like T_c, resistivity, etc. of high T_c cuprate superconductors (in particular Bi-2212) which are non-stoichiometric with respect to oxygen [14–17]. Bi-2212, based on layered perovskite structure, experiences a tensile stress in Bi–O (bismuth) layer due to small Bi^{3+} ion [17]. This tensile stress is relieved by accommodating extra oxygen in bismuth layer [17–19]. Thus, Bi-2212 is always prone to contain excess oxygen [20, 21]. Oxygen, being an electronegative atom serves as a source of hole to the conducting CuO_2 layer and changes carrier concentration. There is a relation between critical temperature T_c and the excess oxygen content in Bi-2212, which resembles a typical bell-shaped curve [22]. The extra nonstoichiometric oxygen is not strongly bound like other oxygen atoms. Its binding energy is very low and is vulnerable to be knocked out by particle irradiation.

We had earlier observed an increase in T_c by 20 MeV α-irradiation at a dose higher than $1 \times 10^{15}\,\alpha/cm^2$ on polycrystalline Bi-2212 overdoped with oxygen ($T_c = 65$ K) [23]. We investigated the irradiation at various doses starting from $1 \times 10^{13}\,\alpha/cm^2$. There was no appreciable increase in T_c up to $1 \times 10^{15}\,\alpha/cm^2$. The increase after $1 \times 10^{15}\,\alpha/cm^2$ was monotonic with dose and was presumed to be due to knock-out of oxygen. Annealing of the irradiated sample in oxygen reverted back to original T_c. Irradiation was carried on one surface of the sample. The range of 20 MeV α in Bi-2212 is $\sim 100\,\mu m$. So, in the sample of around 1 mm thickness (as used in earlier irradiation experiments), the damage did not propagate to much depth. Hence, bulk damage and change in oxygen content could not be ascertained by iodometry as the radiation induced oxygen knock-out could not occur in the bulk. To investigate the bulk damage, we adopted the following modifications: (i) Thickness of the sample was reduced from 1 mm to 0·5 mm. (ii) Energy of α was increased from 20 MeV to 40 MeV to have longer range and hence large depth of damage. (iii) Irradiation was carried out on both surfaces of the sample to obtain a fairly uniform bulk damage.

In this paper, we have analyzed oxygen knock-out from the polycrystalline Bi-2212 pellet caused by light charged particle irradiations, where interaction with oxygen is significant. In case of heavy ions, cross-section of interaction with other atoms and their NIEL will be significant. We have considered cases of 20 and 40 MeV α and also 15 MeV proton, which penetrates the sample of 0·5 mm (range of 15 MeV protons in Bi-2212 is $\sim 0{\cdot}8$ mm) and hence causes bulk damage. We have calculated oxygen vacancies generated by particle induced displacements with the help of the program TRIM-95 and the pressure developed due to the displaced oxygen. We have considered the displacement of loosely bound oxygen as these are vulnerable to be displaced more easily. We have then calculated the diffusion of the displaced oxygen through pores or, intergranular region thereby estimating the oxygen content for these particles at various doses. We have verified the results with oxygen content measured iodometrically for Bi-2212 pellets irradiated with 40 MeV α at various doses.

2. Experimental

Polycrystalline samples of Bi-2212 were prepared from nitrates of the respective elements (in nominal composition) by usual solid state reaction [24]. Excess oxygen content was assayed iodometrically by the method of Appleman *et al* [25]. Often, aerial oxidation of iodide in strong acid solution catalyzed by Cu(II) gives rise to erroneous results. We have eliminated it by holding Cu(II) as citrate. Acidity was adjusted to prevent aerial oxidation. Excess oxygen content of the sample was 0·204, i.e. it was in the overdoped region with respect to oxygen [22].

Samples were prepared in the form of pellets of 0·5 mm thickness. Critical temperature was measured resistively by usual 4-probe method using Lake Shore 120 constant current source and Keithley 181 digital nanovoltmeter. The current was typically 1 mA. $T_c(R=0)$ was around 73 K.

A few pellets were chosen for irradiation with 40 MeV α from variable energy cyclotron (VEC). They were irradiated from both sides. Defocussed beam was taken to guarantee uniformity of dose over the sample. Beam current was typically around 100 nA, i.e. $\sim 3 \times 10^{11}$ particles/sec. The area over which the beam was falling was $\sim 5\,cm^2$. Hence, the rate of the incoming particles was $\sim 6 \times 10^{10}/cm^2$/sec. The target assembly was cooled with flowing water at the back of the flange to minimize the heating effect due to particle irradiation. The temperature of the sample was monitored by a thermocouple and it was around 50°C (± 1°C). The whole assembly of the target and the flange was in vacuum in the order of $\sim 10^{-6}$ torr. The total doses employed on the pellets were 2×10^{15}, 4×10^{15}, 6×10^{15}, 8×10^{15} and $1 \times 10^{16}\,\alpha/cm^2$. The irradiated samples were characterized by XRD like the unirradiated one. Their T_c's were measured like the unirradiated sample.

3. Results and discussion

T_c and oxygen contents of the irradiated and unirradiated samples are given in table 1. The amount of error in iodometric estimation of oxygen contents is indicated in brackets. It is seen that T_c increases up to a certain dose. There is a correlation of $T_c(R=0)$ with excess oxygen content. From table 1, we observe that, oxygen content of the irradiated sample decreases with dose. There is a sharp drop in T_c for the dose of $8 \times 10^{15}\,\alpha/cm^2$ from that of $6 \times 10^{15}\,\alpha/cm^2$. This may be due to a large drop in excess oxygen content (0·06) in the dose of $8 \times 10^{15}\,\alpha/cm^2$. Excess oxygen content 0·06 corresponds to a much underdoped region and hence its T_c is much less compared to

Table 1. T_c and excess oxygen as a function of dose.

Dose (α/cm^2)	$T_c(R=0)$ (K)	Excess oxygen by iodometry
0	73·1	0·204(± 0·003)
2×10^{15}	74·3	0·191(± 0·002)
4×10^{15}	75·8	0·150(± 0·002)
6×10^{15}	76·3	0·102(± 0·002)
8×10^{15}	66·46	0·060(± 0·002)

the samples of other doses [22]. The behaviour of T_c with change in oxygen content is nearly consistent with the picture of Allgeier and Schilling [22]. The absence of one-to-one correspondence with Allgeier–Schilling picture may be due to some additional factors brought by radiation induced disorder. Displacements of other cations like Cu, Bi, etc. may also play a role. But obviously, oxygen knock-out with irradiation plays a major role.

4. Mechanism of oxygen knock-out

The decrease in oxygen content caused by knock-out of oxygen from the sample can be understood to occur through the following steps: (i) Appreciable oxygen vacancies are created by charged particle irradiation induced displacement of loosely bound oxygen of Bi-2212 at a dose higher than 1×10^{15} particles/cm^2. (ii) The displaced oxygen occupies pores and/or the intergranular region, which are energetically favourable to them and in this process generates pressure. (iii) These 'free' or labile oxygen molecules diffuse from pores to outside (of the sample) which is in vacuum. More porous the sample, more is the absorption or desorption of oxygen. We had earlier seen in the case of textured samples that with decrease of porosity, oxygen absorption decreases during annealing which causes a lower value of excess oxygen content [26]. In the synthesis of Bi-2212 through carbonate and nitrate routes, we observed that the carbonate route gave rise to porous sample and oxygen content was much higher which must have come by absorption of the same through pores during annealing stage. Also, excess oxygen in these porous samples is desorbed after heating to 800–850°C as seen by thermogravimetric analysis [27].

During estimation by iodometry, all the excess oxygen (i.e. those in the pores, intergranular region as well as those in Bi–O layer) are estimated. The net decrease of oxygen content will be the oxygen diffusing out of the pores and/or integranular region. Thus, one can get the net excess oxygen content of the irradiated samples by subtracting the oxygen diffused from excess oxygen content of the unirradiated sample.

We have calculated with the help of the simulation program TRIM (TRIM-95) the number of vacancies created by displacement of loosely bound oxygen due to charged particle irradiation. We have taken binding energy of this loosely bound oxygen as 0·073 eV, supported by experimentally observed ΔH value for the liberation of loosely bound oxygen from the compound as obtained from thermogravimetric analysis (TGA) and differential thermal analysis (DTA) [28]. The numbers for loosely bound oxygen atoms displaced per projectile ion for various doses are given in table 2. The displaced oxygen atoms with enough kinetic energy migrate to pores, interstitials, etc.

Table 2. Number of oxygen vacancies/ion and the partial pressure for various projectiles.

Particle	Loose O-vacancies/ion	Partial pressure (for dose 1×10^{15}/cm^2)	ΔG (kcal)
40 MeV α	110·19	0·6464 atm.	12·12
20 MeV α	77·18	0·4528 atm.	11·95
15 MeV proton	35·26	0·2068 atm.	11·47

We have estimated the partial pressure developed due to oxygen vacancies at a dose of 1×10^{15} particle/cm^2 for a typical sample of mass around 100 mg (total oxygen vacancies being obtained by multiplying the number of vacancies/ion by the dose).

It is seen from table 2 that the partial pressure generated by knocked out loose oxygen atoms is quite high. The free energy change associated with migration of oxygen from inside the sample to outside (or, the free energy difference between inside and outside the sample) is given as

$$\Delta G = RT \ln[\{(P_{O_2})\text{inside sample}\}/\{(P_{O_2})\text{outside sample}\}].$$

(P_{O_2}) outside sample is $\sim 10^{-6}$ torr as the target flange containing the sample during irradiation is under vacuum (of the order 10^{-6} torr). As see from table 2, the free energy change for 100 mg of the sample is $\sim$ 12·12 kcal in case of 40 MeV α-irradiation, which is quite enormous. This is the driving force for migration which is controlled by diffusion. The process of diffusion is controlled by porosity of the sample. The more porous a sample, the higher will be the rate of diffusion. The rate of oxygen atoms/ molecules diffusing out is proportional to the atoms/molecules of oxygen present in the pores.

The rate of net oxygen molecules accumulating at the pores as a result of diffusion is the rate of formation of oxygen through knock-out by charged particles minus the rate of diffusion of oxygen out of pores, which can be given by the following equation

$$d[N_0]/dt = I - D[N_0], \tag{1}$$

where N_0 is the number of oxygen molecules remaining in the pores, I is the rate of oxygen atoms formed per second. D is the diffusion coefficient depending on porosity of the sample. At the beam current of 100 nA of 40 MeV α, $I = 1{\cdot}205 \times 10^{14}$/sec for 0·35 cm^2.

Solution of this first order differential equation (1) yields, for any time t,

$$[N_0 e^{Dt}] = (I/D)(e^{Dt} - 1)$$

or

$$N_0 = (I/D)(1 - e^{-Dt}). \tag{2}$$

Diffusion coefficient of oxygen in this system D is given by following equation [29]

$$D(/\text{sec}) = 2{\cdot}618 \times 10^{-4} \exp[-(1{\cdot}3\,\text{kcal/mole})/RT].$$

The activation energy for diffusion of oxygen from pores is 1·3 kcal/mole as confirmed by thermogravimetric analysis of Bi-2212 [27]. The value of D at the temperature of the sample (around room temperature) $= 3 \times 10^{-5}$/sec.

From the solution of the diffusion equation (2), we can estimate the oxygen remaining in the pores. The total oxygen vacancies can be obtained from the dose. The difference between these two gives the amount diffused out or the net knocked out or, lost oxygen. Subtracting this from the excess oxygen content of the unirradiated sample will give the excess oxygen content for the irradiated sample. The values of excess oxygen thus obtained for 40 MeV, 20 MeV α and 15 MeV protons at various doses are given in table 3. The data for 40 MeV α can be compared with the experimental value obtained by iodometry given in table 1. Figure 1 shows the plots of oxygen contents (theoretically calculated from TRIM and experimentally verified by iodometry) as function of doses for 40 MeV α. It is seen that the two are in close agreement. Thus, it

Table 3. Excess oxygen values calculated from TRIM and diffusion for various particles.

Dose (per cm^2)	40 MeV α	20 MeV α	15 MeV proton
2×10^{15}	0·1854	0·1914	0·1982
4×10^{15}	0·1480	0·1648	0·1861
6×10^{15}	0·1034	0·1335	0·1718
8×10^{15}	0·0553	0·0990	0·1564

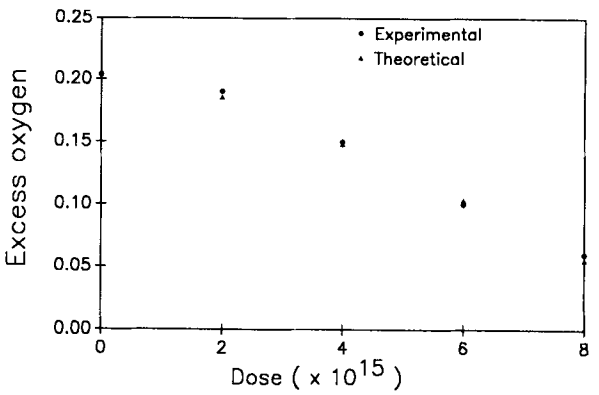

Figure 1. Oxygen contents (experimental and calculated from TRIM) as function of dose.

establishes the mechanism of knock-out of oxygen by charged particle irradiation followed by diffusion from pores. We are now carrying out experiments with 15 MeV proton and 20 MeV α for checking the knock-out of oxygen from bulk polycrystalline Bi-2212 and agreement with the results calculated from TRIM.

For other atoms, displacement energy is ~ 20 eV. TRIM calculation shows number of vacancies to be very less compared to that for loosely bound oxygen (of the order 5/ion). So, the damage due to displacements for other atoms is effective at a dose higher than 1×10^{16} particles/cm^2.

The vacancies of loose oxygen are created mostly in the bulk as little energy is lost at the surface due to ionization. As the projectile particle loses energy with depth, the nonionizing energy loss dominates causing displacement and the knock-out of oxygen. Hence, the knock-out of oxygen is a bulk rather than surface process.

5. Conclusion

We have calculated the knock-out of oxygen by 40 MeV α-irradiation from both sides on polycrystalline Bi-2212 overdoped with oxygen. This was measured experimentally by the difference in oxygen contents of irradiated and unirradiated samples estimated by iodometry. The calculations were done using the code TRIM which showed a large number of vacancies of loose excess oxygen created by α-irradiation. The loose oxygen

occupy pores and create enormous partial pressure as compared to outside vacuum and acts as a driving force for desorption of oxygen through diffusion. The reduction of oxygen content is due to the diffusion of this oxygen. We have calculated oxygen contents for irradiated samples for different cases – 15 MeV protons, 20 and 40 MeV α at various doses. There is fairly good agreement of the calculated results with the oxygen content measured iodometrically in the case of 40 MeV α. We are also carrying out studies with proton to see the knock-out of oxygen and validity of the above mentioned mechanism. The knock-out of oxygen is a bulk process.

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