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POINT DEFECTS AND OXYGEN DIFFUSION IN HIGH T_c SUPERCONDUCTORS*

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ABSTRACT

This paper presents a review of the oxygen tracer diffusion data on the high-temperature oxide superconductors, $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ which have been obtained in our laboratory. The SIMS (Secondary Ion Mass Spectrometry) technique has been used to determine the depth profile of ^{18}O from which the diffusion coefficient was calculated. Measurements in the La-Sr-Cu-O system have been performed for x = 0.1, 0.15 and 0.2 and the self-diffusion coefficient was found to decrease with increasing Sr substitution, a fact explained by a defect model in which oxygen vacancies are bound to Sr clusters. Recent measurements in polycrystals of Y-Ba-Cu-O were made in the temperature range of 300 to 600°C at an oxygen partial pressure of 1 atmosphere; they are given by $D = 9 \times 10^{-6} \exp -(0.89\ eV/kT)\ cm^2/s$.

I. INTRODUCTION

The relationship between the oxygen defect behavior in the cupric oxide perovskite-structure superconductors and the critical superconducting temperature, T_c, is important. The importance is indicated by the dependence of T_c on the deviation from stoichiometry. These compounds are nonstoichiometric oxides, containing oxygen vacancies. In the 37 K superconductor, $La_{2-x}Sr_xCuO_4$, T_c is a sensitive function of x [1], exhibiting a maximum for $x \approx 0.2$. In this case, oxygen vacancies are introduced for charge compensation as Sr^{+2} ions are substituted for La^{+3}. In the 90 K superconductor, $YBa_2Cu_3O_{7-\delta}$, T_c achieves a maximum for $\delta = 0$, but superconductivity is destroyed for $\delta = 0.6$. The dependence of T_c on stoichiometry is illustrated in Fig. 1, taken from reference [2]. Therefore, superconductivity is intimately linked to the oxygen vacancy concentration.

Measurements of oxygen tracer diffusion coefficient, D^*, can yield information concerning the motion of oxygen vacancies and the interactions with their environment that cannot be obtained

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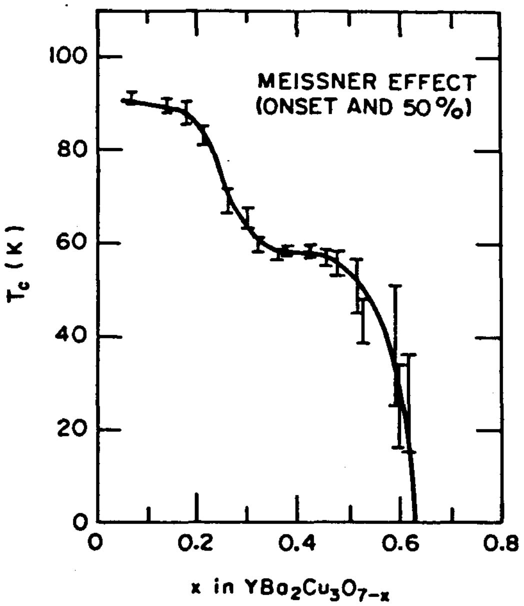

Fig. 1. Plot of T_c vs. deviation from stoichiometry for $YBa_2Cu_3O_{7-\delta}$ from Ref. [2].

by other techniques. However, such measurements are not trivial. Oxygen has no radioactive isotope and therefore the radioactive counting and sectioning technique which is the most commonly used method for measurement of D^* is not applicable. However, Secondary Ion Mass Spectrometry (SIMS) is a modern technique which has been successfully employed for measurements of oxygen diffusion in a wide-variety of ceramic oxides [3-6] and its application to the study of oxygen diffusion in the new high-temperature superconductors has been recently described [7].

This note will be divided into three sections. The first section covers the principal experimental aspects of the SIMS technique. The second section reviews the studies of oxygen diffusion in the $La_{2-x}Sr_xCuO_4$ system [8]. The results yield a fairly complete description of the behavior of oxygen ion vacancies in this compound. The final section deals with oxygen diffusion in the $YBa_2Cu_3O_{7-\delta}$ compound [9,10,11]. The tracer data are compared to results from recently acquired internal friction data [12].

II. EXPERIMENTAL PROCEDURES

Sample Preparation

A detailed description of the preparation of the $La_{2-x}Sr_xCuO_4$ polycrystalline samples has been presented in ref. [8]. Briefly, the $(La,Sr)_2CuO_4$ powder was prepared using the "liquid mix" technique by mixing appropriate quantities of cation nitrates with ethylene glycol and citric acid, heating to dryness, and calcining. Disks, formed by dry pressing the calcined powders, were heated at 100°C/h up to 400°C to burn out the binder, and fired between 1050 and 1100°C for at least 1 hr followed by a 6-12 h anneal in oxygen at 700°C. The diffusion samples, predominantly single-phase superconductors, have densities of approximately 92% of theoretical.

Specimens of $YBa_2Cu_3O_{7-\delta}$ were prepared from powders obtained from Rhone-Poulenc, Inc. Pellets were made by dry pressing the powder and the green pellets were sintered at 975°C for 4 h, cooled to 530°C at a rate of about 5°C/min., and then cooled to 400°C over a span of 15 h, following which the furnace was cooled to room temperature in about 3 h. All heat treatments were performed under flowing oxygen. The superconducting properties of all specimens were routinely characterized.

Diffusion specimens were prepared from the fired ceramics by polishing with diamond paste to 1/4 and 1 μm for the La-Sr-Cu-O and Y-Ba-Cu-O samples respectively. Polished samples of Y-Ba-Cu-O were then equilibrated at the diffusion temperature in one atmosphere of natural oxygen for times long compared to the diffusion anneal. This treatment insures that no chemical potential gradients exist during the diffusion anneal, a condition which is necessary to measure D^*, rather than the chemical diffusion coefficient. The samples were then encapsulated into quartz tubes which were backfilled with a mixture of 95% ^{18}O and 5% ^{16}O at a pressure which would yield an oxygen partial pressure of ≈1 atms at the diffusion temperature. It was found that ^{18}O ion implantation was necessary to overcome a sluggish exchange reaction characteristic of low temperatures for the Y-Ba-Cu-O material. Diffusion anneals were performed in a furnace whose temperature was controlled and measured to ±1°C.

SIMS Analyses

Concentration profiles were measured on the Cameca IMS 3f secondary ion mass spectrometer at the Center for Microanalysis of Materials at the University of Illinois at Urbana. Argon ions with 9.7 keV were used to sputter the La-based compound, while 17 keV Cs ions were used to sputter the Y-Ba-Cu-O material. Crater depths were measured with a profilometer.

The concentration of tracer for each channel was determined by subtracting the ^{18}O background and dividing by the sum of ^{16}O ^{18}O counts. The depth corresponding to each channel was assumed to be the total crater depth divided by the number of channels. The penetration profiles were fitted to theoretical solutions to the diffusion equation with the appropriate boundary conditions [8 and 10] in order to calculate D^* from a nonlinear least-squares regression analysis. In all cases, a fast-diffusion "tail", whose origin remains unknown, was present. A typical SIMS profile is shown in Fig. 2 in which the logarithm of counts is shown as a function of channel number (depth). In the cases of higher temperature anneals, the spot sputtering technique had to be modified because the penetration distances were too large to be easily uncovered by sputtering. In these cases a surface was ground at a small angle to the original surface and the profile was obtained by step scanning [7] along the inclined surface. The penetration distance was calculated from the position of the step scan and the measured angle.

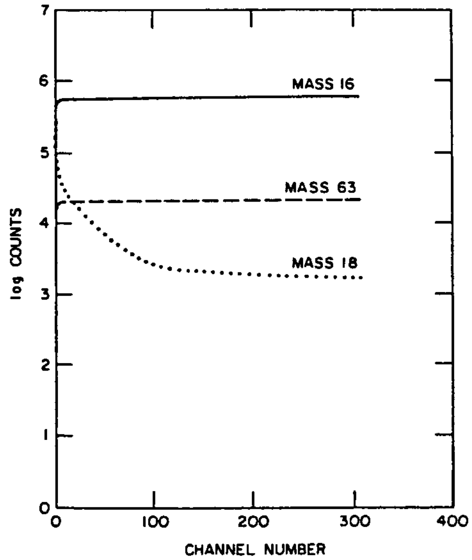

Fig. 2. SIMS data as plot of counts (log scale) vs. channel number for masses 16, 18 and 63 for $YBa_2Cu_3O_{7-\delta}$ annealed 0.5 h at 300°C.

Such an analysis obtained from a spot scan of a $La_{1.8}Sr_{0.2}CuO_4$ sample annealed for 2 h at 400°C is shown in Fig. 3. The criteria of goodness of fit, χ^2 is close to unity. A typical spot scan measured on a $YBa_2Cu_3O_{7-\delta}$ sample annealed for 0.5 h at 300°C is shown in Fig. 4. Line scans indicate more scatter,

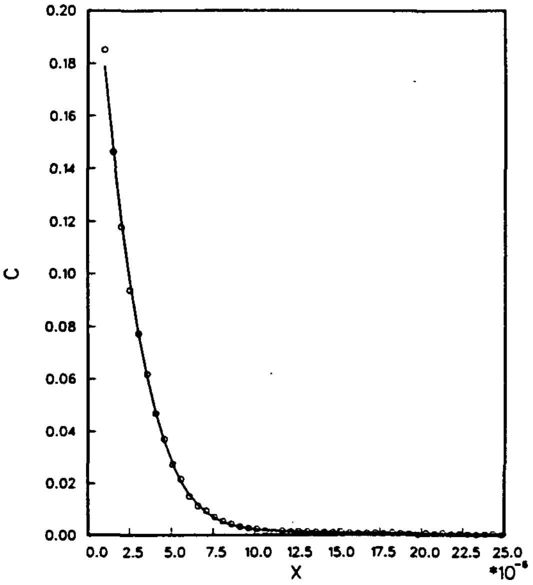

Fig. 3. Penetration plot (concentration of ^{18}O vs. distance) obtained by a spot scan for $La_{1.80}Sr_{0.20}CuO_4$ annealed for 2 h at 400°C.

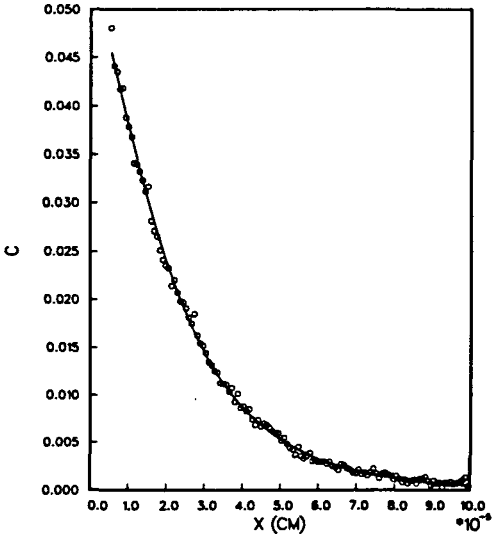

Fig. 4. Penetration plot obtained by a spot scan for $YBa_2Cu_3O_{7-\delta}$ annealed for 0.5 h at 300°C.

probably because of surface roughness, slight uncertainties in position and anisotropic diffusion [7]. However, as shown in Fig. 5, obtained for a $YBa_2Cu_3O_{7-\delta}$ sample annealed for 2 h at 600°C, the deviations about the calculated line are random.

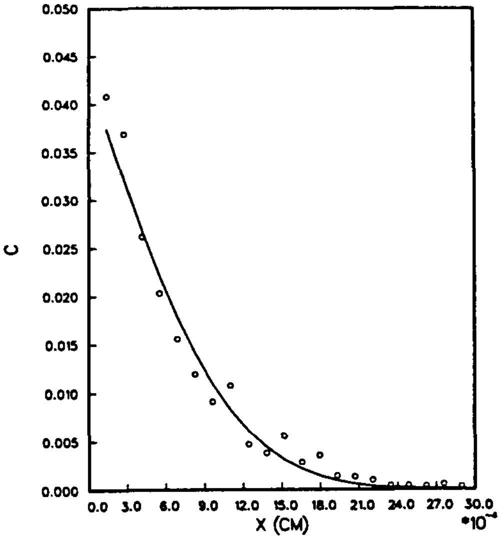

Fig. 5. Penetration plot obtained by a line scan for $YBa_2Cu_3O_{7-\delta}$ annealed for 2 h at 600°C.

III. TRACER DIFFUSION IN $La_{2-x}Sr_xCuO_4$

Arrhenius plots of the oxygen tracer diffusion coefficient for x = 0.10, 0.15 and 0.20 are shown in Fig. 6. The activation energy increases and the oxygen mobility decreases with increasing Sr additions. On the other hand, positron annihilation spectroscopy (PAS) by the Doppler broadening technique at room temperature on the same samples [13] indicated that significant positron trapping occurred for x = 0.20. That is, the vacancy concentration increased significantly as x increased from 0.15 to 0.20 (Fig. 7).

The PAS results are expected because substituting Sr^{+2} for La^{+3} will result in an increase in the oxygen vacancy concentration due to charge compensation. However, D^* might be expected to increase with increasing Sr concentration, rather than decrease. The trapping of positrons by anion vacancies, which are charged positively with respect to the lattice, was also unexpected. Furthermore, the sharp increase in the vacancy concentration and in the activation energy for diffusion occurred at approximately

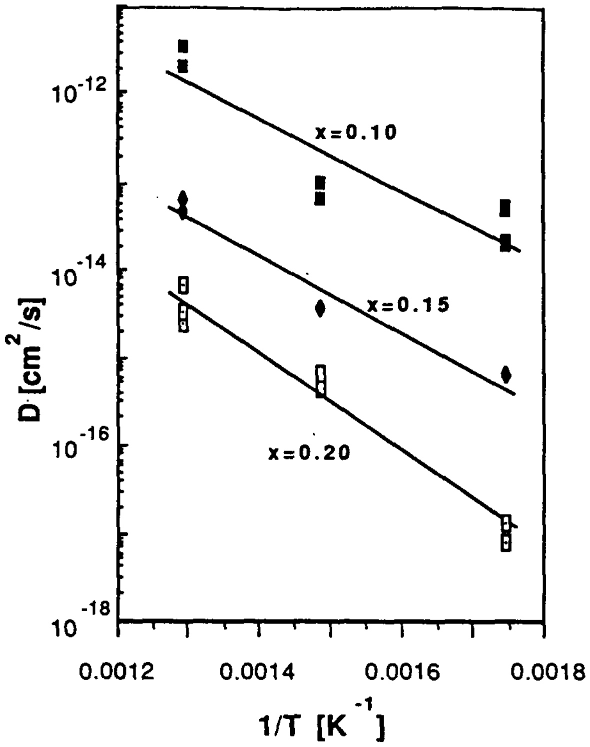

Fig. 6. Arrhenius plots for the tracer diffusion coefficient of oxygen in $La_{2-x}Sr_xCuO_4$ for x = 0.10, 0.15 and 0.20 from Ref. [8].

the same Sr concentration as did the maximum in T_c. These two apparent anomalies and their correlation were explained by the following model [13].

The Sr^{+2} ions are charged negatively with respect to the La^{+3} ions they replace. The excess negative charge of a single Sr^{+2} ion can be compensated by creation of an electron hole. Or the charges of two neighboring Sr^{+2} ions can be compensated by a neighboring oxygen ion vacancy, forming a cluster which immobilizes the vacancy. At low Sr^{+2} concentration, most of the Sr^{+2} ions are single, so the concentration of electron holes increases with increasing Sr additions, hence T_c increases. At a Sr^{+2} concentration of ≈0.2, the concentration of Sr^{+2} ion pairs, and hence, of oxygen ion vacancies, starts to increase rapidly, and the concentration of electron holes begins to decrease. Further additions of oxygen vacancies are likely to be tied up in clusters which slow down the motion of all oxygen ion vacancies so that the activation energy for oxygen diffusion increases. Since the superconducting properties are thought to be linked to the concentration of electron holes, T_c will

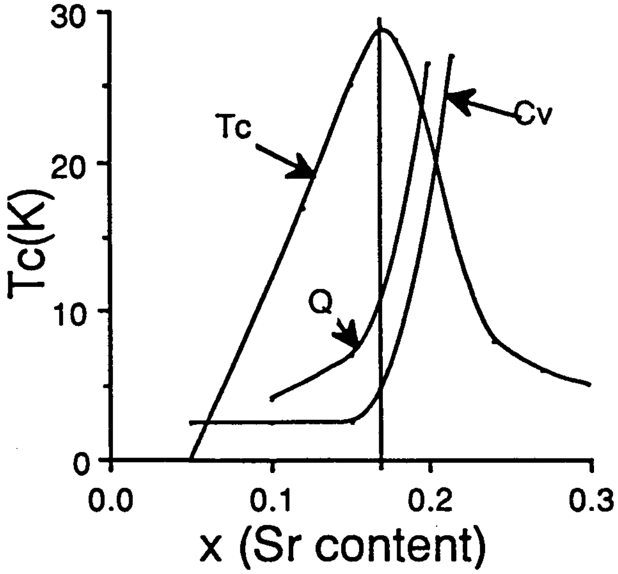

Fig. 7. Variation of the critical temperature T_c, the activation energy for oxygen diffusion Q, and the Doppler broadening lineshape parameter (related to the oxygen vacancy concentration) as a function of x in $La_{2-x}Sr_xCuO_4$ from Ref. [11].

decrease for x > 0.2. Also, the Sr^{+2} ions compensate for the positive charge of the oxygen ion vacancies; hence the latter can trap positrons. This model is completely analogous to the situation when fluorite-structured oxides are doped with divalent or trivalent cations; oxygen ion vacancies are introduced for charge compensation, and above a critical concentration of dopant, the oxygen ion conductivity decreases, and the activation energy for the diffusion of O^{-2} increases with increasing dopant concentration [14]. The temperature dependence of the thermopower and electrical conductivity in $La_{2-x}Ba_xCuO_4$ has been explained by a similar model [15].

IV. TRACER DIFFUSION IN $YBa_2Cu_3O_{7-\delta}$

An Arrhenius plot of the oxygen diffusion coefficients measured in the temperature range of 300-600°C is presented in Fig. 8. The experimental data from both spot and line scanning are represented as circles and can be described by:

$$D^* = (9 \pm 8) \times 10^{-6} \exp (0.89 \pm 0.05 \text{ eV}/kT) \text{ cm}^2\text{s}^{-1}.$$

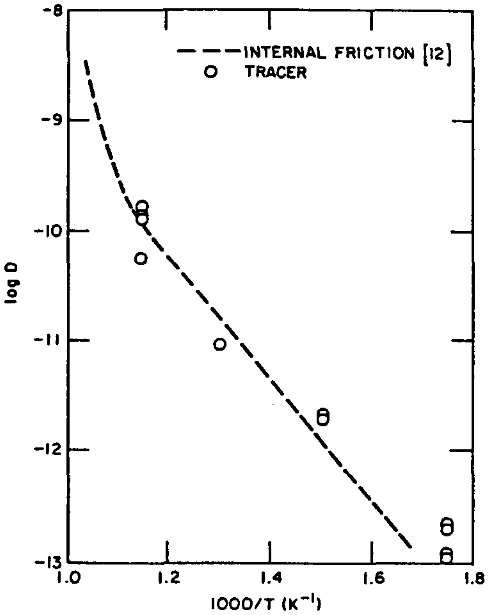

Fig. 8. Arrhenius plot of oxygen tracer diffusion coefficient shown as circles compared to values calculated from internal friction studies [12].

Since as much as 60% of the ^{16}O was exchanged by ^{18}O, we believe that D^* represents volume diffusion since short circuit paths such as grain or mosaic boundaries would probably not provide such a large exchange.

While there have been many measurements of the chemical diffusion coefficient (applicable to heat treatments in which a chemical potential gradient exists), there have been no other direct tracer diffusion measurements. However, Tallon and Staines [12] have measured the internal friction of $YBa_2Cu_3O_{7-\delta}$ at 7.8, 40 and 144 kHz from 300 to 1100 K as a function of oxygen partial pressure. At 40 kHz a relaxation peak occurs at ≈800 K which they ascribe to the hopping of oxygen in the basal plane. The peak can be described by a Debye relaxation from which a relaxation time is calculated. Tallon and Staines then calculate D^* from the relationship, $D^* = f\lambda^2/2d\tau$, where f is the correlation factor, assumed to be unity, λ is the jump distance between adjacent O1 and O5 sites, d is the dimensionality of the diffusion path (d = 2), and τ is the calculated relaxation time. The values of D^* calculated for an oxygen partial pressure of 0.8 are shown on Fig. 8 as the dotted line. The agreement between the two sets of measurements is excellent, but may be fortuitous. Among the principal concerns is that since f depends on the ordering of the oxygen ions in the basal plane, it is temperature dependent, varying from 1.0 at 600°C to ≈0.1 at 300°C [16,17]. Tallon and Staines also point out that there is no apparent peak broadening although some might be expected on the basic of oxygen density fluctuations.

It is clear that more experimental and theoretical efforts on $YBa_2Cu_3O_{7-\delta}$ will be required if the understanding of defects in this compound is to be elevated to the level obtained for the La-Sr-Cu-O compound. In particular, tracer measurements must be made at various oxygen partial pressures, a task which is currently in progress. Furthermore, it is expected that anion diffusion will be very anisotropic [7]. Therefore, measurements on crystals of various orientations are necessary. Despite, the lack of availability of large single crystals of $YBa_2Cu_3O_{7-\delta}$, such measurements are also in progress.

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