Defect Chemistry of Undoped La$_2$CuO$_4$

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La$_2$CuO$_4$ is an oxygen-excess, p-type material over the range 700–900°C and 10^{-2}–10^5 Pa of oxygen. The major defects are interstitial oxygen and holes. The enthalpy of oxidation is near zero, and the hole mobility increases slightly with decreasing temperature, characteristic of band conduction. The preference for oxygen-excess nonstoichiometry is attributed to the presence of an interstitial site that is of adequate size for an oxide ion, to local charge and stress imbalances in the La$_2$CuO$_4$ lattice that favor the presence of holes in the Cu–O planes, and to large, negatively charged oxygen interstitials in the NaCl layers of the intergrowth structure. © 1992 Academic Press, Inc.

Introduction

Superconducting compositions of the type La$_{2-x}$M$_x$CuO$_4$ (M = Sr, Ba) have been studied extensively since the discovery of high temperature superconductivity in a member of this family in 1986 (*1–3*). Doping with the alkaline earth ions, and equilibration with an oxidizing atmosphere, increases the hole concentration to the level necessary to give superconducting properties. The undoped parent compound La$_2$CuO$_4$ has also been found to become superconducting below about 30 K, if it is equilibrated in very high oxygen pressures so as to raise the hole concentration by the incorporation of a stoichiometric excess of oxygen (*4–6*). Thus the defect chemistry of La$_2$CuO$_4$ is of interest both for its own properties and for its being the parent compound of the doped compositions.

In the superconducting solid solutions La$_{2-x}$M$_x$CuO$_4$, where M is a divalent cation that acts as an acceptor impurity, the superconducting transition temperature initially increases with increasing acceptor content and peaks at x = 0.15, after which it decreases with further doping (*7, 8*). For low dopant concentrations and high oxygen activities the acceptor content is compensated by holes, whose concentration thus increases with doping. For x > 0.2, the compensation is increasingly accomplished by oxygen vacancies, and the hole concentration drops. Under oxidizing conditions, undoped La$_2$CuO$_4$ takes up a stoichiometric excess of oxygen that is compensated by holes (*9*). This is analogous to the oxidation of YBa$_2$Cu$_3$O$_{6+y}$, in which the hole concentration is increased by the filling of oxygen vacancies (*10*).

In order to understand the effects of dopants and equilibration conditions on the transport properties of La$_2$CuO$_4$, it is necessary to study its defect chemistry. The ceramic material readily equilibrates with oxygen-containing atmospheres at elevated temperatures, and information on the resulting defect populations can be obtained by high temperature electrical measure-

ments and thermogravimetric analysis. At low oxygen contents, nonsuperconducting single phase materials can be achieved that undergo a structural change from tetragonal to orthorhombic near 530 K. During equilibrium studies at temperatures considerably higher than 530 K, the material will remain in the single-phase, tetragonal, oxygen-excess state that is the origin of superconductivity in this material.

Experimental

Powders of La_2CuO_4 were prepared by two techniques to ensure reproducibility: the conventional solid state reaction technique involving the calcination of a mixture of La_2O_3 and CuO powders at 1000°C and a liquid-mix method similar to that described by Pechini (11), in which metal salts are dissolved and mixed in citric acid and ethylene glycol and then dried and calcined. The resulting single-phase powders, as determined by X-ray diffraction, were pressed into rectangular bars, $0.15 \times 0.6 \times 1.5 \, cm^3$, and sintered at 1200°C in air for 12 hr. The sintered samples were dense and mechanically sturdy. The equilibrium 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 mixtures 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. Thermoelectric power was measured in natural temperature gradients achieved by varying the temperatures in two heating zones. Nearly identical results were given by samples prepared by the two processing techniques.

Results and Discussion

The Stoichiometric Composition

The proper discussion of redox behavior and nonstoichiometry requires the defini-

tion of a stoichiometric composition as a reference state. This is the composition for which there are neither excess electrons nor excess holes and for which these electronic carriers arise only by ionization across the band gap. Under these circumstances, and when there are no trapping states in the band gap, the total electron and hole concentrations are necessarily equal. Thus charge neutrality must also include charge balance among the various charged lattice defects. When the stoichiometric composition is oxidized, excess oxygen is added to the material and empty electronic states are introduced into the valence band, i.e., holes. The resulting p-type conduction increases with increasing oxygen partial pressure, $P(O_2)$. On the other hand, reduction leads to oxygen deficiency and excess electrons. The resulting n-type conductivity increases with decreasing $P(O_2)$. The stoichiometric composition thus corresponds to the minimum value of the electronic conductivity plotted as a function of $P(O_2)$, insofar as the electron and hole mobilities are similar in magnitude, and when these species are not trapped by any oppositely charged lattice defects in the crystal. In La_2CuO_4, Cu^{2+} is the only oxidizable and reducible species, and there is only one type of lattice site for the copper, at the center of an oxygen octahedron. Therefore, there should be only one oxidation state for Cu at the stoichiometric composition, which is clearly La_2CuO_4, which corresponds to the combination of the stoichiometric binary oxides, La_2O_3 and CuO. This composition corresponds to the ideal K_2NiF_4 structure, which is thus the reference structure from which lattice defects are defined.

High Temperature Defect Chemistry

The equilibrium electrical conductivity of La_2CuO_4 is shown in Fig. 1. The conductivity increases with increasing $P(O_2)$ across the entire experimental range ($10^{-2} \gtrsim P(O_2) \gtrsim 10^5$ Pa and 700–900°C), characteristic of
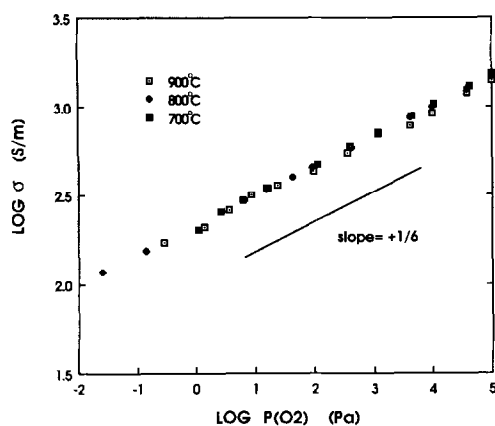
FIG. 1. Electrical conductivities of undoped La₂CuO₄ as a function of oxygen partial pressure at 700–900°C.

p-type conduction related to a stoichiometric excess of oxygen. The results are very similar in both magnitude and oxygen pressure dependence to those described previously by Su *et al.* and by Tsai *et al.* (*12, 13*). The excess oxygen could be accommodated by the filling of oxygen vacancies, by the formation of cation vacancies, or by the occupation of interstitial sites. The amount of nonstoichiometry exceeds any reasonable impurity level or uncertainty in the La/Cu ratio, so the filling of extrinsic vacancies is not likely. The cation vacancy model does not fit the observed $P(O_2)$ dependence, so it is assumed that the interstitial model is correct. This is in accord with a neutron diffraction study of the isostructural La₂NiO₄ by Jorgensen *et al.* (*14*) in which it was determined that a stoichiometric excess of oxygen is located in interstitial sites. For comparable equilibration conditions, La₂NiO₄ has a considerably higher content of excess oxygen than does La₂CuO₄, because of the greater ease of oxidation of Ni^{2+} compared with Cu^{2+}. This higher defect concentration made it possible to determine the location of the excess oxygen in the lattice, and it is reasonable to assume that similar accommodation occurs in La₂CuO₄ (*9*). Thus the oxidation reaction is

$$\tfrac{1}{2}O_2 \rightleftharpoons O''_I + 2h^{\cdot} \tag{1}$$
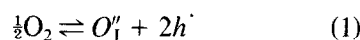
with the mass action expression

$$[O''_I]\, p^2\, P(O_2)^{-1/2} = K_p e^{-\Delta H_p / kT}, \tag{2}$$

where $p = [h^{\cdot}]$ and ΔH_p is the enthalpy of oxidation per oxygen. If Eq. (1) is the major source of defects, then the condition of bulk charge neutrality can be approximated as

$$p \approx 2[O''_I]. \tag{3}$$

Combination of Eqs. (2) and (3) gives

$$p \approx (2K_p)^{1/3} e^{-\Delta H_p / 3kT} P(O_2)^{1/6} \tag{4}$$

which is in excellent agreement with the experimental results. This is the same model proposed by Su *et al.* (*12*). Thus it appears that the excess oxygen occupies interstitial sites and that the oxygen interstitials and the corresponding holes are the major defects over the entire range of experimental conditions studied. The conductivity shows no significant temperature dependence for these equilibrium conditions.

The thermoelectric power of La₂CuO₄ was measured within the same experimental range and the results are shown in Fig. 2 in the form of the normalized Seebeck coeffi-
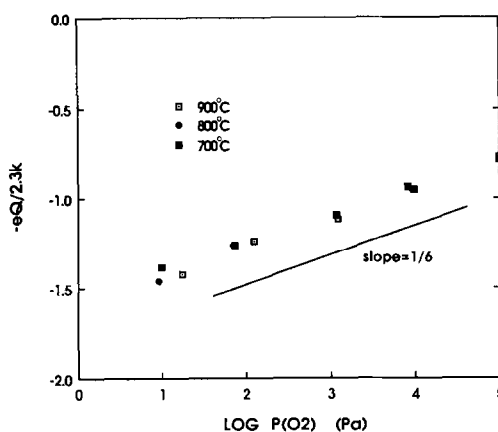

FIG. 2. Normalized Seebeck coefficients of undoped La₂CuO₄ as a function of oxygen partial pressure at 700–900°C.

cient, which is proportional to the log of the carrier concentration, as a function of log $P(O_2)$. The results are again similar to those reported previously (12, 13), although the magnitudes of our coefficients agree best with those of Tsai et al. (13). The Seebeck coefficient is always positive, in accord with the expected p-type conductivity. It is also proportional to $P(O_2)^{1/6}$, as was the conductivity, indicating that the hole mobility is independent of the defect concentration. It is important to note that both the conductivity and the carrier concentration are essentially independent of temperature. This implies that ΔH_p, the enthalpy of the oxidation reaction, is near zero and that the hole mobility has little or no temperature dependence. These points will be discussed in greater detail later.

The equilibrium conductivity of La_2CuO_4 follows the same $P(O_2)$ dependence down to the lowest partial pressures shown. There is no indication of a transition to a regime where holes and oxygen interstitials are not the major charged defect species. For $P(O_2)$ values below about 10^{-3} Pa it is very difficult to obtain reproducible conductivities, and this is assumed to be associated with a decomposition of the compound. Thus the stoichiometric composition of La_2CuO_4 does not appear to be stable at these temperatures, and the presence of either interstitial oxygen or holes in the valence band may be necessary to stabilize the structure. Su et al. (12) have collected the available information on the amount of excess oxygen as a function of $P(O_2)$ and have shown that it continues to follow the $P(O_2)^{1/6}$ dependence up to 23 kbars, the highest pressure for which data are available. At that pressure the composition corresponds to the formula $La_2CuO_{4.05}$.

The defect chemistry of La_2CuO_4 can be viewed as a narrow range of a generalized Kroger–Vink diagram of the type shown in Fig. 3, where anion Frenkel defects are assumed to be the preferred type of intrinsic ionic disorder and the band gap is assumed
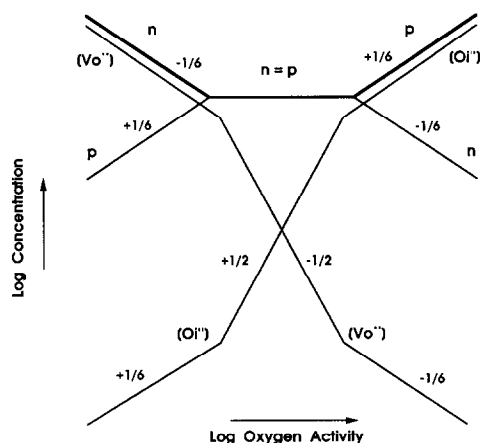

FIG. 3. Schematic equilibrium defect diagram for an ideally pure oxide with $K_i = np \gg K_F = [V_O^{\cdot\cdot}][O_i'']$.

to be smaller than the enthalpy of formation of anion Frenkel disorder. The stability range of La_2CuO_4 exists only at the far right-hand side of this diagram, where holes and oxygen interstitials are the major defects.

The Structural Accommodation of Excess Oxygen in La_2CuO_4

La_2CuO_4 has the K_2NiF_4 structure in which single perovskite-type layers are separated by a double sequence of NaCl-type layers, as shown in Fig. 4. This corresponds to the first member, $n = 1$, of the Ruddlesden–Popper sequence of structures that have the generic formula $AO–nABO_3$ (15). It has been shown that this sequence is a special case with $m = 1$ of a more general family of structures involving coherent intergrowths of the NaCl and perovskite structures with the generic formula $mAO–nABO_3$ (16). Most of the Bi- and Tl-containing superconducting cuprates also belong to this family of structures. Since these are relatively close-packed structures, it may seem unlikely that they can accommodate oxygen on interstitial sites. The interstitial site suggested by Jorgensen et al.,
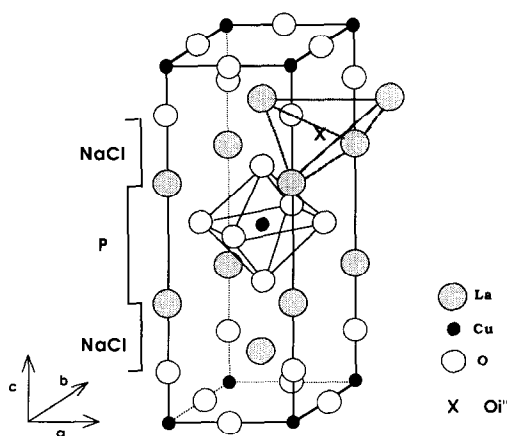
FIG. 4. Crystal structure of La₂CuO₄ showing the position of interstitial oxygen (×).

based on their neutron diffraction study of the isostructural La_2NiO_4, is indicated by " × " in Fig. 4 (*14*). It corresponds to the tetrahedrally coordinated interstitial site in the NaCl part of the structure. In the ideal NaCl structure, this site can accommodate an ion with a radius that is 0.225 that of the close-packed anions, but the NaCl layer in La_2CuO_4 is far from ideal because the cations and anions are nearly the same size, 0.134 nm for La^{3+} (9-coordinate) and 0.126 for O^{2-} (6-coordinate) (*17*). Thus the interstitial site takes on more of the appearance of a body-centered cubic interstice, in which the diameter of the ideal interstice is 0.732 times that of the cubic ions. From the ionic radii listed above, this interstice can accommodate an ion with a radius of 0.095 nm, while from the lattice dimensions of La_2CuO_4 (*9*), the ideal size of the interstitial ion is 0.094 nm. Moreover, the La–O distance for the interstitial ion is then 0.229 nm, which is very close to the closest La–O separation of 0.230 nm in the lattice (*18*). Jorgensen *et al.* also found that the first coordination sphere around the interstitial oxygen in La_2NiO_4 is slightly distorted so that the surrounding oxide ions have moved away from the interstitial (*14*). If it is assumed

that the amount of distortion is similar in La_2CuO_4, about 6% in the face-diagonal direction, the radius of the interstitial site is increased to about 0.104 nm, and the La–O separation for the interstitial is then 0.238, larger than the shortest La–O distance in the La_2CuO_4 lattice. Thus the size of the interstitial site in the NaCl layer of La_2CuO_4 is adequate for the accommodation of an interstitial oxide ion.

It may also be noted that the NaCl layer carries a net positive charge relative to the perovskite layer and hence is particularly receptive to the introduction of a negatively charged defect. While in the isostructural compound Sr_2TiO_4, or $2SrO–TiO_2$, the NaCl layers are made up of electrically neutral SrO, and the perovskite layers from electrically neutral $SrTiO_3$, in La_2CuO_4 these layers consist of LaO^+ and $LaCuO_3^-$, respectively. In addition, Goodenough and Manthiram have pointed out that there is a substantial mismatch in bond lengths between the perovskite and NaCl layers in La_2CuO_4, such that the perovskite layer is under compression and the NaCl layer is under tension (*19*). The incorporation of oxygen interstitials in the NaCl layer is thus favored by the tensile stress in that part of the lattice. This interaction with imbalances in both stress and charge by the oxygen interstitials, plus the attraction of the net negative charge in the perovskite layer for the introduction of positively charged holes into Cu states, may explain the tendency for La_2CuO_4 to favor oxygen excess over oxygen deficiency, as well as the observation that the stoichiometric composition does not seem to be stable under equilibrium conditions.

Electrical Properties

It was shown in Figs. 1 and 2 that the equilibrium conductivity and the Seebeck coefficient are both relatively independent of temperature, indicating that the enthalpy
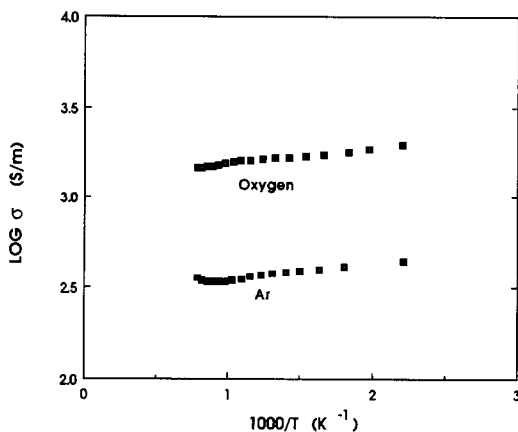
FIG. 5. Electrical conductivities as a function of temperature for undoped La_2CuO_4 in 1 atm O_2 and Ar.

of oxidation, ΔH_p, is near zero and that the hole mobility has little if any temperature dependence. The latter has been explored further by measurement of the same two parameters over the extended temperature range of 200–1000°C in fixed atmospheres of oxygen or argon at 1 atm. The oxygen content of the argon is in the range 10–100 ppm (1–10 Pa). As shown in Figs. 5 and 6, the conductivity increases slightly with
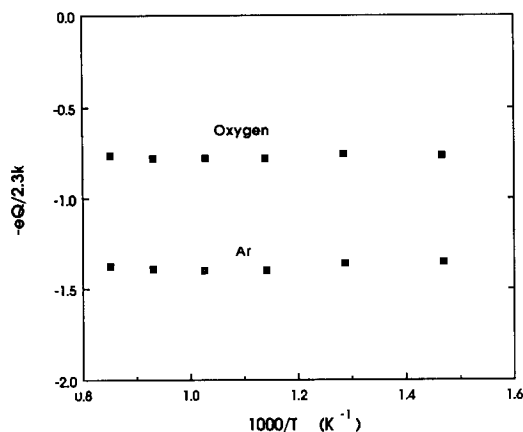

FIG. 6. Normalized Seebeck coefficients as a function of temperature for undoped La_2CuO_4 in 1 atm O_2 and Ar.

decreasing temperature, as would be expected for metallic-type conductivity with a constant carrier concentration. The thermopower measurements confirm that the hole concentration is essentially independent of temperature. It thus appears that the hole mobility increases slightly with decreasing temperature, as is characteristic of band conduction. Jorgensen et al. have reported a composition of $La_2CuO_{4.01}$ for material equilibrated in 1 atm of oxygen at 900°C (9). Based on extrapolation of this value to the lowest oxygen pressures at which stable conductivities could be measured, this material appears to be unstable for oxygen contents below $La_2CuO_{4.001}$. Based on the presence of two holes per excess oxygen, and our experimental results, the hole concentration can be expressed as

$$p = 3.08 \times 10^{19} P(O_2)^{1/6}\, cm^{-3}, \qquad (5)$$

where $P(O_2)$ is expressed in Pa and the mobility is given by

$$\mu = 16800 T^{-3/2}\, cm^2/V \cdot s. \qquad (6)$$

From these results, the hole mobility at 900°C is 0.42 $cm^2/V \cdot s$. This is on the borderline between what are generally considered typical values for band and small polaron conduction. Based on the lack of any indication of thermal activation for the hole mobility, the behavior most closely resembles band conduction.

The nature of the conductivity in La_2CuO_4 has been examined by a density of states versus energy diagram for σ-bonding by Singh et al. (20). They proposed that there exists an overlap between the empty split $\sigma^{*2}_{x^2-y^2}$ band and $d^2_{z^2}$ energy levels, which leads to metallic behavior. The metallic state could also be attributed to a half-filled, unsplit $\sigma^{*}_{x^2-y^2}$ band. However, for either of these models in which a substantial fraction of the uppermost occupied band is filled, the hole concentration as a function of oxygen activity would not follow the mass-action expression for the oxidation reaction.

Therefore, it is more consistent to attribute the temperature independence of the hole concentration to the observed zero enthalpy of oxidation. This can occur by a balance between the enthalpy of formation of holes and oxygen interstitials according to the expression

$$\Delta H_{\mathrm{p}} = 2E_{\mathrm{h}} + \Delta H_{\mathrm{i}}, \qquad (7)$$

where E_{h} is the enthalpy for creating a hole in the valence band and ΔH_{i} is the enthalpy of formation of an oxygen interstitial. Unless both of these contributions to the enthalpy of oxidation are zero, one of them must be negative.

Acknowledgment

References

1. J. G. BEDNORZ AND K. A. MULLER, *Z. Phys. B* **64**, 189 (1986).
2. C. W. CHU et al., *Phys. Rev. Lett.* **58**, 405 (1987).
3. R. J. CAVA et al., *Phys. Rev. Lett.* **58**, 408 (1987).
4. J. BEILLE et al., *Physica B* **146**, 307 (1987).
5. J. E. SCHIRBER et al., *Physica C* **152**, 121 (1988).
6. G. DEMAZEAU et al., *Physica C* **153**, 824 (1988).
7. R. B. VAN DOVER et al., *Phys. Rev. B* **35**, 5337 (1987).
8. D. G. HINKS et al., *Mater. Res. Soc. Symp. Proc.* **99**, 9 (1988).
9. J. D. JORGENSEN et al., *Phys. Rev. B* **38**(16), 11,337 (1988).
10. D. J. L. HONG, A. MEHTA, P. PENG, AND D. M. SMYTH, *Ceram. Trans.* **13**, 129 (1990).
11. M. PECHINI, U.S. Patent 3,330,697 (1967).
12. M. Y. SU, E. A. COOPER, C. E. ELSBERND, AND T. O. MASON, submitted for publication.
13. M. J. TSAI, E. J. OPILA, AND H. L. TULLER, *Mater. Res. Soc. Symp. Proc.* **169**, 65 (1990).
14. J. D. JORGENSEN et al., *Phys. Rev. B* **40**(4), 2187 (1989).
15. S. N. RUDDLESDEN AND P. POPPER, *Acta Crystallogr.* **11**(1), 54 (1958).
16. D. M. SMYTH, "Ceramic Superconductors II" (M. F. Yan, Ed.), p. 1, The American Ceramic Society, Westerville, OH (1989).
17. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. B* **25**, 925 (1969).
18. HK. MULLER-BUSCHBAUM, *Angew. Chem. Int. Ed. Engl.* **16**, 674 (1977).
19. J. B. GOODENOUGH AND A. MANTHIRAM, *J. Solid State Chem.* **88**, 115 (1990).
20. K. K. SINGH, P. GANGULY, AND J. B. GOODENOUGH, *J. Solid State Chem.* **52**, 254 (1984).