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Defect Chemistry of $La_{2-x}Sr_xCuO_{4-x/2}$ $(0 < x \leq 1)$

D. J. L. HONG AND D. M. SMYTH

Materials Research Center, Building 5, Lehigh University,
Bethlehem, Pennsylvania 18015

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The hole concentration in oxygen-equilibrated $La_{2-x}Sr_xCuO_{4-x/2}$ increases linearly with x up to $x \approx 0.15$, passes through a maximum value, and then decreases for further increases in x. This change in behavior is attributed to a shift in the charge-compensating defect from holes to oxygen vacancies. However, classical defect chemistry indicates that the hole concentration should only shift to a less rapid rate of increase with x, but not decrease. The observed decrease is caused by an increase in the enthalpy of the oxidation reaction that fills vacancies and replaces them with holes. This occurs because large concentrations of oxygen vacancies are effective in relieving imbalances in stress and charge that exist in the intergrowth structure of La_2CuO_4. As a result, the vacancies become increasingly favored over holes as the charge-compensating defect in the highly acceptor-doped material. The increase in the enthalpy of oxidation results in maximum values for both the hole concentration and T_c as functions of the acceptor content. © 1993 Academic Press, Inc.

Introduction

La_2CuO_4 is an oxygen-excess, p-type semiconductor that shows bulk superconductivity if a sufficient excess of oxygen is incorporated into the lattice by equilibration in high oxygen pressures (*1–3*). It has been shown elsewhere that the oxidation process involves the incorporation of interstitial oxygen that is charge-compensated by holes (*4, 5*)

$$V_i + \tfrac{1}{2}O_2 \rightleftarrows O_i'' + 2h^{\cdot}. \qquad (1)$$

The enthalpy of this oxidation reaction is near zero (*5*), indicating that it is highly favored. The oxygen excess slightly exceeds 1% after equilibration in 23 kbar of oxygen (*6*). The correspondingly high hole concentration is the probable source of the superconducting properties. Acceptor-doped La_2CuO_4 can also become superconducting when the negatively charged acceptor centers are compensated by holes. Ba-doped La_2CuO_4 was the first such material discovered (*7*), and was the forerunner of an extensive family of cuprate superconductors whose chemistry is dominated by oxidized, acceptor-doped, p-type compositions.

In $La_{2-x}Sr_xCuO_4$ solid solutions, equilibrated under oxidizing conditions, the superconducting transition temperature initially increases with increasing Sr content up to $x \approx 0.15$ and then decreases with further doping (*8, 9*). This compositional dependence is undoubtedly related to the defect chemistry and to the resulting hole concentrations. Thus it is important to understand the effects of doping and equilibration on the defect concentrations and on the transport properties of the material.

An acceptor dopant, such as Sr^{2+} substi-

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tuted for La^{3+} in La_2CuO_4, is a negatively charged center, Sr'_{La}, that must be compensated by a positively charged defect to maintain bulk charge neutrality. Since interstitial cations are not expected to be major defects in this compound, the choice is restricted to oxygen vacancies and holes. The stoichiometric compositions of the doped compositions correspond to combinations of the stoichiometric binary oxide constituents, i.e., $(1 - x/2)La_2O_3 + xSrO + CuO$ or $La_{2-x}Sr_xCuO_{4-x/2}$. The compensating defects in the stoichiometric compositions are oxygen vacancies, and the substitution of SrO for La_2O_3 for this case can be written as

$$x\mathrm{SrO} \xrightarrow{x/2\,(\mathrm{La_2O_3})} x\mathrm{Sr}'_{\mathrm{La}} + x\mathrm{O_0} + \frac{x}{2}V_0^{\cdot\cdot}. \quad (2)$$

By interaction with oxygen in the ambient, the oxygen vacancies may be partially or completely filled and replaced by holes as the charge-compensating defect

$$V_0^{\cdot\cdot} + \tfrac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{O_0} + 2h^{\cdot}. \quad (3)$$

In the case of complete replacement of oxygen vacancies by holes, the sum of Eq. (2) and $x/2$ times Eq. (3) gives the alternative reaction for the incorporation of SrO with the formation of holes:

$$x\mathrm{SrO} + \frac{x}{4}\mathrm{O_2} \xrightarrow{x/2(\mathrm{La_2O_3})} x\mathrm{Sr}'_{\mathrm{La}} + \frac{3x}{2}\mathrm{O_0} + xh^{\cdot}. \quad (4)$$

Equations (2) and (4) represent limiting cases of charge compensation linked by the oxidation reaction, Eq. (3). For the optimum superconducting properties, it is expected that one should oxidize the material as much as possible toward the limiting case of Eq. (4).

It has been determined that Eq. (1) is the oxidation reaction for undoped La_2CuO_4 (*5*, *6*). The corresponding mass-action expression is

$$\frac{[\mathrm{O}''_{\mathrm{I}}]\mathrm{p}^2}{[V_{\mathrm{I}}]} = K_{\mathrm{p}}e^{-\Delta H_p/kT}P(\mathrm{O_2})^{1/2} \quad (5)$$

where $p = [h^{\cdot}]$ and ΔH_p is the enthalpy of oxidation, which has been found to be essentially zero; i.e., there is no temperature dependence to the concentrations of oxygen interstitials and holes for equilibration at a fixed oxygen activity (*5*).

As La_2CuO_4 is reduced, it appears to decompose while still in the oxygen-excess, *p*-type state; i.e., the stoichiometric composition is not stable at the equilibration temperatures (*5*). Thus reduction to oxygen-deficient compositions does not actually occur; however, it is still convenient to propose a fictive reduction reaction for the purpose of thermodynamic analysis. In the absence of direct information, it is convenient, and reasonable, to assume that the preferred form of intrinsic ionic disorder is anion Frenkel, and that the reduction reaction would thus involve the formation of oxygen vacancies. The equilibrium reactions and mass-action expressions for these processes are

$$V_{\mathrm{I}} + \mathrm{O_0} \rightleftarrows \mathrm{O}''_{\mathrm{I}} + V_0^{\cdot\cdot} \quad (6)$$

$$\frac{[\mathrm{O}''_{\mathrm{I}}]\,[V_0^{\cdot\cdot}]}{[V_{\mathrm{I}}]\,[\mathrm{O_0}]} = K_{\mathrm{F}}e^{-\Delta H_F/kT} \quad (7)$$

$$\mathrm{O_0} \rightleftarrows \tfrac{1}{2}\mathrm{O_2} + V_0^{\cdot\cdot} + 2e' \quad (8)$$

$$[V_0^{\cdot\cdot}]n^2/[\mathrm{O_0}] = K_n e^{-\Delta H_n/kT}P(\mathrm{O_2})^{-1/2} \quad (9)$$

where $n = [e']$. The defect picture is completed by consideration of intrinsic electronic disorder

$$\mathrm{nil} \rightleftarrows e' + h^{\cdot} \quad (10)$$

$$np = K_i e^{-E_g^\circ/kT} \quad (11)$$

where E_g° is the enthalpy of the intrinsic ionization reaction, commonly referred to as the band gap at 0 K. These defects must be present in concentrations that maintain bulk charge neutrality.

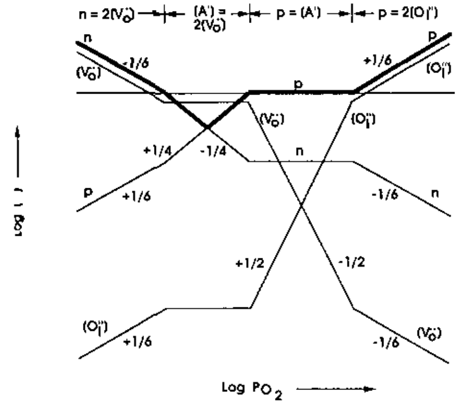

FIG. 1. Schematic equilibrium defect diagram for an ideal oxide MO doped with the acceptor oxide A_2O with $K_i >> K_F$.

$$2[O_i''] + n + [Sr_{La}'] = 2[V_0^{\cdot\cdot}] + p \quad (12)$$

which includes the charged acceptor center, Sr_{La}'. The mass-action expressions and the condition of charge neutrality can be used to construct an idealized defect diagram for acceptor-doped La_2CuO_4, as shown in Fig. 1, in which it has been assumed that E_g° is significantly less than ΔH_F.

The defect diagram can be divided into four regions, each of which corresponds to a simplification of the charge neutrality expression such that it is dominated by only two defects of opposite charge. Intrinsic nonstoichiometry exists only in the region at the highest oxygen activities, at the far right of Fig. 1, such that the charge neutrality expression can be approximated by $p = 2[O_i'']$. Both undoped and acceptor-doped La_2CuO_4 decompose on reduction before the stoichiometric composition, where $n = p$, is reached. It will be seen that the behavior of the acceptor-doped compositions corresponds to the central part of the diagram, near the boundary between the regions where holes and oxygen vacancies are the major compensating defects. In the region dominated by acceptor impurities and oxygen vacancies, such that

$$[Sr_{La}'] \approx 2[V_0^{\cdot\cdot}] \quad (13)$$

combination of Eqs. (5) and (7) gives

$$p \approx \left\{\frac{K_p[Sr_{La}']}{2K_F[O_0]}\right\}^{1/2} e^{-(\Delta H_p - \Delta H_F)2kT} P(O_2)^{1/4} \quad (14)$$

while at higher oxygen activities, the hole concentration shifts to

$$[Sr_{La}'] \approx p. \quad (15)$$

It should be noted that in both of these regions, the hole concentration always increases with increasing acceptor content at constant $P(O_2)$ if the system behaves ideally. This will be an extremely important point in the subsequent discussion.

The relationship in Eq. (14) can be obtained directly from the mass-action expression for Eq. (3):

$$p^2[O_0]/[V_0^{\cdot\cdot}] = K_{ox}e^{-\Delta H_{ox}/kT}P(O_2)^{1/2}. \quad (16)$$

This can be combined with Eq. (13) to give

$$p \approx \left\{\frac{K_{ox}[Sr_{La}']}{2[O_0]}\right\}^{1/2} e^{-\Delta H_{ox}/2kT} P(O_2)^{1/4}. \quad (17)$$

Comparison of Eqs. (14) and (17) demonstrates the important relationship

$$\Delta H_{ox} = \Delta H_p - \Delta H_F \quad (18)$$

which states that the enthalpy of the oxidation reaction for filling extrinsic oxygen vacancies is less than the enthalpy for oxidation of the undoped material, and that the difference is the enthalpy for anion Frenkel disorder. Since ΔH_p has been determined to be zero, and since ΔH_F must be positive, ΔH_{ox}, the enthalpy for the vacancy-filling reaction, must be negative, i.e., exothermic, and thus very highly favored.

La_2CuO_4 has the K_2NiF_4 structure which is an intergrowth structure consisting of individual perovskite unit cells separated by layers of the NaCl structure. It corresponds to the first member of the homologous series of Ruddlesden–Popper structures that have the generic formula $AO\text{-}nABO_3$ (*10*). In the more conventional isostructural analog Sr_2TiO_4, the component parts are SrO and $SrTiO_3$, and the NaCl and perovskite parts of the structure are both electrically neutral. In addition, the Sr–O and Ti–O bond lengths are such that the two parts fit together almost exactly without stress. However, in La_2CuO_4 the component parts are LaO^+ and $LaCuO_3^-$, so that the layers bear net charges. In addition, Goodenough and Manthiram have pointed out that there is a serious mismatch in bond lengths between the layers, such that the perovskite part of the structure is under compression, while the NaCl part is under tension (*11*). One result of this stress mismatch is that the high-temperature, tetragonal structure of La_2CuO_4 distorts on cooling to a low-temperature, orthorhombic structure in which the CuO_6 octahedra in the perovskite layer are tilted so as to relieve the compressive stress. Our equilibrium measurements on both doped and undoped La_2CuO_4 have been made at temperatures above this structural transition, where the materials are always tetragonal. It will be seen that these imbalances in both stress and charge have a profound influence on the defect chemistry of acceptor-doped La_2CuO_4. For example, the very high solubility of Sr in $La_{2-x}Sr_xCuO_{4-x/2}$, up to $x = 1.34$ (*12*), can be attributed to the favorable aspects of substituting a larger ion of lesser charge, Sr^{2+} for La^{2+}, in a layer that is under tension and bears a net positive charge.

Experimental

Ceramic powders of composition $La_{2-x}Sr_xCuO_{4-x/2}$ $(0 < x \leq 1)$ were prepared by the conventional solid-state reaction method involving repeated calcinations of a mixture of La_2O_3, $SrCO_3$, and CuO powders at 1000°C. The resulting single-phase powders, as determined by XRD, were pressed into rectangular bars, $0.15 \times 0.60 \times 1.50$ cm^3, and sintered at 1200°C in air for 6–12 hr. The sintered samples were dense and mechanically sturdy. Platinum leads and paint were attached for electrical measurements. The equilibrium electrical conductivities were measured by a standard dc, four-probe technique, as a function of temperature and oxygen partial pressure. Variations in atmosphere were achieved by flowing a mixture of oxygen and argon, or carbon dioxide and carbon monoxide, through the sample chamber, and the oxygen partial pressure was monitored by a zirconia cell. The thermoelectric power was measured in the natural temperature gradient between two heating zones while the average sample temperature was kept constant.

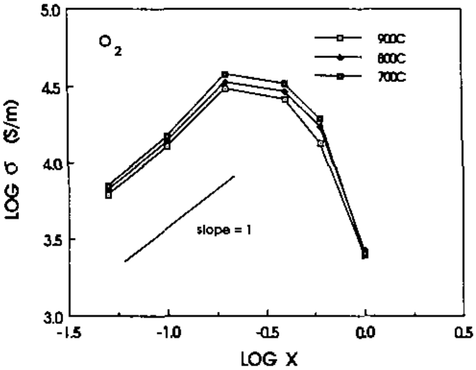

FIG. 2. Equilibrium conductivities as a function of Sr concentration for Sr-doped La_2CuO_4 equilibrated in 1 atm O_2 at 700–900°C.

Results and Discussion

The electrical conductivity of $La_{2-x}Sr_xCuO_{4-x/2+y}$ in equilibrium with 1 atm (10^5 Pa) of O_2 over the temperature range 700–900°C is shown as a function of x, the Sr content, in Fig. 2. y represents the stoichiometric excess of oxygen that results from the oxidation reaction, Eq. (3). There is only a small temperature dependence, with the conductivity increasing slightly with decreasing temperature. For values of x up to about 0.2, the conductivity increases

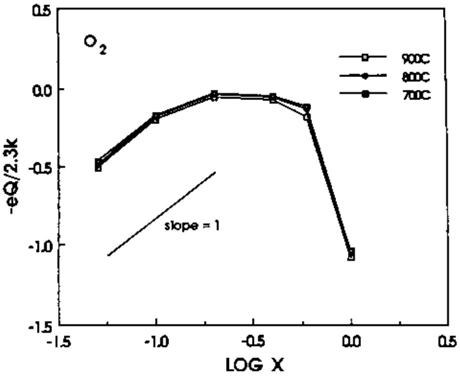

FIG. 3. Normalized Seebeck coefficients as a function of Sr concentration for Sr-doped La_2CuO_4 equilibrated in 1 atm O_2 at 700–900°C.

with x, with a slope of unity. This indicates that the conductivity is linear with x, characteristic of compensation of the acceptor centers by holes, according to Eq. (15). For $x > 0.2$, the conductivity shows an accelerating decrease with increasing x. Charge compensation of the acceptors must have been taken over by oxygen vacancies in this region. A plot of the normalized Seebeck coefficient, assumed to be proportional to the log of the hole concentration, is shown in Fig. 3 for the same experimental range. These values are less precise than the conductivities, because the carrier concentrations are so large that some of the thermoelectric voltages are close to zero. However, the general trend is similar. There is no significant temperature dependence, but this could result from a loss in accuracy in determining the hole concentration from the Seebeck coefficient when the concentration is very high.

The Seebeck coefficient confirms that the hole concentration is decreasing with increasing acceptor content at high concentrations, and that the corresponding decline in conductivity is not primarily due to a change in the mobility. It will be recalled from Eq. (17) that the hole concentration should be increasing with $[Sr'_{La}]^{1/2}$ when the acceptors are compensated by oxygen vacancies, and that in no case should the hole concentration be decreasing with increasing acceptor content. This behavior cannot be explained by ideal defect chemistry and will be discussed in detail at a later point.

1. The Electronic Compensation Region, $La_{2-x}Sr_xCuO_4$, $0 < x < 0.2$

Equilibrium conductivities as a function of oxygen partial pressure over the temperature range 800–1000°C are shown in Fig. 4 for Sr-doped samples with $x = 0.05$ and 0.1 (2.5 and 5% replacement of La^{3+} by Sr^{2+}). It was not possible to obtain reproducible measurements below about 1 Pa (10^{-5} atm), and this was attributed to decomposition of the samples. The conductivities are independent of $P(O_2)$ over the entire range for both samples, except for a very slight downturn for the more highly doped sample for the lowest oxygen activities and highest temperatures, i.e., for the most severely reducing conditions. Also, as x is increased by a factor of 2, the conductivity increases by the same factor. The overall behavior is that expected for the region where the acceptors

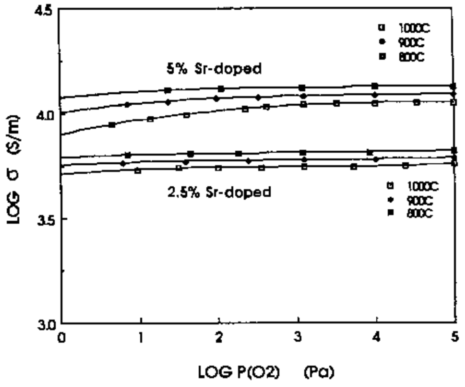

FIG. 4. Equilibrium conductivities as a function of oxygen partial pressure for $La_{1.95}Sr_{0.05}CuO_4$ and $La_{1.9}Sr_{0.1}CuO_4$ at 800–1000°C.

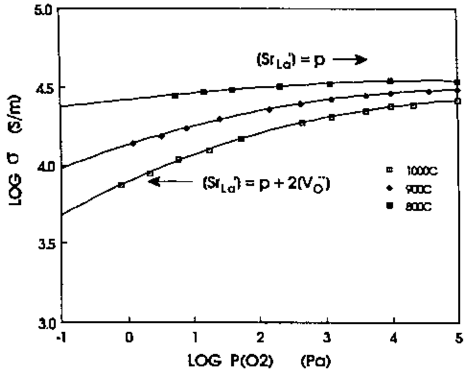

FIG. 5. Equilibrium conductivities as a function of oxygen partial pressure for $La_{1.8}Sr_{0.2}CuO_4$ at 800–1000°C.

are compensated by holes according to Eq. (15). Once again, the conductivities decrease slightly with increasing temperature, most likely due to the temperature dependence of the hole mobility.

When the Sr content is doubled again to $x = 0.2$, as shown in Fig. 5, the conductivity at high oxygen activity also doubles, but the tendency to decrease with decreasing oxygen activity has become more pronounced, as has the temperature dependence in the region of low $P(O_2)$. This suggests that the compensating defects are changing from holes to oxygen vacancies with increasingly reducing conditions. According to Eq. (17), the oxygen activity dependence of the hole concentration should be approaching $P(O_2)^{1/4}$, and should also be decreasing with increasing temperature, as observed, since the oxidation reaction is exothermic, i.e., ΔH_{ox} is negative, according to Eq. (18). The general behavior for this range of acceptor contents is summarized in a defect diagram for two different dopant levels in Fig. 6, where it has been assumed that dilute solution thermodynamics are still valid, i.e., that the thermodynamic parameters are independent of concentration. It is apparent that the boundary between the regions where the acceptors are compensated by oxygen vacancies and by holes moves to higher $P(O_2)$ with increasing acceptor content, as observed in Figs. 3 and 4.

2. *The Mixed Compensation Region, $La_{2-x}Sr_xCuO_{4-x/2+y}$, $0.2 < x < 0.6$*

As seen in Fig. 2, the hole concentration no longer increases with increasing acceptor content when $x > 0.2$, and Eq. (15) is thus no longer an adequate approximation to charge neutrality. Both oxygen vacancies and holes are involved in charge compensation of the acceptors, and charge neutrality can best be expressed as

$$[\mathrm{Sr}'_{\mathrm{La}}] = 2[V_{\mathrm{o}}^{\cdot\cdot}] + p. \tag{19}$$

Equilibrium conductivities of samples with $x = 0.4$ and 0.6 are shown in Figs. 7 and 8. For $x = 0.4$ the conductivities are less than for the sample with $x = 0.2$, even at the highest oxygen activities, and this trend is much more pronounced for the sample with $x = 0.6$. The pertinent equilibrium reaction for these samples is clearly Eq. (3), as oxygen vacancies are gradually filled with increasing oxygen activity.

The most striking behavior in this range of dopant concentrations is that the hole

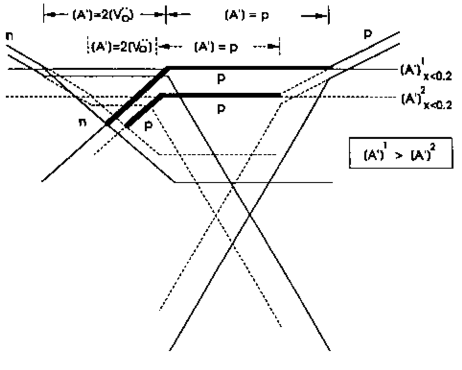

FIG. 6. Schematic defect diagram for Sr-doped La_2CuO_4 with low Sr concentrations.

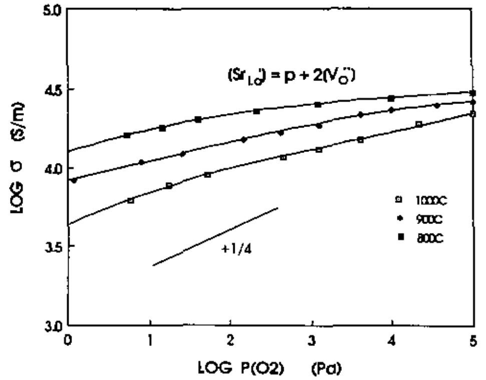

FIG. 7. Equilibrium conductivities as a function of oxygen partial pressure for $La_{1.6}Sr_{0.4}Cu_{4-y}$ at 800–1000°C.

concentration has started to decrease with increasing acceptor content at constant oxygen activity. As pointed out earlier, based on Eq. (17), this cannot be accounted for by the straightforward application of defect chemistry, as seen in the idealized defect diagram, Fig. 6. It must be considered that the use of dilute solution thermodynamics is no longer valid, and that some of the thermodynamic parameters of the equilibrium state are no longer independent of acceptor concentration.

If the hole concentration is less than expected in the region dominated by the oxygen vacancy filling reaction, Eq. (3), this implies that it has become more difficult to fill the vacancies; i.e., the enthalpy for this reaction, ΔH_{ox}, has become larger. The following discussion will be based on the assumption that for $x > 0.2$, the defect concentrations are sufficient to have a significant effect on the stress and charge imbalances in the La_2CuO_4 structure, and that as a result, the enthalpies for some of the equilibrium reactions will become concentration dependent. Experimental evidence will be given that supports this hypothesis.

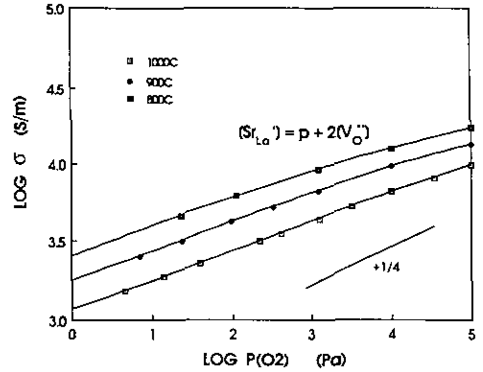

FIG. 8. Equilibrium conductivities as a function of oxygen partial pressure for $La_{1.4}Sr_{0.6}CuO_{4-y}$ at 800–1000°C.

It was suggested in earlier work that oxygen vacancies in acceptor-doped La_2CuO_4 are preferentially located in the basal planes, i.e., in the Cu–O planes (*9, 12*), and that various vacancy ordering schemes are present in the basal planes for compositions with $x > 1$ (*12*). This preferential location of the vacancies is quite reasonable because their presence in the basal planes will relieve both the compressive stress and the net negative charge of those planes. Thus when the vacancy concentration becomes high enough to have a finite effect on relieving this imbalance in stress and charge, the enthalpy for their replacement by holes should increase, and they will become an increasingly favorable defect. When the vacancies are replaced by holes, which are assumed to be located in Cu-derived states in the basal planes, the net charge effect is unchanged, but the relief of the compressive stress by the vacancies is lost. As a result, vacancies become increasingly favored over holes, and the enthalpy of the oxidation reaction is increased. Since this reaction is exothermic, and ΔH_{ox} is negative, this means that it becomes less negative with increasing acceptor content. It should also be remembered that the presence of the Sr^{2+} itself in the NaCl layers serves to relieve the tensile stress and net positive charge in those layers.

There are two direct pieces of evidence

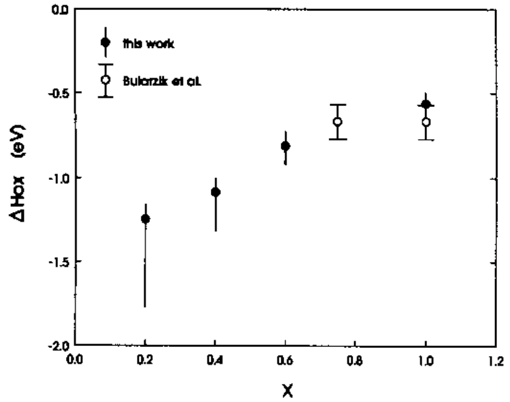

FIG. 9. Enthalpy of the oxidation reaction for filling oxygen vacancies as a function of Sr content (x) for $La_{2-x}Sr_xCuO_{4-y}$ with $0.2 \leq x \leq 1$.

that support the model described above. First of all, it has been observed that for $x > 0.2$ there is no longer a transition to the orthorhombic structure at low temperatures (*12*). This transition has been attributed to a cooperative tilting of the CuO_6 octahedra in a way that relieves the compressive stress in the Cu–O planes. Apparently this stress has been sufficiently relieved by the presence of oxygen vacancies in the basal planes, and of Sr^{2+} in the NaCl layers, that the structural relief is no longer necessary. The second bit of evidence is shown in Fig. 9, where the apparent enthalpy of the vacancy-filling reaction, ΔH_{ox}, is plotted as a function of acceptor content. The enthalpy increases (becomes less negative) with increasing acceptor content, indicating that it is becoming increasingly difficult to replace oxygen vacancies by holes. These apparent enthalpies were obtained from the temperature dependence of the conductivities at the lowest oxygen activities for each acceptor concentration. The full temperature dependence has not been fully developed for the samples of smaller acceptor content, so that for those samples the apparent enthalpies are higher (less negative) than the true values. Thus the concentration dependence of ΔH_{ox} is actually larger than that shown in Fig. 9, especially in the low concentration range. To obtain more accurate estimates for the enthalpies of oxidation for the lower acceptor contents, the curvature in Figs. 5, 7, and 8 have been mathematically extrapolated to lower $P(O_2)$ until the ideal $\frac{1}{4}$ slopes have been developed. The enthalpies were then obtained from the temperature dependencies at those points. These values correspond to the lower tips of the extended error bars in Fig. 9, and demonstrate a greater-than-observed dependence on the acceptor content. No estimates of ΔH_{ox} are available for $x < 0.2$, because the hole concentration is equal to the acceptor concentration in that region, and the only contribution to the temperature dependence of the conductivity is due to that of the hole mobility. Since ΔH_p has been found to be zero for undoped La_2CuO_4, these results and Eq. (18) suggest that the enthalpy for anion Frenkel disorder in the undoped material, ΔH_F, is of the order of 2 eV.

Values of the enthalpy of oxidation obtained from calorimetry by Bularzik *et al.* are included in Fig. 9, and the results are in reasonable agreement with ours (*13*). These authors found no dependence of the enthalpy on the acceptor content within the precision of their measurements, which were made at high acceptor contents where the effect on the enthalpy appears to be saturating.

3. The Ionic Compensation Region, $La_{2-x}Sr_xCuO_{4-x/2}$, $x \geq 1$

The equilibrium conductivity of a sample with $x = 1$ is shown in Fig. 10. The behavior has now evolved into that expected for complete charge compensation by vacancies, according to Eq. (13), in that the hole concentration is now proportional to $P(O_2)^{1/4}$, as indicated by Eq. (17). The hole concentration has continued its decrease, and the enthalpy of oxidation is even less negative. The composition of this sample is then $LaSrCuO_{3.5}$. Electron diffraction studies of sam-

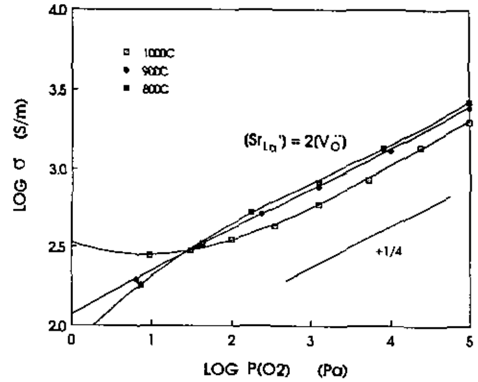

FIG. 10. Equilibrium conductivities as a function of oxygen partial pressure for $\mathrm{LaSrCuO}_{4-y}$ at 800–1000°C.

ples with this acceptor content and higher have shown superlattice structures that are attributed to ordering of the oxygen vacancies on the basal planes (*12*).

The equilibrium conductivities of this sample under the most highly reducing conditions show evidence of the development of a conductivity minimum, where $n = p$, below which oxygen-deficient, n-type behavior would be expected if the material did not decompose. The reversal of the temperature dependence to an endothermic behavior in this region is consistent with the expected thermally activated behavior of the band gap. It will be seen that as the hole concentration decreases with increasing acceptor content, the stoichiometric composition, as indicated by the condition $n = p$, is expected to move to higher values of $P(O_2)$. In this case, the stoichiometric composition appears to have moved into the stability range of the highly acceptor-doped compound.

4. *The Complete Defect Model*

In the preceding discussion, it was proposed that the enthalpy of the oxidation reaction that involves the filling of extrinsic oxygen vacancies, Eq. (3), increases with increasing acceptor content for $x > 0.2$, because the oxygen vacancies are more effective than holes in relieving the compressive stress in the Cu–O planes. This hypothesis is directly confirmed by the observed dependence of ΔH_{ox} on the acceptor content, as shown in Fig. 9. However, there are relationships among the various reaction enthalpies, and ΔH_{ox} cannot increase without causing changes in some of the other enthalpies. One such relationship is given by Eq. (18), where it is seen that if ΔH_{ox} increases, either ΔH_p must increase, or ΔH_{F} must decrease, or both. Another relationship is obtained by the addition of the intrinsic oxidation and reduction reactions, Eqs. (1) and (8), which indicates the following relationship:

$$\Delta H_p + \Delta H_n = \Delta H_{\mathrm{F}} + 2E_g^0. \qquad (20)$$

It is easily demonstrated from the appropriate diagram that ΔH_{ox} can increase only if (i) ΔH_n decreases or (ii) E_g^0 increases, or both. Since there is no obvious reason for the band gap to increase significantly with dopant concentration, it will be assumed that ΔH_n decreases while the band gap remains unchanged. This is reasonable since the oxygen vacancies created by reduction will relieve both the compressive stress and excess negative charge in the Cu–O planes, while the charge due to the electrons will only cancel the charge relief due to the vacancies, and the stress relief will remain and will result in making the reduction reaction more favorable. This situation is summarized in the form of a defect diagram in Fig. 11. This diagram demonstrates a point made earlier; in these circumstances, the stoichiometric composition, where $n = p$, moves to higher $P(O_2)$ with increasing acceptor content. It also shows that the transition from compensation of the acceptors by oxygen vacancies to compensation by holes also moves to higher $P(O_2)$, as observed.

According to Eq. (20), if ΔH_n decreases and the band gap is unchanged, then either ΔH_p must increase, or ΔH_{F} must decrease, or both. In the absence of direct informa-

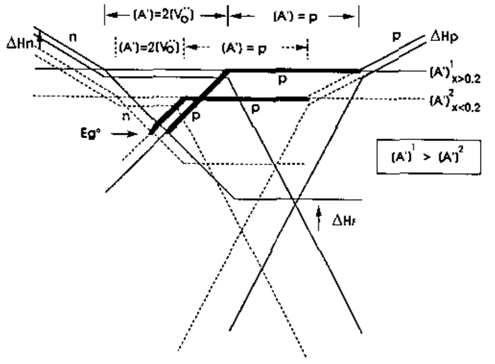

FIG. 11. Schematic defect diagram for Sr-doped La_2CuO_4 with high Sr contents ($0.2 \le x \le 1$).

tion, Fig. 11 has been drawn for the case that ΔH_F decreases, and ΔH_p is unchanged. This can be rationalized by the consideration that oxygen vacancies are a favored defect, so that anion Frenkel disorder has become more favorable. This assumption is consistent with the required change in Eq. (18) when ΔH_{ox} decreases. If oxygen interstitials also become energetically favored because they relieve the tensile stress and excess positive charge in the NaCl layers, then ΔH_p could also decrease. According to Eq. (20), ΔH_F would then have to decrease even further, as expected since the anion Frenkel disorder would then involve two highly favored defects. These various alternatives are not important for the basic model proposed here, because there is no experimental evidence to distinguish between them.

Summary

For values of x up to 0.2, the defect chemistry of $La_{2-x}Sr_xCuO_4$ is an extension of that of the undoped La_2CuO_4, with thermodynamic parameters for the various equilibrium reactions that are essentially independent of, or at least not strongly dependent on, the defect concentrations. Oxygen excess compositions are favored over oxygen deficiency because oxygen interstitials are favored in the NaCl layers because of the local tensile stress and excess positive charge, and holes are favored in the negatively charged Cu–O planes. Theoretical calculations support the difference in the enthalpic cost of creating electrons and holes (*14*). As a result, the stoichiometric composition lies at very low oxygen activities, below the decomposition of the compound, except possibly for extremely high acceptor contents. While the enthalpy of oxidation of undoped La_2CuO_4 according to Eq. (1) has been found to be zero, the enthalpy of oxidation of the acceptor-doped material according to Eq. (3) is reduced by the enthalpy of anion Frenkel disorder and is negative, i.e., exothermic. The hole mobility decreases slightly with increasing temperature over this range of acceptor concentrations, as is characteristic of band-type conduction.

For compositions with $x > 0.2$, the defects have a significant effect on the imbalance of stress and charge in the structure, and the enthalpies of the equilibrium reactions are no longer independent of the defect concentrations. The experimental results require that the enthalpy of the vacancy-filling oxidation reaction, Eq. (3), increase. This is attributed to an increased preference for oxygen vacancies because of their effect in relieving the stress and charge imbalance in the Cu–O planes. The relationship among the various enthalpies is satisfied by the assumption that the enthalpy of reduction decreases with acceptor content, while the band gap is essentially unchanged. The absence of the transition to an orthorhombic structure at these high acceptor concentrations is attributed to the stress relief afforded by the oxygen vacancies and acceptor impurity such that a buckling of the Cu–O planes is no longer needed as a further mechanism of stress relief. Direct experimental evidence for the proposed increase in the enthalpy of oxidation with increasing acceptor content is demonstrated.

The proposed defect model is in accord with the observed peak in the superconducting transition temperature as a function of acceptor content. For oxidizing conditions, the hole concentration increases linearly with the acceptor content up to about $x = 0.15$. The hole concentration peaks at about this concentration and then decreases with further increases in the acceptor content. The superconducting transition temperature follows a similar dependence on the acceptor content as would be expected if it is a function of the hole concentration. Thus the dependence of the enthalpy of oxidation on the acceptor content is the primary reason for the occurrence of a maximum value of the superconducting transition temperature in acceptor-doped La_2CuO_4.

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