

Direct Calorimetric Determination of Energetics of Oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_x$

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The enthalpy of oxidation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($5.97 \leq x \leq 6.94$) was measured directly by high-temperature reaction calorimetry. The partial molar enthalpy of oxygen dissolving in the structure is constant at -237 ± 5 kJ/mole O_2 over the whole composition range. No change in $\Delta\bar{h}_{\text{O}_2}$ is observed at either the tetragonal/orthorhombic transition or at $x = 6.5$, the composition in which all copper could be divalent. This behavior supports structural models in which the change in speciation from $x = 6$ to $x = 7$ is very gradual, with Cu^+ and Cu^{3+} (or their electronic equivalents in the oxygen p -band) coexisting in concentrations which vary smoothly with composition. It is also consistent with models which consider the solid solution series to be a complex intergrowth of microdomains of oxidized and reduced end members. The observations rule out that the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is any sort of "titration endpoint" with very different defect chemistry on either side. © 1989 Academic Press, Inc.

Introduction

Since late 1986, the crescendo of excitement and blizzard of publications in high T_c oxide superconductors have placed solid-state chemistry in a new perspective. To date, three families of superconducting compounds, all containing perovskite-re-

lated structural elements, have been found. The first is a series of doped materials based on the K_2NiF_4 structure (1-3). Starting with the composition La_2CuO_4 , doping with a large alkaline earth results in a series of compounds $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-t}$ or $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-t}$. The substitution of Sr^{2+} for La^{3+} is charge-compensated by the conver-

sion of Cu^{2+} to Cu^{3+} , at least in terms of formal oxidation state. However, loss of some oxygen converts part of the Cu^{3+} back to Cu^{2+} . The second group of compounds is the so-called 1:2:3 materials, $\text{YBa}_2\text{Cu}_3\text{O}_x$ (4, 5). The oxygen content x varies between limits of approximately six and seven corresponding, nominally, to 2Cu^{2+} and 1Cu^+ for $x = 6$ and to 2Cu^{2+} and 1Cu^{3+} for $x = 7$. The structure again is related to perovskite, and oxygen content is controlled by temperature and oxygen fugacity (6–9). Systematic vacancy formation appears essential to the structure and defines two sets of oxygen sites, one which contains mainly or entirely Cu^{2+} and one which is quite variable in oxygen coordination and seems to accommodate the changing average copper oxidation state. The third class of materials, having the highest critical temperatures (>120 K) of any discovered thus far, are complex oxides with alkaline earths (Ca, Ba) and large ions other than rare earths, namely Bi and Tl (3, 10). They are layer structures analogous to previously known phases (11), with superconductivity related to the number of copper planes sandwiched between perovskite-like layers.

Rather little is known yet about the thermodynamic properties of these new materials. Thermodynamic stability involves at least three questions—namely, stability with respect to other phases in the multi-component (typically 3–5 component) oxide systems to which these phases belong, stability with respect to reactions with water and carbon dioxide (a major problem for Ba-rich phases), and stability with respect to oxygen content within a homogeneous solid solution. The first two questions have received some attention in the Y–Ba–Cu–O system. Studies relating oxygen fugacity, temperature, and oxygen content, x , in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ have been reported, and the tetragonal–orthorhombic transition has been mapped as a function of T , x , and P_{O_2} (6–9).

It is clear that the highest values of x (and highest T_c) are achieved by low-temperature anneals, but it is not certain whether these oxygen-rich phases are stable or are metastable with respect to decomposition to other phase assemblages at 300–500°C. Heats of formation and of some chemical reactions involving $\text{YBa}_2\text{Cu}_3\text{O}_x$ and La_2CuO_4 have recently been measured by acid solution calorimetry (12).

The purpose of the present work is to explore the energetics of oxygen stoichiometry in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ system using high-temperature reaction calorimetry. This is a sensitive tool for determining the dependence of partial molar enthalpy of oxygen on composition. That dependence, in addition to providing useful thermochemical data, may help relate changes in chemical bonding to difference in average oxidation state and in crystal symmetry. Such understanding is relevant to understanding the detailed crystal chemistry and possible mechanisms of electron transport and superconductivity.

Experimental Procedures

Sample preparation and analysis. Samples were obtained from three sources. A series of samples was prepared from reagent-grade BaCO_3 , Y_2O_3 , and CuO by E. Takayama-Muromachi at NIRIM in Japan. After preliminary heating and grinding, 1-g batches were equilibrated in small alumina tubes in a vertical furnace at the desired temperature and atmosphere for 10 hr or more and then quenched into liquid nitrogen. They were analyzed by wet chemical analysis (iodometry). Results are shown in Table I. A second set of several samples was prepared by P. K. Davies of the University of Pennsylvania by annealing previously synthesized samples with $x = 6.98$ for 16 hr at temperatures ranging from 400 to 850°C under Cu-gettered flows of high-purity argon (see Table I). A third set of sam-

TABLE I
PREPARATION AND ANALYSIS OF $\text{YBa}_2\text{Cu}_3\text{O}_x$
SAMPLES

Source	Annealing		Oxygen content (x)
	T (°C)	Atmosphere	
AJ ^a	600–650	Sealed tube	5.97
ETM	850	N ₂	6.01
PD	875	Ar	6.02
AJ	600–650	Sealed tube	6.04
AJ	600–650	Sealed tube	6.11
ETM	980	Air	6.10
AJ	600–650	Sealed tube	6.20
ETM	900	Air	6.20
ETM	850	Air	6.22
PD	550	Ar	6.31
AJ	600–650	Sealed tube	6.35
ETM	800	Air	6.30
ETM	750	Air	6.25
ETM	779	Air	6.36
AJ	600–650	Sealed tube	6.42
ETM	700	Air	6.43
ETM	650	Air	6.49
PD	450	Ar	6.60
ETM	600	Air	6.62
ETM	550	Air	6.62
AJ	600–650	Sealed tube	6.64
AJ	600–650	Sealed tube	6.79
ETM	500	Air	6.82
AJ	600–650	Sealed tube	6.94
ETM	400	Air	6.88
ETM	300	O ₂ , slow cooled	6.93

^a AJ, Allan Jacobson's samples; ETM, Eiji Takayama-Muromachi's samples; PD, Peter Davies' samples.

ples, made by Allan Jacobson of Exxon, had somewhat different thermal histories. Previously prepared and analyzed end members, with $x = 5.97$ and $x = 6.94$, were mixed in known proportions, sealed in silica tubes, annealed at 600–650°C for 16 hr, and then cooled slowly (16–24 hr) to room temperature. The stoichiometry of the mixture fixed the stoichiometry of the final product, whose composition was checked by thermogravimetry (see Table I).

It is worth noting that the three sets of samples were synthesized and analyzed

completely independently in three different laboratories. The precision of the reported oxygen contents is ± 0.01 to ± 0.02 , but there may be a slight systematic difference (of ± 0.03 to ± 0.04) between the oxygen contents reported by Takayama-Muromachi and by Jacobson (see below).

X-ray studies. X-ray measurements were performed on a Scintag Pad V automatic diffractometer using $\text{CuK}\alpha$ radiation and a solid-state detector. Background correction was done together with stripping the $\text{K}\alpha_2$ peaks. Lattice parameter measurements were performed with a scan rate of $0.5^\circ 2\theta$ per minute and a chopper increment of $0.02^\circ 2\theta$. Peak positions were corrected and calculated using the first four lines of metallic aluminum ($a = 4.0494 \text{ \AA}$ at 23°C) as an internal standard. The lattice dimensions were refined by a version of the Appelman and Evans least-squares procedure using 20 reflections.

Calorimetry. The aim of the calorimetric experiments was to convert a sample with a given value of x (obtained by quenching or sealed tube synthesis) into one with a known, reproducible, and rapidly attained value of x attained by dropping the sample into a calorimeter operating in air at a high temperature. Preliminary TGA experiments showed that oxygen equilibration was obtained in less than 15 min at 780°C regardless of whether initial samples were more or less oxidized than this value. Thus 784°C afforded a convenient calorimetric temperature at which a Calvet-type microcalorimeter (13) was already operating in Navrotsky's laboratory. For the transposed-temperature-drop experiments, 25-mg samples of $\text{YBa}_2\text{Cu}_3\text{O}_x$ were placed in Pt crucibles made of 0.0001-mm-thick foil approximately 3 mm in diameter by 10 mm long. These crucibles or pouches were closed by folding over their top edge. This prevented sample from spilling out during the drop, but did not limit gas access. The crucibles were then dropped from room

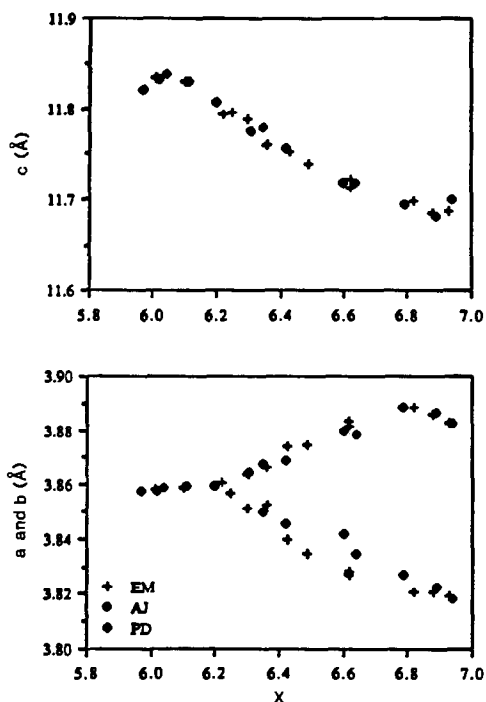


FIG. 1. Lattice parameters versus composition for $\text{YBa}_2\text{Cu}_3\text{O}_x$ phases.

temperature into the calorimeter at 784°C . Sample drops were sometimes alternated with calibration drops, in which similar capsules, containing dry well-crystallized Al_2O_3 powder (corundum), were used. In addition, calibrations using capsules with Al_2O_3 and using cylindrical Pt weights were performed separately from the drop experiments. The general method has been described previously (13, 14).

The measured heat effect consisted of three contributions: the heat content of the platinum, that of the sample, and the enthalpy of oxidation (exothermic, for $x < 6.36$) or reduction (endothermic, for $x > 6.36$). The heat effect due to Pt was about 30% of the total measured enthalpy.

The composition of samples once they were dropped into the calorimeter could not be checked directly because the capsules could not be retrieved quickly enough

from the calorimeter to prevent reequilibration on cooling. A capsule identical to that used for calorimetry was placed in a TGA and heated at about $35^\circ\text{C}/\text{min}$ (the maximum heating rate attainable) to 784°C . By the time 784°C was reached (about 20 min), the weight already indicated equilibrium, and no further weight changes were seen. Since, during calorimetry, each experiment lasts 30–35 min, with the sample at 784°C for all this time, it is likely that the oxidation or reduction is complete in the first 10 min or less. The shape of the calorimetric curves also indicates rapid reaction, with no secondary step related to oxidation–reduction detectable after the initial heat pickup. Indeed virtually all experiments looked normal, with rapid return to instrumental baseline. Five to twelve experiments were performed for each composition. The standard deviation of the mean (see Table II) was generally less than 1%.

Results and Discussion

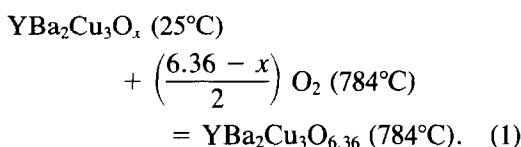
Lattice Parameters

Measured lattice parameters are shown in Fig. 1. All the compounds analyzed were single phase orthorhombic or tetragonal belonging, respectively, to the $Pmmm$ or $P4/mmm$ space groups. Lattice parameters for different samples fall on a common trend well although there may be a small systematic offset (0.03 to 0.04 in x) between the Takoyama-Muromachi and Jacobson samples. This might be related to a difference in the structural state (vacancy ordering) between quenched and slowly cooled samples but more likely represents a small systematic difference in oxygen analysis. In our study, the tetragonal–orthorhombic transformation is seen in quenched samples slightly below $x = 6.3$. This is somewhat lower than reported by others (6–9), who place the transformation about $x = 6.4$. In our three samples, $x = 6.36$ (ETM), 6.35

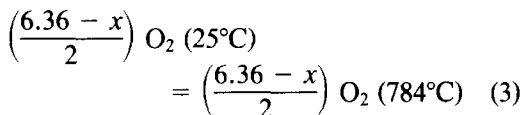
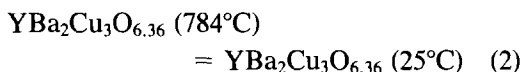
(AJ), and 6.30 (ETM), the (200) reflection near $47^\circ 2\theta$ ($\text{CuK}\alpha$ radiation) is obviously split, which we have interpreted as the (020) and (200) peaks of the orthorhombic modification. Because the X-ray patterns are based on $\text{CuK}\alpha_1$ radiation only, the observed splittings are not α_1 - α_2 doublets. The exact composition at which the peak splitting is observable may be quite sensitive to sample preparation, quench rate, and the diffractometer used. The reasons for our rather low value of x for the transition are not obvious. Our X-ray data were taken at room temperature on a rather sensitive new diffraction system. We may have picked up the beginning of peak splittings earlier than for samples run on diffraction systems with lower signal-to-noise. Alternately, differences in preparation conditions may be responsible, but since all three sets of samples we used, which were prepared somewhat differently, gave concordant results, this is perhaps less likely.

Calorimetry

Results are shown in Table II. The measured enthalpy (J/g) refers to the reaction



This may be related to an isothermal process, oxidation at 25°C , by the following thermodynamic cycle.



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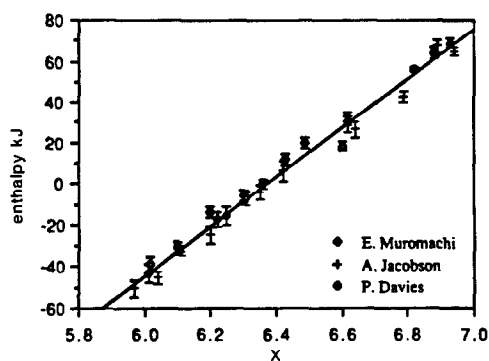
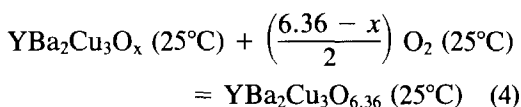
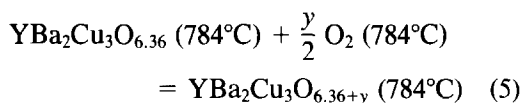


FIG. 2. Enthalpy of oxidation or reduction for reaction (4) at 298 K as measured by high-temperature calorimetry.

with $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$. ΔH_1 can be calculated per mole $\text{YBa}_2\text{Cu}_3\text{O}_x$ from the data in Table II. ΔH_2 is the negative of the measured enthalpy (per mole) for the one composition which neither reduces nor oxidizes at 784°C ($x = 6.36$). ΔH_3 is the enthalpy of $(6.36 - x)/2$ moles of oxygen gas, readily obtained from standard tables (15). Resulting values of ΔH_4 are given in Table II and Fig. 2.

We should consider one potential source of ambiguity in our data. Suppose the composition of the equilibrated samples in the calorimeter was not 6.36 but some slightly different value, $6.36 + y$ (y either positive or negative). This might conceivably be the case if the high T oxidation state was not completely quenchable. As long as all samples equilibrated rapidly to the same oxygen content (same value of y), as the rapidity of equilibration in the TGA suggests, the thermochemical cycle which sums to reaction (4) would still be valid, since one would then add an oxidation-reduction step



to reaction (1) and subtract it from reaction (2). The composition 6.36 is really an arbitrary

TABLE II
LATTICE PARAMETERS AND CALORIMETRIC RESULTS

Composition (x)	Lattice Parameters (Å)			Enthalpy	
	a	b	c	Observed J/g	kJ/mole
5.97 (AJ) ^a	3.8578(7)		11.8211(31)	286.7 ± 6.0(8) ^b	-50.4 ± 4.6 ^c
6.01 (ETM)	3.8583(6)		11.8344(13)	297.0 ± 7.1(12)	-43.1 ± 5.2
6.02 (PD)	3.8578(4)		11.8318(15)	303.2 ± 1.7(6)	-38.8 ± 2.6
6.04 (AJ)	3.8587(4)		11.8373(21)	292.8 ± 4.6(6)	-45.3 ± 3.8
6.10 (ETM)	3.8586(4)		11.8305(13)	313.2 ± 4.7(6)	-30.9 ± 3.9
6.11 (AJ)	3.8592(1)		11.8293(5)	310.8 ± 2.7(6)	-32.4 ± 2.9
6.20 (AJ)	3.8598(4)		11.8077(19)	320.4 ± 6.1(6)	-24.6 ± 4.7
6.20 (ETM)	3.8594(4)		11.8068(16)	336.5 ± 3.6(6)	-14.0 ± 3.3
6.22 (ETM)	3.8607(7)		11.7939(21)	330.9 ± 5.1(6)	-17.3 ± 4.1
6.25 (ETM)	3.8572(5)		11.7959(18)	332.6 ± 6.9(12)	-15.7 ± 5.1
6.30 (ETM)	3.8514(15)	3.8640(12)	11.7889(28)	346.0 ± 4.4(12)	-6.0 ± 3.8
6.31 (PD)		3.8643(7)	11.7761(28)	344.2 ± 3.0(7)	-7.0 ± 3.1
6.35 (AJ)	3.8502(12)	3.8675(13)	11.7798(15)	347.5 ± 5.4(6)	-4.1 ± 4.3
6.36 (ETM)	3.8525(21)	3.8666(16)	11.7605(40)	353.5 ± 3.7(8)	0.0 ± 3.4
6.42 (AJ)	3.8454(7)	3.8688(9)	11.7563(18)	361.4 ± 7.2(6)	+6.2 ± 5.4
6.43 (ETM)	3.8400(16)	3.8742(15)	11.7528(38)	369.5 ± 4.2(8)	+11.8 ± 3.7
6.49 (ETM)	3.8349(6)	3.8747(6)	11.7403(15)	380.1 ± 4.4(5)	+19.8 ± 3.8
6.60 (PD)	3.8415(13)	3.8795(19)	11.7185(75)	374.5 ± 2.0(10)	+18.2 ± 2.7
6.62 (ETM)	3.8283(5)	3.8814(4)	11.7227(20)	393.1 ± 3.0(6)	+30.8 ± 3.1
6.62 (ETM)	3.8270(5)	3.8833(5)	11.7131(20)	391.9 ± 6.7(8)	+30.0 ± 5.1
6.64 (AJ)	3.8347(16)	3.8785(36)	11.7191(28)	386.2 ± 5.9(6)	+26.6 ± 4.6
6.79 (AJ)	3.8273(3)	3.8886(3)	11.6938(11)	406.5 ± 4.0(6)	+42.8 ± 3.5
6.82 (ETM)	3.8212(9)	3.8888(7)	11.6989(13)	425.4 ± 1.8(6)	+56.0 ± 2.7
6.88 (ETM)	3.8208(10)	3.8858(16)	11.6841(22)	463.3 ± 3.9(6)	+64.3 ± 3.5
6.89 (AJ)	3.8226(11)	3.8864(9)	11.6803(24)	440.3 ± 4.6(6)	+67.2 ± 3.8
6.93 (ETM)	3.8195(6)	3.8831(17)	11.6871(41)	441.5 ± 3.6(6)	+68.7 ± 3.4
6.94 (AJ)	3.8184(9)	3.8832(7)	11.6991(44)	435.6 ± 2.5(6)	+65.1 ± 2.9

^a AJ, Allan Jacobson's samples, TGA analysis; ETM, Eiji Takayama-Muromachi's samples, analysis by iodometry; PD, Peter Davies' samples, analysis by TGA.

^b Error is twice the standard deviation of the mean; the number in parentheses is the number of experiments performed. The effect due to Pt has been subtracted.

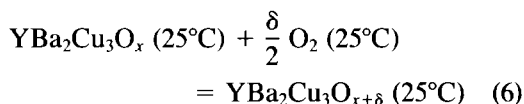
^c Error calculated by propagation of errors for a given sample and a sample with $x = 6.36$; see text.

trary reference state, and we could have written the reaction referred to some other composition, for example, the most oxidized or most reduced. However, the cycle as written is conceptually useful since it stresses that during the calorimetric experiment some samples are oxidized and others reduced. What is important for further discussion is the slope of the enthalpy relation in Fig. 2; that would be the same regardless of the choice of the reference state.

The figure shows several striking features. First, the data for three different sets of samples coincide reasonably well, although there may be a small systematic offset between those prepared by fast quench and by slow cooling in sealed tubes. This might represent a difference in structural state (vacancy ordering) but it more likely represents a small systematic difference (of $x = 0.02$ to 0.04) in oxygen analysis. On the whole, it is the agreement among various

samples, rather than their differences, which is noteworthy.

Second, the enthalpy of oxidation is best represented by a straight line. The slope of that line gives the partial molar enthalpy of oxygen (per mole O) reacting with the structure. We calculate thermodynamic parameters for the reaction



Twice the slope gives -237 ± 5 kJ/mole as the partial molar enthalpy of O_2 , in good agreement with the values of -200 to -221 kJ/mole estimated from the temperature dependence of oxygen content (16) and of -190 ± 20 kJ/mole estimated from calorimetric cycles involving solution of several samples in aqueous acid (12). Because the present values are measured by a more direct thermochemical cycle and because they cover a large number of compositions, these data can be considered more detailed and accurate than previous work.

A more detailed analysis of the data from the several different sets of samples is summarized in Table III. All the samples taken together (27 samples), E. Takayama-Muro-machi's 14 samples, and A. Jacobson's 10 samples taken separately give partial molar enthalpies of oxygen in the range -237 to -241 kJ/mole O_2 .

The linearity of enthalpy with composition means that the enthalpy of oxidation, and the partial molar enthalpy of oxygen, is constant throughout the entire range of stoichiometry. There are neither steps in the enthalpy nor changes in slope at the orthorhombic-to-tetragonal transition which, for these samples (see lattice parameters in Fig. 1), is near $x = 6.3$. Thus, if the orthorhombic-tetragonal transition is first order, its enthalpy is less than the resolution of our measurements, namely about ± 4 kJ/mole of $\text{YBa}_2\text{Cu}_3\text{O}_x$. This small en-

TABLE III
ANALYSIS OF ENTHALPY DATA FOR SEVERAL SETS
OF SAMPLES

Data set	Enthalpy of reaction (4) (kJ/mole)	$\Delta \bar{h}$ of O_2 (kJ/mole)
All	$-755.1(\pm 16.8) + 118.5(\pm 2.6)x$	-237.0
ETM samples, iodometry	$-758.9(\pm 13.1) + 119.5(\pm 2.0)x$	-239.0
AJ samples, TGA analyses	$-771.0(\pm 20.9) + 120.6(\pm 3.2)x$	-241.2

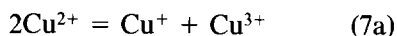
thalpy of transition is not surprising when one considers the small magnitude of enthalpies of distortional transitions in other perovskite-related components, e.g., 0.1 kJ/mole in BaTiO_3 (16). If the transition from orthorhombic to tetragonal were higher order, rather than a step in the enthalpy of oxidation, one might expect a change in slope in the enthalpy curve. Once more, no change is seen, and the partial molar enthalpy of oxygen in the two structures is essentially the same. Another possibility is that the higher symmetry phase in fact has lower symmetry on the unit cell scale, with the tetragonal symmetry being an average seen by X-rays because of extensive twinning. Then in terms of local oxygen environments, no sharp phase transition would really exist.

Equally striking is the lack of any discontinuity or change in slope near $x = 6.5$, the composition at which all the copper could nominally be divalent. For $x < 6.5$, oxidation formally represents the reaction $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$; for $x > 6.5$, oxidation formally represents the reaction $\text{Cu}^{2+} \rightarrow \text{Cu}^{3+}$. The calorimetric data strongly suggest that the enthalpy of oxidation is the same on both sides of $x = 6.5$. The correct description of actual species in the copper superconductors is still a subject of active discussion. In terms of formal valence states, the description using Cu^+ , Cu^{2+} , and Cu^{3+} follows the more ordinary chemical custom. Other descriptions, involving Cu^+ , Cu^{2+} , and O^- (holes in the oxygen $2p$ -band), have also been suggested (22-24), as have models in-

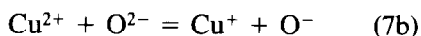
volving species such as O_2^- (23). We illustrate below that our calorimetric data are generally consistent with models which predict a gradual change in electron distributions with increasing x , with no major change in species present at $x = 6.5$.

The constant partial molar enthalpy of oxygen could arise in several ways. One possibility is that the enthalpy of oxidation of Cu^+ to Cu^{2+} is identical to that of Cu^{2+} to Cu^{3+} , but that the oxidation occurs stepwise with Cu^{2+} the only species present at $x = 6.5$. This seems an unlikely coincidence, especially since Cu^+ and Cu^{2+} are common oxidation states while Cu^{3+} occurs only under special conditions in other oxides. If the equilibrium were between Cu^+ , Cu^{2+} , and O^- , then the above argument could be rephrased to require that the enthalpy of oxidation of Cu^+ to Cu^{2+} is the same as the enthalpy of formation of O^- from O^{2-} , with Cu^{2+} again the only species present at $x = 6.5$. This seems equally unlikely.

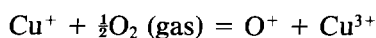
A second possibility is that the disproportionation reaction



or



occurs significantly even at the stoichiometric composition ($x = 6.5$). Thus that composition does not represent a unique compound with only one valence state but is simply one point in a gradual progression where, with increasing x , the amount of Cu^+ decreases and the amount of Cu^{3+} (or of O^-) increases. A defect model has been proposed by Su *et al.* (19) which is based on Cu^+ , Cu^{2+} , and Cu^{3+} . It is supported by measurements of thermoelectric power and electrical conductivity. This model gives an equilibrium constant for reaction (7a), $K_d = 0.40$ (independent of T , x), and for

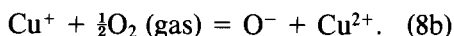


$$\ln K_{ox} = -10.08$$

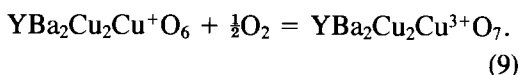
$$+ 10885/T \text{ (independent of } x). \quad (8a)$$

Therefore, for reaction (8a), $\Delta G^\circ = -90498 + 83.81 T$ (J/mole) and $\Delta H^\circ = -90500$ J/mole, $\Delta S^\circ = 83.8$ J/mole \cdot K.

In terms of O^- instead of Cu^{3+} , Eq. (8a) would be



The oxidation can also be represented by the reaction



From the calorimetric measurements, ΔH° for reaction (9) is -118.5 ± 2.5 kJ/mole, in reasonable agreement with the -90.5 kJ above. The entropy of oxidation, -83.8 J/mole \cdot K per mole O, is in the range commonly seen for many oxidation reactions, -92 ± 17 J/mole \cdot K, as discussed by Navrotsky (20).

Can one reconcile an equilibrium between Cu^+ , Cu^{2+} , and Cu^{3+} (or between Cu^+ , Cu^{2+} , O^{2-} , and O^-) and the observed linear variation of enthalpy with composition? Because of the small temperature dependence of K_d seen by Su *et al.* (19), and the relatively small range of temperatures over which K_d was studied, one cannot reliably separate enthalpy and entropy terms for the disproportionation reaction. If K_d was truly temperature-independent, then reaction (7a) or (7b) would be athermal, with $\Delta H = 0$ and entropy effects alone driving the disproportionation. Then the enthalpy of oxidation would not be influenced by the degree of disproportionation, and a strictly linear variation of enthalpy with x would occur.

For illustrative purposes, consider the other extreme case, namely that the equilibrium constant is dominated by the enthalpy term. Then, with $K_d = 0.4$ and $T = 750$ K,

$$\Delta G^\circ \sim \Delta H^\circ = -RT \ln K_d = +5.7 \text{ kJ/mole.} \quad (10)$$

For the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, Su *et al.* (19) suggest that the site which would contain 1 mole of Cu^{2+} if there was no dissociation actually contains 0.4 mole of Cu^{2+} and 0.3 mole each of Cu^+ and Cu^{3+} . The degree of dissociation is thus 60% and, if the enthalpy of dissociation was 5.7 kJ/mole, an enthalpy of $0.4 \times 5.7 = 2.3$ kJ/mole would be subtracted from the observed enthalpy of oxidation of account for the back-reaction to form Cu^{2+} . This would be at the level of resolution of the calorimetric data and would not produce definitely detectable curvature in the plot of enthalpy of oxidation versus x . At other values of x , this correction term would be even smaller. Thus the above defect model is consistent with the calorimetric results.

If the above defect model was rephrased in terms of Cu^+ , Cu^{2+} , O^{2-} , and O^- as species, it is not clear whether that formulation could satisfactorily explain all of Su *et al.*'s electrical measurements. Such a formulation, with equilibrium constants for reactions (7b) and (8b) similar to those for (7a) and (8a), respectively, would be consistent with the calorimetry by arguments similar to those above. Thus the calorimetric results cannot be used to distinguish a defect structure involving discrete Cu^+ , Cu^{2+} , and Cu^{3+} species from models containing holes in the oxygen p -band, or from several other possible models. However, the calorimetric results show conclusively that the composition $x = 6.5$ is not energetically unique, and is not a titration equivalence point separating two regions of strikingly different defect chemistry.

Galy *et al.* (21) describe the $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$ system as "triperoykite" derived phases showing extended oxygen defects and yttrium/barium ordering. In their scheme, phases between $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ are generally intergrowths of regions of

discrete compositions. These intermediates, rather than representing a homogeneous solid solution, are more like intergrown two- (or multi-) phase mixtures. A linear enthalpy for such a series might then be expected as the result of "mechanical" mixing of different microphases. This structural model predicts powder X-ray patterns satisfactorily and is consistent with our thermochemical measurements.

Indeed the reports of locally ordered structures close to $x = 6.5$ tend to support the occurrence of disproportionation at these compositions. It has been suggested that ordered superstructures observed in the electron microscope for oxygen-deficient samples result from systematic absences of the copper chains (17, 18). For example, for $x = 6.5$, removing the oxygen ions from every other Cu chain leads to a doubling of the cell along the a direction. The local geometry of the copper ions in these ordered structures is such that half the copper ions are in square-planar coordination, with the remaining ions in the vacant chains adopting linear coordination. Because two-fold coordination is the stable coordination for Cu^+ , it seems likely that for $x = 6.5$, while the overall Cu valence is 2, the average valence of Cu in the chains is 1.5, allowing the sheets to maintain an average valence in excess of 2 (2.25 for $x = 6.5$). These observations would support a model in which the stoichiometric composition ($x = 6.5$) does not represent a unique state with only one valence state but is simply one point in a gradual progression where, with increasing x , the amount of Cu^+ in the Cu chains decreases and the amount of Cu^{3+} (if such exists) in the sheets increases.

The calorimetric results also show no change in slope of the enthalpy of oxidation curve near the limits of homogeneity of the phase, namely, $x = 6.0$ and $x = 7.0$. This might suggest that these limits of stability arise, not from any sudden destabilization of the 1:2:3 phase by too high or too low

an oxygen content, but by a delicate balance of free energy between the 1:2:3 phase and other phases in the BaO–Y₂O₃–Cu–O system. High-temperature oxide melt solution calorimetry is in progress to clarify these questions.

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