

In-plane oxygen diffusion in single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Abstract

We have determined the in-plane diffusion coefficient for nonstoichiometric oxygen in single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212). This was done by measuring the superconducting diamagnetic transition of the crystals by AC susceptometry, following repeated annealing of the crystals at a range of temperatures. We find that the chemical diffusion coefficient for oxygen in Bi-2212 is well described by $D_{ab}^* = (1.5_{-0.7}^{+1.4}) \times 10^{-3} \exp[-(1.23 \pm 0.06) \text{ eV}/k_{\text{B}}T] \text{ m}^2/\text{s}$.
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1. Introduction

As is the case with many HTS cuprates, the oxygen content in Bi-2212 can be varied, and directly influences the carrier concentration and in turn the physical properties of the material. The oxygen content (C) may be changed by annealing the material at fixed temperatures and oxygen partial pressures ($p\text{O}_2$), permitting it to be studied at closely spaced doping levels across the accessible region of the phase diagram. However, for pure Bi-2212 – i.e., without substituting cations such as Pb in place of Bi – accessing the heavily overdoped region requires annealing under high oxygen partial pressures and at comparatively low-temperatures. For experiments involving single crystals and a number of different hole concentrations, it is essential to know what annealing conditions will ensure oxygen homogeneity. Since the oxygen diffusion coefficient increases strongly with temperature, the necessary anneal times may easily be of the order of weeks, for large crystals and low-temperatures. In some cases, this may even deter-

mine which experiments are feasible and which are not. In practice, ensuring oxygen homogeneity requires an accurate estimate of the chemical diffusion rate D_{ab}^* in the ab -plane, since it is already well established that in Bi-2212, D_{ab}^* exceeds D_c^* by some orders of magnitude [1] and will therefore dominate any diffusion process.

Chemical and/or self-diffusion coefficients in HTS compounds have been estimated by a number of methods, including thermogravimetry [2], ultrasonic oscillator studies [3], and secondary ion mass spectrometry (SIMS) [1], usually by measuring the rate of ^{18}O diffusion into samples over a range of temperatures. However, for Bi-2212, these all involve measurements on polycrystalline samples. As a result, many estimates rely upon assumptions regarding the size and shape distribution of the grains [1,2]. Also, they may be affected by any unusual layer forming on the surface of grains as a result of exposure to air and water vapour, potentially forming a barrier to oxygen diffusion in or out of the superconductor. We therefore require a method which measures the diffusion in single crystals with dimensions of order mm. For the re-equilibration of such a sample, the quantity of greatest practical interest is the chemical diffusion coefficient D^* , since this describes hopping of ions in a sample that is temporarily out of chemical

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equilibrium, i.e., in the presence of a concentration gradient. The self-diffusion coefficient D corresponds to hopping in a system in chemical equilibrium, such as may be studied in an ^{18}O tracer-diffusion experiment. The two coefficients are related by the Darken equation [2]

$$D^* = D \cdot F \cdot h \quad (1)$$

where the Haven factor h will be approximately 1 (assuming that for Bi-2212 we may ignore any in-plane anisotropy) and the thermodynamic factor F depends on both the concentration of oxygen in the sample and the temperature. F may be estimated from the phase diagram for the oxygen content in the crystal as a function of the annealing conditions as follows [2]:

$$F = \frac{1}{2} \frac{d \ln \left(\frac{p\text{O}_2}{p^\circ\text{O}_2} \right)}{d \ln C} \bigg|_T \quad (2)$$

where $C = 8 + \delta(T_{\text{anneal}}, p\text{O}_2)$ is the total oxygen content in the crystal, $p\text{O}_2$ is the oxygen partial pressure in the atmosphere with which the material is in chemical equilibrium, and $p^\circ\text{O}_2$ is an arbitrary standard partial pressure. Since F may be large, the chemical diffusion coefficient may be several orders of magnitude larger than the self-diffusion coefficient.

In this experiment we will infer the oxygen content of the material from its T_c , since for Bi-2212, as with many HTS compounds, T_c is related to the hole concentration p by the well-known empirical function [4]

$$T_c = T_c^{\text{max}} \left[1 - 82.6(p - 0.16)^2 \right] \quad (3)$$

We may in turn obtain δ and C by assuming that $\delta = p + 0.08$ as implied by the thermogravimetry and resistivity measurements of Fujii et al. [5]. Any uncertainties in this result will have minimal effect on our values for F and D_{ab} , since the non-stoichiometric oxygen content δ is far less than the total oxygen content of the crystal. Similarly, the exact form of the relationship between T_c and p (and thus C) will have little effect on the values of D_{ab}^* deduced from our results.

Yang et al. [6] have performed c -axis resistivity measurements on single crystals with the temperature being swept over ranges from 70 to 856 K, thereby allowing the oxygen re-equilibration of the sample to be observed in real time. This yielded significantly different results for oxygen in- and out-diffusion, possibly implying the existence of a surface barrier layer.

However, measurements involving temperature sweeps necessarily pose difficulties of interpretation, since the diffusion coefficient is a strongly varying function of both temperature and oxygen concentration, and some form of deconvolution must be performed in order to extract the diffusion coefficient as a function of temperature. Also, it is unclear what effect the electrical contacts may have on the chemistry of the crystal at elevated temperature and thus on the diffusion coefficient. We note in passing that

resistivity measurements performed on sintered YBCO suggest that substituting small amounts of Zn for Cu greatly increases the oxygen diffusion coefficient [7]. In this work we therefore estimate D_{ab} by observing the change in the superconducting AC susceptibility signal of a single crystal after successive periods of annealing at various temperatures. We compare our results with those obtained by other methods, and also study the effects of Co impurities on the diffusion coefficient.

2. Methodology

Since the oxygen concentration significantly affects T_c , the oxygen content of the material – or at least changes therein – may be obtained with considerable precision via the measurement of the superconducting transition. If the oxygen level is inhomogeneous, then this will be visible as a broadening of the transition width.

Single crystals of Bi-2212 were grown by the travelling solvent floating zone method (TSFZ), using feed rods with a nominal stoichiometry of $\text{Bi}_{2.15}\text{Sr}_{1.85}\text{CaCu}_2\text{O}_{8+\delta}$. The stoichiometry of the resulting single crystals was found to be $\text{Bi}_{2.01}\text{Sr}_{1.82}\text{CaCu}_{2.03}\text{O}_{8.2}$ as determined by EPMA (performed with the assistance of Dr. Chris Hayward of the University of Cambridge Department of Earth Sciences). Crystals free of twins or visible defects were selected and cut to dimensions approximately $8 \times 1 \times 0.2$ mm, with the thinnest dimension being along the crystalline c -axis. The 8:1 length to width ratio ensured that the effects of oxygen diffusion into the ends of the crystal would be negligible, and that for analytical purposes the equilibration process could be regarded as one-dimensional diffusion into a flat plate along the short in-plane axis of the crystal (corresponding to the axis around 1 mm in length). For reasons mentioned above, c -axis diffusion into the crystal could be ignored.

The crystals were annealed in oxygen in a quartz tube furnace at 650 °C in flowing N5.0 grade O_2 for one week to ensure that oxygen homogeneity was achieved before starting the diffusion measurement. All anneals were performed with the crystals placed in small Au boats within a clean alumina boat. The crystals were then quenched by removing them from the furnace as quickly as possible and tipping them out of the boats on to a clean Cu block at room temperature.

The in-phase AC susceptibility of the crystal was then measured from 4.2 K to above T_c at a sweep rate of 1 K/min in an applied RMS field of 1G, at 333.3 Hz. The measurements were performed with \mathbf{H} parallel to the long in-plane axis of the crystal. This ensured that the superconducting transition – and any information it contained regarding the superfluid density – would be spread over the widest temperature range possible. For a homogeneous superconducting crystal, the average magnetisation (given by Eq. (10)) deviates significantly from its low-temperature limit only when $\lambda(T)$ becomes comparable to the width of

the crystal. This is more readily achieved when $\mathbf{H} // ab$, since $\lambda_c \gg \lambda_{ab}$ for Bi-2212.

The crystal was then re-annealed at 600 °C in O₂ to allow additional oxygen to diffuse into it, and the ACS curve re-measured. This was repeated until the shape of the superconducting transition in the ACS signal showed no further change, implying that the crystal had reached a new state of oxygen equilibrium. The anneal times were chosen such that after the n th anneal at 600 °C, the total anneal time at 600 °C was proportional to n^2 .

This process was repeated with successive anneals at 550 °C in O₂, then at 500 °C, at 450 °C, and finally at 400 °C. The annealing conditions were chosen such that at the start of the experiment the crystal was on the slightly overdoped side of the maximum value for T_c , and that T_c was always decreased, typically by a few Kelvin during each re-equilibration process. In this way, we could ensure that there would never be any normal region at the centre of the crystal being magnetically screened by a superconducting layer on the outside. If T_c were increased by a few K during each re-equilibration, then misleading results could be obtained. Also, our approach ensured that the oxygen content, and thus the thermodynamic factor, would never change significantly in the course of each re-equilibration. At temperatures above 600 °C, oxygen re-equilibration takes place in a matter of minutes, comparable to the time needed for the crystal to thermally equilibrate upon insertion into the furnace. Consequently, above 600 °C we may no longer assume that oxygen re-equilibration is effectively occurring at a fixed temperature, meaning that application of Eq. (4) may give systematic errors. On the other hand, at temperatures below 400 °C, re-equilibration for a crystal of this size becomes impractically slow for the purposes of this experiment, taking in excess of a week.

3. Results and interpretation

The solution for diffusion in one dimension into the flat plate extending from $+b/2$ to $-b/2$, shown in Fig. 1, is given by

$$C(x, D, t) = C_0 + (C_\infty - C_0) \times \left[1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-(2n+1)\pi^2 \frac{Dt}{b^2}} \cos \left[(2n+1) \frac{\pi x}{b} \right] \right] \quad (4)$$

where C_0 and C_∞ are respectively the initial oxygen concentration present in the crystal and the concentration at the surface (dictated by the annealing conditions), x is the distance from the centre of the crystal, D is the diffusion coefficient, and t is the annealing time [2].

Let us consider a highly anisotropic HTS crystal of the approximate dimensions $a \times b \times c$ described previously, with one comparatively long in-plane axis (hereafter referred to as the a -axis), and extending along the other in-plane axis (henceforth referred to as the b -axis) from $+b/2$ to $-b/2$. If a field $H_{z0} < H_{c1}$ is applied parallel to

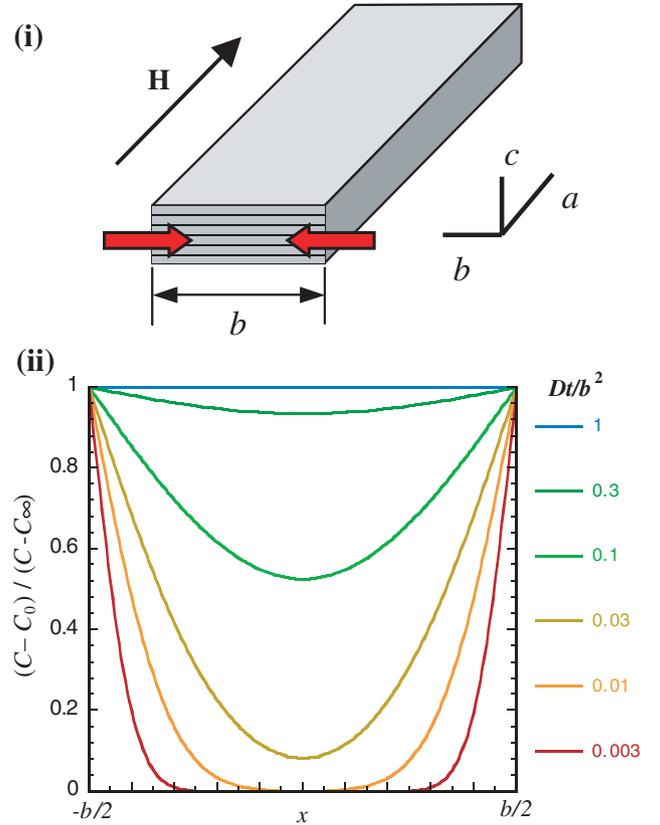


Fig. 1. (i) Assumed direction of diffusion of oxygen into crystal, as shown by red arrows. We assume that the diffusion process is dominated by diffusion in from the edges along the shortest in-plane axis of the crystal, which we shall refer to as the b -axis. (ii) Hole concentration as predicted by Eq. (4) for increasing values of Dt/b^2 . C_∞ is the oxygen concentration at the surface of the crystal, while C_0 is the initial concentration in the centre. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the a -axis such that the crystal is in the Meissner state, and the London penetration depths λ are such that $\lambda_c(T) \gg \lambda_{ab}(T)$, then B_z will penetrate into the crystal predominantly along the b -axis only. It follows from the London equations that

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B} \quad (5)$$

Assuming that λ_c is uniform and the crystal is sufficiently long such that we may ignore any effects at the ends, then inside the volume of the crystal Eq. (5) has solution

$$B_z(x) = \mu_0 H_{z0} \frac{\cosh(x/\lambda_c)}{\cosh(b/2\lambda_c)} \quad (6)$$

Hence the average magnetisation of the crystal (in the z -direction) is given by

$$m_z = \int_V (B_z - \mu_0 H_{z0}) d^3 \mathbf{r} \quad (7)$$

$$= -abc \mu_0 H_{z0} \left[1 - \frac{2\lambda_c}{b} \tanh \left(\frac{b}{2\lambda_c} \right) \right] \quad (8)$$

For b sufficiently large, then in the limit as $T \rightarrow 0$, $\lambda_c \ll b$, (consistent with $\chi_{av} \rightarrow -1$ as $T \rightarrow 0$) and Eq. (8) gives

$$m_z(T=0) = -abc\mu_0 H_{z0} \quad (9)$$

We may therefore write

$$-\chi_{av}(T) = \frac{m_z(T)}{m_z(0)} = 1 - \frac{2\lambda_c}{b} \tanh\left(\frac{b}{2\lambda_c}\right) \quad (10)$$

From Eq. (10) and the ACS signals for the crystal in the initial and final equilibrium states we can respectively extract $\lambda_c(T, C_0)$ and $\lambda_c(T, C_\infty)$.

We obtain C_0 and C_∞ via Eq. (3) and the crystal's critical temperatures at the start and end of the re-equilibration process. When the crystal is between these two equilibria in an intermediate, inhomogeneous doping state (i.e., $C_0 \leq C(x) \leq C_\infty$) we assume that we can linearly interpolate the penetration depth as

$$\begin{aligned} \frac{1}{\lambda_c^2[T/T_c(C), C]} &\approx \frac{1}{\lambda_c^2[T/T_c(C_0), C_0]} \\ &+ \frac{C - C_0}{C_\infty - C_0} \left(\frac{1}{\lambda_c^2[T/T_c(C_\infty), C_\infty]} \right. \\ &\left. - \frac{1}{\lambda_c^2[T/T_c(C_0), C_0]} \right) \end{aligned} \quad (11)$$

where $T_c(C)$ is once again calculated via Eq. (3). This is in fact a far less strong assumption than it might first appear, since all we effectively assume is that the superfluid density within a few Kelvin of T_c – the region of interest upon which our estimates of D_{ab}^* will be based – can be linearly interpolated between the curves measured for two closely spaced doping states.

Hence substituting Eq. (4) into Eq. (11) we obtain an expression $\lambda_c(C(x, D, t), T)$ for the position-dependent flux penetration depth of the inhomogeneous crystal at any given temperature. We must now solve

$$\frac{d^2}{dx^2} B_z(x) = \frac{1}{\lambda_c^2(x, T)} B_z(x) \quad (12)$$

numerically at each temperature (subject, as before, to the boundary condition $H_z(x = \pm b/2) = H_{z0}$) and integrate it with respect to x to generate a predicted curve for $[m_z(T)/m_z(0)](t, D, T)$. In this way, given a set of curves of $[m_z(T)/m_z(0)](t, T)$ measured for various anneal times t , a non-linear least-squares fit can be made to the observed data, with D_{ab}^* as the only free parameter.

Fig. 2 shows measured AC susceptibility curves near T_c (normalised by their low-temperature limits) for a crystal with dimensions $7.43 \times 1.09 \times 0.19$ mm ($a \times b \times c$) after successive re-equilibration anneals at 400 °C in 100% N5.0 grade O₂. Using the above non-linear optimisation procedure, we estimate the chemical diffusion coefficient $D_{ab}^*(673 \text{ K}) = (1.1 \pm 0.2) \times 10^{-12}$ m²/s, and the curves predicted from this value by the method described previ-

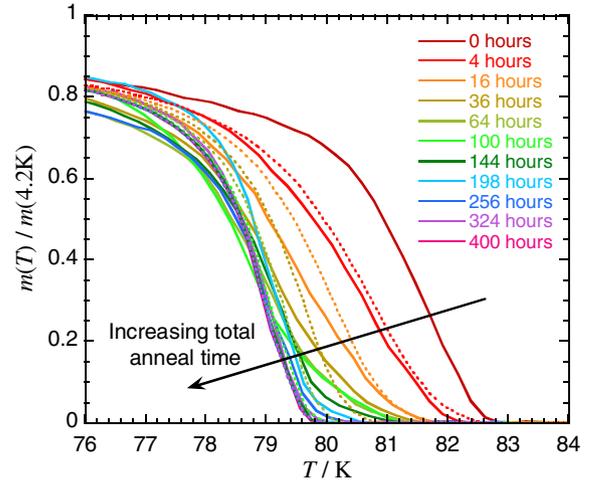


Fig. 2. Superconducting transition of overdoped single crystal, after successive anneals at 400 °C; as measured by AC susceptibility at 333.3 Hz, 1G RMS, with $H \perp c$. The susceptometer background signal has been corrected for. The legend shows total annealing times at 400 °C, while dotted lines are calculated curves for these annealing times, the crystal dimensions, and the fitted in-plane chemical diffusion coefficient $D_{ab}^*(673 \text{ K}) = (1.1 \pm 0.2) \times 10^{-12}$ m²/s. The agreement between the predicted and actual curves – especially near the start and towards the end of the re-equilibration process – is surprisingly good. At intermediate annealing times, re-equilibration effects at the ends of the crystal become more significant, and the assumptions outlined previously no longer hold.

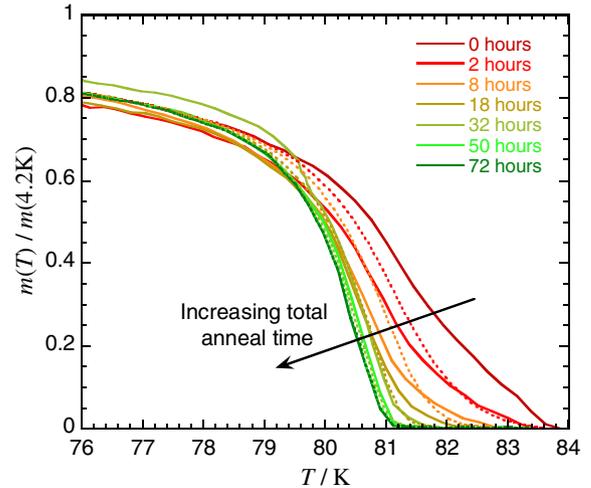


Fig. 3. AC susceptibility of the same single crystal as shown in Fig. 2, measured under the same conditions. This time, successive re-equilibration anneals were performed at 450 °C, and the estimated diffusion coefficient is $D_{ab}^*(723 \text{ K}) = (3.5 \pm 1) \times 10^{-12}$ m²/s.

ously are shown dotted. Fig. 3 shows the equivalent data and fits for re-equilibration of the crystal at 450 °C.

Our results for the range of temperatures investigated by this method are summarised in Table 2, together with estimates of the thermodynamic factor F obtained from the phase diagram for $C(T, pO_2)$ shown in Fig. 4 using Eq. (2). The greatest contribution to the uncertainty in the estimates for the self-diffusion coefficient D_{ab} is the uncertainty in the estimates for F . It is difficult to reduce this without measuring T_c for an impractically large number of different

Table 1

Values of T_c measured by AC susceptometry as described previously, and values of p obtained using Eq. (3) for the annealing conditions investigated in this work

T (°C)	pO_2 (bar)	T_c (K)	p
400	1	79.5	0.1913
400	0.0001	84.3	0.1775
450	1	81.0	0.1877
450	0.2	82.5	0.1877
450	0.002	85.0	0.1745
450	0.0001	85.2	0.1735
500	1	82.4	0.1840
500	0.2	84.3	0.1775
500	0.002	86.3	0.1653
500	0.0001	85.9	0.1508
550	1	84.0	0.1787
550	0.2	84.7	0.1759
550	0.002	86.3	0.1547
550	0.0001	85.9	0.1508
600	1	84.8	0.1754
600	0.2	86.5	0.1600
600	0.002	84.7	0.1441
600	0.0001	84.0	0.1413
650	1	85.1	0.1740
650	0.2	84.6	0.1437
650	0.002	82.8	0.1325
650	0.0001	81.1	0.1325
700	1	85.6	0.1712
700	0.2	82.7	0.1370
700	0.002	82.2	0.1355
700	0.0001	79.6	0.1289

The various oxygen partial pressures were achieved using mixtures of O_2 in N_2 at 1 bar. The values listed in this table were all measured on the same crystal. We find that measurements of T_c made on crystals taken from the top 2/3 of a TSFZ growth rod and then annealed under the same conditions agree to within errors. These values for T_c also closely agree with measurements made on polycrystalline samples annealed under the same conditions and quenched into liquid nitrogen.

Table 2

Estimated values for chemical diffusion coefficient implied by re-equilibration experiments in 100% O_2 , values for the thermodynamic factor F at $pO_2 = 1$ bar inferred from Fig. 4, and corresponding estimates for the self-diffusion coefficient

T (°C)	Chemical diffusion coefficient D_{ab}^* (m^2/s)	F	Self-diffusion coefficient D_{ab} (m^2/s) ($=D_{ab}^*/F$)
400	$(1.1 \pm 0.2) \times 10^{-12}$	2011.8	$(5.5 \pm 1.0) \times 10^{-16}$
450	$(3.5 \pm 1) \times 10^{-12}$	1609.4	$(2.2 \pm 0.6) \times 10^{-15}$
500	$(1.5 \pm 0.6) \times 10^{-11}$	1005.9	$(1.5 \pm 0.6) \times 10^{-14}$
550	$(5.6 \pm 3) \times 10^{-11}$	714.72	$(7.8 \pm 4) \times 10^{-14}$
600	$(1.1 \pm 0.5) \times 10^{-10}$	423.53	$(2.6 \pm 1.4) \times 10^{-13}$
650		217.49	
700		191.60	

annealing conditions. Such a large variation in F over the region investigated – nearly an order of magnitude – may seem surprising, but Conder et al. measure a variation in F more than twice as large in YBCO [2]. Since the chemical diffusion coefficient is the parameter of greatest interest for the purposes of this project, we calculate the implied self-diffusion coefficient primarily in order to compare our results with those obtained by other methods, especially those obtained in [1].

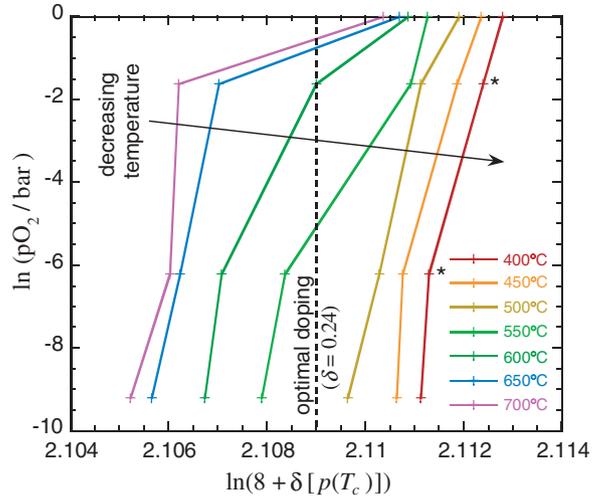


Fig. 4. Map of crystal oxygen content as inferred from measurements of T_c by AC susceptometry for various (T, pO_2) annealing conditions, using data taken from Table 1. The crystal used was the same as that used for the estimates of the chemical diffusion coefficient. The thermodynamic factor F at any given point in (T, pO_2) -space may be calculated from the slope of the isotherms. Due to the extreme length of time necessary to equilibrate the crystal at 400 °C, the two points marked with the asterisk are extrapolations from the remainder of the points measured for pO_2 of 0.2 bar and 0.002 bar. Note the region centred at around 600 °C and 0.2 bar in which the crystal stays close to optimal doping over a large region of (T, pO_2) -space. We therefore estimate $F(T = 550$ °C, $pO_2 = 1$ bar) by interpolating $F(600$ °C) and $F(500$ °C), since the value implied above by the 550 °C isotherm is clearly non-physical.

Similarly, we have made a linear least-squares fit to our data for the chemical diffusion coefficient $D_{ab}^*(T)$ (even though it is not strictly valid to do this, since F is a strongly varying function of T) to permit direct comparison with other works in which only D_{ab}^* has been estimated. We obtain

$$D_{ab}^* = (1.5_{-0.7}^{+1.4}) \times 10^{-3} \times \exp[-(1.23 \pm 0.06) \text{ eV}/k_B T] m^2/s \quad (13)$$

shown by the dotted line in Fig. 5. Yang et al. [6] have obtained $D_{ab}^*(T)$ by measuring the change in the c -axis resistivity at constant temperature of a single crystal which had been brought out of equilibrium with the atmosphere in which it was annealed by thermal cycling. They estimated the chemical diffusion coefficient to be

$$D_{ab}^* = 6 \times 10^3 \exp[-2.20 \text{ eV}/k_B T] m^2/s \quad (14)$$

McKernan and Zettl [8] have performed in-diffusion estimates, obtaining

$$D_{ab}^* = 1.17 \times 10^{-3} \exp[-1.16 \text{ eV}/k_B T] m^2/s \quad (15)$$

This was also obtained by measuring the resistivity of a single crystal, but by keeping the temperature constant while measuring the change in the ab -plane resistivity following switching the atmosphere from Ar to O_2 . (Note that while these two measurements estimated different hopping energies, the observed diffusion coefficients themselves were of

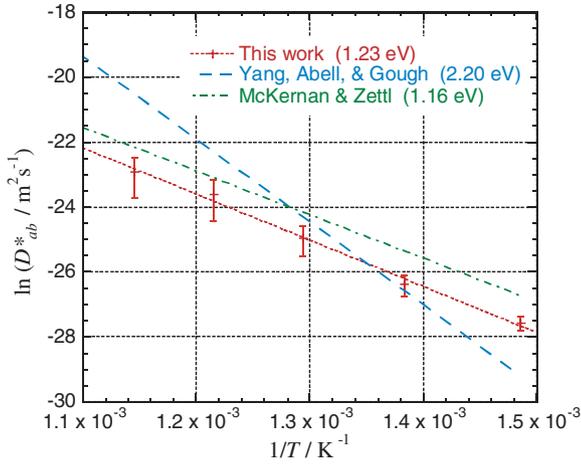


Fig. 5. Arrhenius plot of in-plane chemical diffusion coefficient. The dotted line is a least-squares fit to the points listed in Table 2. The dashed and dot-dashed lines are respectively estimates made by Yang et al. [6] and McKernan and Zettl [8].

similar magnitude over the temperature range studied, accounting for the difference of several orders of magnitude in the prefactors.) Both of these methods may introduce systematic errors, since in the latter approach the oxygen content and thus the thermodynamic factor will change dramatically during the course of the re-equilibration, and in the first case the initial oxygen distribution in the sample is unclear. The three estimates are plotted in Fig. 5 for comparison. The agreement between our ACS-derived results and the estimates of McKernan and Zettl derived from the resistivity (particularly with regard to the hopping energy, where the agreement is within errors) is remarkable, especially considering that the two sets of estimates were obtained by completely different methods.

From our estimates of $D_{ab}^*(T)$ and $F(T, pO_2 = 1 \text{ bar})$, we may extract an estimate for the oxygen self-diffusion coefficient $D_{ab}(T)$, obtaining

$$D_{ab} = (4.5^{+4.0}_{-3.0}) \times 10^{-4} \times \exp[-(1.60 \pm 0.09) \text{ eV}/k_B T] \text{ m}^2/\text{s} \quad (16)$$

Runde [1] estimated the self-diffusion coefficient directly by performing ^{18}O tracer-diffusion measurements upon Bi-2212 polycrystalline samples (using SIMS) which implied

$$D_{ab} = (1.7^{+1.5}_{-0.8}) \times 10^{-9} \times \exp[-(0.93 \pm 0.04) \text{ eV}/k_B T] \text{ m}^2/\text{s} \quad (17)$$

The two estimates are plotted in Fig. 6 for comparison.

4. Conclusions

The good agreement between our results and those estimated by *in situ* resistivity measurements suggests that any systematic errors in our estimates of the chemical diffusion coefficient D_{ab}^* – or indeed those of McKernan and Zettl – are unlikely to be significant. Our extraction of the

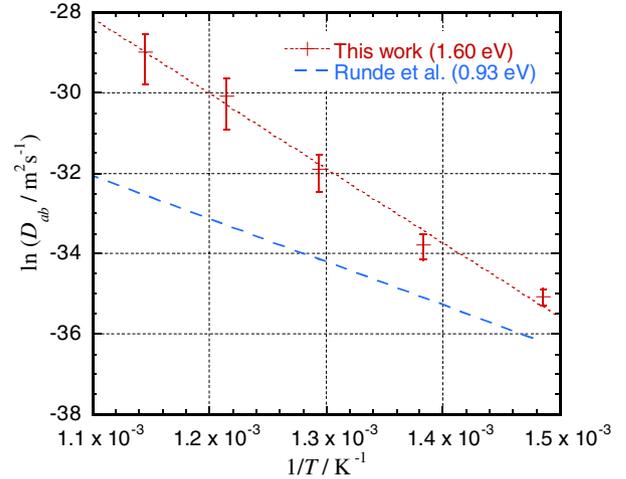


Fig. 6. Arrhenius plot for estimate of in-plane self-diffusion coefficient. The dotted line is the fit to the points in this work, while the dashed line is that fitted by Runde et al. to ^{18}O tracer-diffusion measurements.

self-diffusion coefficient is likely to be more problematic due to the uncertainty in estimating the thermodynamic factor F . We also note that our estimate of D_{ab} corresponds to diffusion via the fastest possible route – probably along the BiO planes – since that is all that is necessary to alter the superconducting properties, whereas tracer-diffusion measurements will represent an average across all possible diffusion routes by which ^{18}O may replace ^{16}O . This explanation may account for the systematically lower tracer-diffusion estimate obtained by Runde [1] for D_{ab} at all temperatures. However, it cannot account for the lower hopping energy estimated by tracer-diffusion, unless the averaging process systematically invalidates the fitting procedure of ^{18}O concentration versus diffusion depth performed in [1]. Grain-boundary effects in the polycrystalline samples used in [1] may influence the results also.

In any case, the parameter of greatest interest for equilibrating single crystals is D_{ab}^* , and the agreement between our results and those obtained by different methods gives us reason to trust them. Comparison between the annealing times after which no further systematic change in the ACS signal could be observed, and the estimates for D_{ab}^* obtained from explicitly fitting the data, suggests that the crystal will be equilibrated when the diffusion length $\sqrt{D_{ab}^* t}$ is equal to at least three times the maximum distance that the oxygen must diffuse. In practice, this will be the shortest in-plane distance from the edge of the crystal to the centre. The exact form of $T_c(p)$ is in general unknown for impurity-substituted Bi-2212, making it difficult to apply the above analysis to impurity-substituted crystals. However, we have investigated the annealing times necessary to achieve no further change in T_c for TSFZ-grown Bi-2212 crystals in which 2% of the Cu atoms have been substituted with cobalt, cut to the same dimensions as the unsubstituted crystals studied above. The necessary anneal

times are nearly identical to those for the unsubstituted crystals, indicating that impurity substitution at this level has no significant effect on D_{ab} .

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