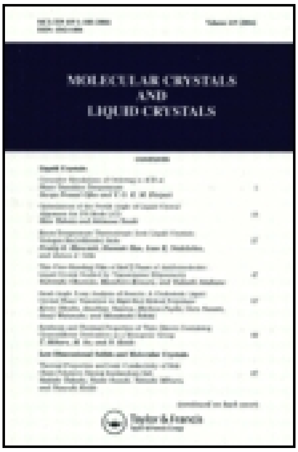

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VALENCE-DEFECT CHEMICAL EQUILIBRIA IN NONSTOICHIOMETRIC $YBa_2Cu_3O_{7-\delta}$

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Abstract Most of the superconducting oxides are nonstoichiometric. The range of homogeneity varies, but in $YBa_2Cu_3O_{7-\delta}$ it is extensive, $0 \leq \delta \leq 1$, so that the phase can serve as a prototype to illustrate the roles of chemical equilibria among the nominal valence states and defects in predicting the normal state properties. Through models which are essentially nearest-neighbor lattice statistics in the Hamiltonian, one can describe quantitatively the variation of the partial pressure of oxygen with temperature and composition. And one can predict the role of localized thermodynamic equilibrium in the transport of electrical charge.

Several measurements of the oxygen partial pressure-composition isotherms [$P_{O_2}(\delta,T)$] of $YBa_2Cu_3O_{7-\delta}$ have been reported,[1-8] but no interpretation based on the defect chemistry has been effected. In this report, we apply a defect model of nonstoichiometry to derive the energy to create vacancies and the energy of interaction between vacancies. This is a first step in eventually connecting $P_{O_2}(\delta,T)$ with conductivities and in identifying the role of chemical equilibria among the valence states and defects in the conductive mechanism.

All of the determinations derived from thermogravimetric measurements (TGA) have been summarized by Lindemer and Sutton,[7] except for two recently obtained values. An examination of the data in this compilation indicates that the structures of the isotherms are all similar. For the present purpose, we believe that it is adequate to use the data given by Lindemer et al.[7] and by Kishio et al.[8]

The partial molar enthalpy of solution of oxygen in $YBa_2Cu_3O_{6.5}$ determined from solution calorimetry is -190±20 kJ/mol.[9] Recently, Parks et al.[10] have reported measurements of the enthalpy of oxidation of $YBa_2Cu_3O_{7-\delta}$ for $0.06 \leq \delta \leq 1.03$; they obtain a constant value at -190±5 kJ/mol of molecular oxygen. The values for the enthalpies of sublimation of oxygen derived from Lindemer and Sutton's and from Kishio's data are 164 and 173 kJ/mol, respectively.

An examination of the pressure-composition isotherms obtained by TGA reveals that they cover, with no phase changes, the same range of composition as the neutron diffraction[11] data. The total fractional occupancy from the structural data and the TGA data are in reasonably good agreement. Most of the differences can be accounted for by the errors, approximately ±0.05 in the structural data and at least ±0.02 in the TGA measurements.

The features of the data indicate that the thermodynamic system is essentially that of two components, two phases (gas and solid), and two molecularities (orthorhombic and tetragonal structures) in the solid. The system is open with respect to oxygen, but closed with respect to copper, yttrium and barium. Furthermore, because the variable oxygen occurs only in the basal plane, it is plausible to represent the formula of the phase by $[YBa_2Cu_2O_6]^- [CuO_{1-\delta}]^+$.

The sublimation of oxygen can be represented by the reaction:

$$4Cu^{3+}cs + 2O^{2-}as \rightarrow 4Cu^{2+}cs + O_2(g) + 2as, \qquad (1)$$

where cs and as refer to cation site and anion site, respectively.

It is obvious that the experimental isotherms are rather simply shaped with a suggestion of an inflection near $\delta = 0.5$. Hence, a rather simple model should suffice. Because the inflection corresponds to the necessity of considering the first neighbor interactions only, one can write the Hamiltonian as Bell[12] has done but without the inclusion of second neighbors. In a very general way, one can write that each vacancy has Z neighbors, and with N_v vacancies and N_s sites and with random arrangements each site has a probability of N_v/N_s of being vacant. The average number of neighbors for a given N_v is ZN_v/N_s; this counts each pair twice. If E_{vv} is the energy of interaction between nearest-neighbor vacancies, E_{vv}/Z is the energy per pair. Hence, for E_v equal to the energy required to creat a vacancy,

$$H = E_V N_V + E_V N_V^2/N_S. \qquad (2)$$

For the degeneracy one can write

$$g = N_s!/N_v!(N_s - N_v)!. \qquad (3)$$

If g and H are substituted into the semigrand partition function and if one evaluates the maximum term, one finds with $\theta_v = N_v/N_S$:

$$\log P_{O_2} = 0.8684 \ln(1-\theta_v)/\theta_v) + \frac{4E_{vv}}{R'T}\theta_v + \frac{(-2E_v + D_T)}{R'T} + \ln(kTQ), \qquad (4)$$

where R' = 19.15 J/deg, D_T is the dissociation energy of oxygen , and Q is the partition function of O_2.

The isotherm is such that for $E_{vv}>0$ and for sufficiently low temperatures, it has a minimum and a maximum with an inflection inbetween at $\theta_v = 1/2$. Thus, under these conditions, it resembles the van der Waals' equation and is correspondingly interpreted as representing a separation into two solid phases. A least-squares' treatment with the use of this equation and the data by Lindemer et al. and by Kishio et al. yields the parameters in

TABLE I Isotherm: $\log P_{O_2} = 0.8684 \ln\left(\frac{1-\theta_v}{\theta_v}\right) + A\theta_v + K$ [See Eqn. (4)].

T	-A	K	$-E_{vv}$(kJ/mole)	E_v(kJ/mole)
773	1.794	-2.086	6.6	454 L
	3.436	-1.364	12.7	448 K
823	2.222	-1.286	8.7	460 L
	3.292	-0.753	16.4	456 K
873	2.070	-0.711	8.2	468 L
	2.722	-0.2639	11.4	464 K
973	2.844	0.737	13.2	479 L
	2.834	0.892	13.2	478 K
1073	2.196	1.146	11.3	498 L
	2.465	1.121	12.7	499 K

$E_{vv} = AR'T/4$; $2E_v = 504.6 + R'T(-K+25.12)$ kJ/mol x 10^{-3}

[See Thorn and Winslow, *J. Chem. Phys.*, *44* (1966) 2646 for RTlnkTQ].

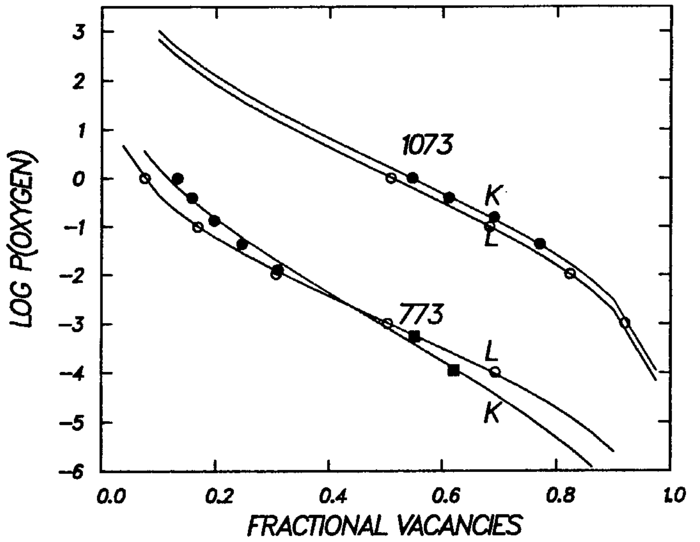

FIGURE 1 Log P_{O_2} vs fractional vacancies (δ) for $YBa_2Cu_3O_{7-\delta}$; circles are from data by Lindemer et al. (7); solid circles are from data by Kishio et al (8); solid squares are from extrapoation of log P_{O_2} vs T^{-1} by Kishio et al. Curves are derived through least-squares' analyses of the isotherms.

Table I. The isotherms are shown in Figure 1. Because all values of E_{vv} are negative with no indication of an extrapolation to $E_{vv}>0$, no phase separation is indicated.

Through the use of models similar to the one used above, except that second neighbor interactions have been included, several studies have treated the orthorhombic-tetragonal structural change as an order-disorder transition within the solid phase.[12-16] Bakker et al.[14] fitted their model equation to the lattice-parameter vs. temperature measurements of Jorgensen et al.[11] and obtained a value of -224 kJ/mol for the enthalpy of solution of molecular oxygen at 1 atm and $\delta \sim 0.4$. Bell[12] constructed a configurational Hamiltonian to describe an assembly of oxygen atoms and vacancies on a square lattice with interactions between first and second neighbors. Calculations with his model yield a variation of lattice-parameter vs. temperature which duplicates the variations for the a and b axes vs. temperature for the orthorhombic structure, but predicts constant values for the tetragonal axis; a linear decrease is observed by Jorgensen et al.[11] Kubo et al.,[15] using the same model-equations used by Bakker et al., applied their measurements of the oxygen deficiency vs temperature to trace the variation with temperature of the orthorhombic-tetragonal transition defined by the inflection in the $\delta(T)$ curves at various pressures (0.01 to 1 atm). The results predict a small decrease in the deficiency (δ) with increasing temperature, -4.7×10^{-4}/K at near 0.38.

In an investigation of the resistivity at temperatures ranging from 300° to 800°C and at pressures ranging from 0.2 to 0.0005 atm., Frietas and Plaskett[17] found breaks in ρ vs. T such that $d\rho/dT$ vs. T displays a λ-type variation. Through an Ising-type model, they interpreted the peak in the λ-type curve as the orthorhombic-tetragonal transition. A plot of ln P_{O_2} (at the transition) vs. T^{-1} of the transition is linear; the slope corresponds to an enthalpy of solution of molecular oxygen equal to -220 ± 6.8 kJ/mol.

Structural studies[18,19] show no change between 300 and 4 K. However, metastability may occur on cooling, but in any event, the structural studies and the TGA measurements probably apply to similar materials, whether they are metastable or equilibrated.

Photoelectron spectroscopic measurements indicate that the binding energies for the outer electrons on $Cu^{2+}cs$ and $O^{2-}as$ are close to each other.[20,21] Hence, the energy for the reaction (cs refers to cation sites; as refers to anion sites),

$$Cu^{2+}cs + O^{1-}as \rightarrow Cu^{3+}cs + O^{2-}as, \tag{5}$$

is small, so that if $O^{1-}as$ [or $(O^{2-}as)_2$] exists in the solid, then so does $Cu^{3+}cs$. In addition, one surmises that the vacancies can become negatively charged, so that the reaction,

$$O^{2-}as + as \rightarrow O^{1-}as + as^{1-} \qquad (6)$$

may have a small energy. The two equilibria make possible the thermally activated transfer of charge along the long and short axes, respectively, in the basal plane; the second makes possible the transfer of charge in the tetragonal structure under thermodynamically established equilibria. Thus, a thermally activated, dynamic charge transfer should exist in the Cu-O network in the basal plane so that if electrons or holes are injected into one end of the network (under a potential gradient and reversible conditions), they are ejected from the other because the chemical equilibrium cited above must be maintained locally. In a sense, there is a flux of local chemical thermodynamic equilibria during conduction.

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