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Oxygen-vacancy behavior in $La_{2-x}Sr_xCuO_{4-y}$ by positron annihilation and oxygen diffusion

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Oxygen-diffusion and positron-annihilation results for $La_{2-x}Sr_xCuO_{4-y}$ compounds are reported. A qualitative explanation of the observed results is given on the basis of a model in which the oxygen-vacancy concentration in $La_{2-x}Sr_xCuO_{4-y}$ is determined by Sr^{2+} ion clustering on the La sublattice. This model also leads to a maximum in the Cu^{3+} ion concentration as a function of the Sr^{2+} ion concentration.

Oxygen vacancies are thought to play a key role in the appearance or disappearance of superconductivity in both the $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-\delta}$ compounds. In the former, oxygen ion vacancies can compensate for the charge introduced by doping with Sr^{2+} ions, which occupy La^{3+} sites. Charge compensation for doping with Sr^{2+} can also be accomplished by oxidation of Cu^{2+} to Cu^{3+}. This paper reports a study of oxygen-vacancy behavior in $La_{2-x}Sr_xCuO_{4-y}$ by measurements of positron annihilation spectroscopy (PAS) and oxygen diffusion; it is suggested that the oxygen-vacancy behavior is related to Sr^{2+} ion clustering.

The samples were prepared by cold-pressing and sintering powders prepared by solid-state reactions. The diffusion samples ($x=0.15$ and 0.20) were predominantly single phase, and both were superconducting. The density was approximately 92% of theoretical; the porosity was closed and more widely spaced than the diffusion distance. The grain distribution was bimodal; angular grains 10–20 μm long with an aspect ratio of about 5, and grains about 100 μm long with varying aspect ratios. For the diffusion measurements,[1] the samples were polished, annealed to remove the damage caused by polishing, and annealed in quartz tubes backfilled with ^{18}O at a pressure of about 1 atm at the annealing temperature. The ^{18}O penetration profiles were measured using a Cameca IMS 3*f* secondary-ion-mass spectrometer (SIMS).[2] The data were fitted to a solution of the diffusion equation for an exchange reaction controlled by first-order kinetics as the surface boundary condition,[3] plus a grain-boundary-type term to account for a small "tail."

The diffusion coefficients for both $x=0.15$ and $x=0.20$ are plotted in Fig. 1 in coordinates corresponding to the standard Arrhenius form $D=D_0\exp(-Q/RT)$. The least-squares values for the parameters are for $x=0.15$, activation energy $Q=81\pm11$ kJ/mol, preexponential $D_0=2\times10^{-8}$ cm^2s^{-1}; for $x=0.20$, $Q=109\pm12$ kJ/mol, $D_0=1\times10^{-7}$ cm^2s^{-1}. The uncertainties in D_0 are a factor of 8. The important observation is that oxygen diffusion occurs more rapidly for $x=0.15$ than for $x=0.20$ at all temperatures in this range, and that this is because the activation energies are significantly different.

The PAS was carried out at room temperature with the Doppler broadening technique.[4] The instrument was stabilized using the ^{103}Ru isotope.[5] The line-shape parameter was measured for samples with $x=0.05$, 0.10, 0.15, and 0.20, where the 0.15 and 0.20 samples are the same as those used for the diffusion measurements. The results are shown in Fig. 2 and indicate that for $x=0.20$ a significant positron trapping takes place. The change in the line-shape parameter is similar to that caused by saturation trapping of the positron in vacancies in Cu. The result is unexpected, since the majority of the vacancy population in the sample would be oxygen vacancies, and anion vacancies are normally not expected to trap positrons.

The PAS data and the diffusion data may be understood if one assumes that the oxygen vacancies are associated with Sr^{2+} ion clusters on the La sublattice; one may, for example, consider two neighboring Sr^{2+} ions, their associated two Cu^{3+} ions in equilibrium with two neighboring Sr^{2+} ions and a single oxygen vacancy. The vacancy charge is then locally compensated, explaining why posi-

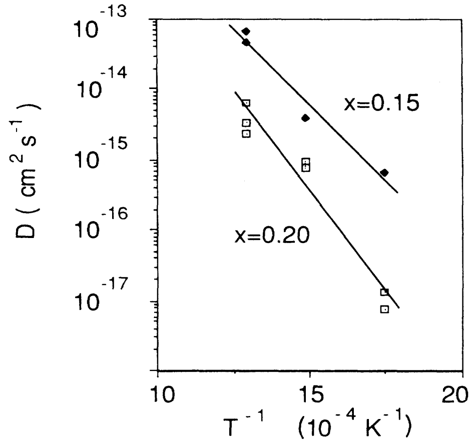

FIG. 1. Diffusion coefficient, $D(cm^2s^{-1})$ of ^{18}O in $La_{2-x}Sr_xCuO_{4-y}$ vs reciprocal temperature $1/T$ (K^{-1}). Upper curve: $x=0.15$, lower curve: $x=0.20$.

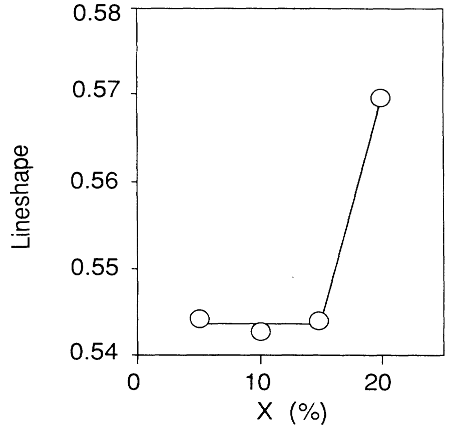

FIG. 2. Doppler broadening lineshape vs x for $La_{2-x}Sr_xCuO_{4-y}$.

trons can trap in the vacancies, and the diffusion results can be understood in terms of the oxygen vacancies being bound to these clusters.

The partition function for the system could be calculated, and from it the vacancy concentration, if one knew the density of states and enthalpy for the various $(Sr^{2+}+Cu^{3+}+V)$ aggregates; not knowing these, we postulate that every cluster of $n Sr^{2+}$ ions on the La sublattice is associated with a vacancy, where the cluster size n is to be determined later. The concentration of clusters of size n may be calculated assuming a random Sr^{2+} occupancy on the La sublattice. For example, we assume that for $n=2$ and $P \geq n$, a cluster of size P contains on the average P/n oxygen vacancies. This approximation is justified since the number of clusters with $P=2$ is much larger than the number with $P=3$. We then obtain $C_v(n=2, Z, x) \approx [1-(1-x/2)^Z]x/8$, where Z is the coordination number. Similar expressions can be calculated for $n>2$. Such expressions overestimate the vacancy concentration, since the Sr^{2+} ions will tend to order, thereby reducing the number of clusters. Also, the coordination number Z to be used in the calculation may differ significantly from the geometrical coordination for two reasons. First, the neighboring positions of a Sr^{2+} ion are not equivalent, and the energy of a pair of Sr^{2+} ions will thus depend on the orientation of the pair. Second, the assumption of one vacancy per cluster of size n differs from reality in that a vacancy may not always be associated with the cluster. Thus, Z is considered to be an adjustable parameter and is anticipated to be smaller than the geometrical coordination.

The oxygen-vacancy concentration $C_v(n, Z, x)$ calculated from this model for $n=2$ and $Z=3$ (Fig. 3), is in good agreement with the thermogravimetric[6] and neutron-diffraction[7] data, considering the experimental scatter and the approximate nature of the model. The concentration for larger cluster sizes was calculated as well and was found to fall below the curves shown in Fig. 3.

The two Sr^{2+} ions ($n=2$) will be neutralized by an oxygen vacancy only if neutralization by Cu^{3+} is energetically unfavorable. By approximating the Sr^{2+}-Cu^{3+} ion pair as a dipole, we can estimate the Sr^{2+} ion interactions on neighboring sites. We find that the dipole-dipole pair interaction energies are ≈ 0.6 eV for neighboring Sr^{2+} ions in different c planes not separated by a Cu-O plane (there are four such neighbors), ≈ 1.5 eV for the Sr^{2+} ions in the same c plane (four neighbors), and large (>10 eV) for Sr^{2+} ions separated by a Cu-O plane. The latter energy is so large that one anticipates that this configuration is unlikely whether a vacancy is present or not and, therefore, the coordination should be either $Z=8$ or $Z=4$, depending on the energies. The present model is known to overestimate the actual vacancy concentration, and a fit of the model to experimental data should, therefore, lead to systematically low values of $Z (Z=3<4)$. The result $n=2$, $Z=3$ is thus supported by our estimate of the interaction energies of the Sr^{2+} ions on the La sites, and indicates that a vacancy is bound to two neighboring Sr^{2+} ions in the same c plane.

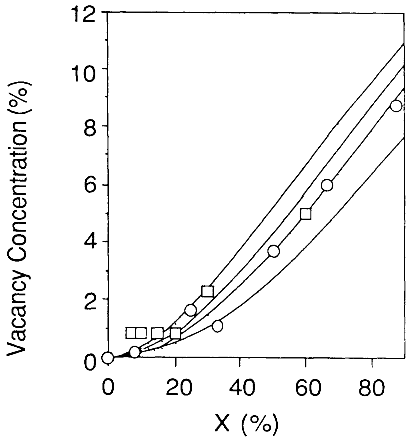

FIG. 3. Oxygen-vacancy concentration vs x for $La_{2-x}Sr_xCuO_{4-y}$. Experimental points: □, from Ref. 7; ○, from Ref. 6. Curves from model (from top to bottom): $(n,Z)=(2,6)$, $(2,4)$, $(2,3)$, and $(2,2)$.

The notion of a vacancy being bound to two Sr^{2+} ions may also qualitatively explain the diffusion results. The simultaneous increase of the concentration of oxygen ion vacancies and decrease of the diffusion coefficient of ^{18}O observed on increasing the Sr^{2+} doping from 0.15 to 0.20 is similar to what takes place when fluorite-structured oxides (ZrO_2, CeO_2, and ThO_2) are doped with divalent and trivalent cations above a critical concentration, and oxygen ion vacancies are introduced for charge compensation.[8] In these materials, it can only be stated generally that the presence of a large concentration of charged defects slows down the motion of other charged defects. No simple calculation of the effect is possible; the dopant and vacancy concentrations, which are equal in the fluorite oxides, are too high. A numerical calculation[9] taking account of 30 different atomic configurations around the vacancy has produced qualitative agreement with experiment. As in the present case, the activation energy for oxygen ion motion was found to increase with dopant and oxygen-vacancy concentration. The present case differs from fluorite-structured oxides, of course, in that the crystal structure $La_{2-x}Sr_xCuO_{4-y}$ is much more complicated

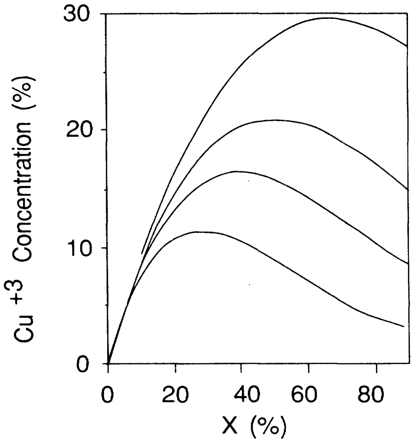

FIG. 4. Cu^{3+} ion concentration vs x for $La_{2-x}Sr_xCuO_{4-y}$. Curves from model (from top to bottom): $(n,Z)=(2,2)$, $(2,3)$, $(2,4)$, and $(2,6)$.

than the fluorite structure.

Finally, the Cu^{3+} ion concentration may be calculated from the present model and the result is shown in Fig. 4. It is seen that the Cu^{3+} ion concentration goes through a maximum at $x \approx 0.5$ ($n=2$, $Z=3$). The present model thus suggest optimal superconductive properties at a Sr^{2+} ion concentration $x \approx 0.5$. This composition is, however, likely to be too large for two reasons. First, the assumption of a noncorrelated occupancy of the La sublattice leads, especially for small x, to an overestimate of the vacancy concentration. A more realistic calculation, taking ordering into account, would lead to maxima at Cu^{3+} ion concentrations well below those found in Fig. 4, and to a more pronounced "vacancy-onset" behavior in Fig. 3. Second, the vacancy concentration, if large, may possibly have an adverse influence on the superconducting properties, thus also leading to an optimal Cu^{3+} concentration below those found in Fig. 4. We note here that the c lattice parameter has a maximum at $x \approx 0.3$,[6] and this was interpreted[6] as being due to a maximum in the Cu^{3+} ion concentration.

In conclusion, we have suggested that the oxygen-vacancy concentration, and hence, the Cu^{3+} ion concentration, in $La_{2-x}Sr_xCuO_{4-y}$ are determined by Sr^{2+} ion clustering on the La sublattice. This model leads to a qualitative explanation of the results observed on diffusion, PAS, and the vacancy concentration. A maximum in the Cu^{3+} ion concentration as a function of Sr^{2+} ion concentration is also predicted from this model. If T_c correlates with the Cu^{3+} ion concentration, our model qualitatively explains the variation of T_c with Sr^{2+} concentration in $La_{2-x}Sr_xCuO_{4-y}$.

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