Site–planar effect in oxygen isotope exchange in the $YBa_2Cu_3O_{7-\delta}$ system

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Oxygen isotope exchange between a gas phase and a $YBa_2Cu_3O_{7-\delta}$ crystal can pass through several stages. This effect is observed during isochronous annealings of a sample. It stems from the presence of sites and planes of different types in the crystal lattice. The site–planar effect observed here might be utilized to study the mechanism for the diffusion of oxygen atoms and also to synthesize crystals with given isotope compositions in the various sites of the oxygen sublattice.

The oxygen atoms in the crystal lattices of high-T_c superconductors with a quasiplanar structure occupy several types of equilibrium sites, which are grouped in certain planes. In the compound $YBa_2Cu_3O_{7-\delta}$, for example, there are the O1 and O5 sites in $CuO_{1-\delta}$ planes, the O4 sites in BaO planes, and the O2 and O3 sites in CuO_2 planes.[1] If a crystal synthesized in the natural mixture of oxygen isotopes is placed in an atmosphere enriched in the isotope ^{18}O at a sufficiently high temperature, there will be a progressive replacement of ^{16}O atoms by ^{18}O atoms. The kinetics of this isotope exchange may differ substantially from one equilibrium site to another. Evidence for this suggestion comes from, in particular, the pronounced anisotropy of the oxygen diffusion in the yttrium[1] and bismuth[2,3] superconductors. If the properties of the crystal which govern the mobility of the oxygen atoms satisfy certain relations, there may be cases in which ^{18}O atoms occupy sites or planes of only a certain type in the course of isotope exchange. To the best of our knowledge, there is no information in the literature on the occurrence of such planar, site, or site–planar effects. The detection and study of such effects would put us in a better position to obtain information on the mechanism for the diffusion of oxygen atoms. Such effects might also be utilized to obtain information on high-T_c superconductors with special properties.

In this letter we are reporting a study in this direction by a method of isochronous annealings. According to the literature, this method is widely used to study the behavior of nonequilibrium point defects in solids.[4] In these experiments, one studies the concentration of defects as a function of the annealing temperature, $C(T)$. A plot in the coordinates $\partial C/\partial T$, T has one or several peaks corresponding to the annealing out of defects. Each peak is localized in a narrow temperature interval, no more than 20–30 °C wide. The physical reasons for this behavior are extremely general. At low temperatures the derivative $\partial C/\partial T$ is small because the defect migration velocity is low. This derivative is also small at high temperatures, in this case because essentially all the defects have disappeared near the characteristic temperature. One might suggest an analogy between the processes involved in the annealing out of nonequilibrium point defects in crystals, on the one hand, and oxygen isotope exchange in the system of a high-T_c superconductor and a gas, on the other.

In the present experiments we used a $YBa_2Cu_3O_{7-\delta}$ ceramic with a density of 70% of the theoretical value, a grain size of about 10 μm, a superconducting transition temperature of 93 K, and a transition width of less than 1 K. The reason for the use of low-density samples is that gaseous oxygen covers each crystallite from all sides during an annealing, so the boundary conditions correspond to the diffusion of ^{18}O atoms into a sample of finite dimensions. The annealings were carried out in a quartz tube in oxygen enriched to $\gamma=0.8$ in the isotope ^{18}O at a pressure of 1 atm. The isotopic composition of the gas phase was monitored in some special experiments; it was found that this composition does not change during an annealing. As the annealing temperature was raised, we increased the pressure of the gas phase in order to keep the total number of oxygen atoms in the samples constant.[5] Unfortunately, the capabilities of our apparatus were such that we could not raise the pressure much above 1 atm, and the isotope exchanged occurred in a situation with driving forces. In other words, the oxygen atoms underwent something less than a completely random walk in the crystal. For the $YBa_2Cu_3O_{7-\delta}$ system at 1 atm, this deviation from ideal conditions could hardly be significant.[6] Nevertheless, in interpreting the results we must bear in mind the significant increase in the oxygen deficiency δ in a $CuO_{1-\delta}$ plane as the annealing temperature is raised.

The duration of the isothermal holds in our experiments was 4 h. The temperature of each annealing was 20 °C above the temperature of the previous annealing. The samples were cooled to room temperature between annealings. The cooling time was $\sim$1 min; the time taken to reach the annealing temperature was $\sim$10 min. The temperature was measured within ± 1 °C by a Chromel–Alumel thermocouple. Profiles of the ^{18}O concentration down to a depth $\sim$1.5 μm in the sample were measured after each isothermal hold by a nuclear microanalysis method using the reaction $^{18}O(p,\alpha)^{15}N$. The energy of the protons of the primary beam was 762 keV. The mean square error was about 10% in the measurement at low concentrations, and about 3% at high concentrations.

The experimental data in Fig. 1 correspond to a depth of about 0.15 μm in a sample. The particular depth is not important in this case, since there was essentially no gradient of the ^{18}O concentration down to a depth of 1.5 μm under these annealing conditions. We clearly see four isochronous-annealing peaks. The ^{18}O concentrations C_i reached at the end of these peaks are 11.4, 33.7, 61.0, and 74.0 at.%. The areas under the peaks are, in units of $\Delta C_i/\gamma$, 14.2, 27.9, 34.1, and 16.3 at.%, respectively. By way of comparison, the concentrations (X_i) of oxygen atoms in the sites of the oxygen sublattice of $YBa_2Cu_3O_{7-\delta}$ are $14.28(1-\delta)$ at.% in O1 (O5) sites, 28.57 at.% in O2 sites, 28.57 at.% in O3 sites, and 28.57 at.% in O4 sites. A concentration of 100% means that all the sites in the oxygen sublattice are filled.

Comparison of the X_i and $\Delta C_i/\gamma$ values implies that O1 (O5) sites in the $CuO_{1-\delta}$ plane are the first to be filled. We tend to believe that O4 sites are the next to

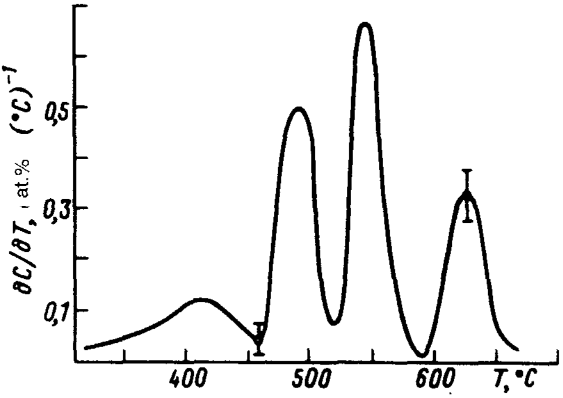

FIG. 1. Isochronous-annealing peaks.

be filled, since they are geometrically closer to the O1 and O5 sites than the O2 and O3 sites are. The results on $\Delta C_i/\gamma$ for the third and fourth peaks were unexpected. A small amount (a few percent) of the orthorhombic phase has apparently converted into the tetragonal phase at the temperatures corresponding to the third peak; in this tetragonal phase the ^{18}O atoms occupy both types of sites in the CuO_2 plane. Since the lattice constant in the basal plane of the tetragonal phase is considerably closer to the lattice constant along the *b* axis in the orthorhombic phase, it is assumed that the third peak corresponds to a replacement of oxygen in O3 sites by the ^{18}O atoms. The total area under the peaks, $\Sigma\Delta C_i/\gamma$, is a few percent less than 100%. This result is attributed to the oxygen deficiency δ at the pressure of 1 atm. This effect can be classified as a site–planar effect. The observation of this effect may have some important implications. Since the peaks are clearly separated, we can use methods developed for an isochronous-annealing study to measure the activation energies for each elementary process characterizing the migration of atoms in the lattice of the superconductor. This cannot be done by the conventional methods for studying diffusion. There is the possibility that the capability to synthesize crystals with an isotope composition controllable by site and by plane in the lattice, will prove useful for research on the nature of superconductivity.

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