

OXYGEN DESORPTION FROM HIGH AND LOW T_c SUPERCONDUCTORS

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High temperature oxygen evolution data are used to calculate the thermodynamic parameters related to the oxygen bonding and oxygen-oxygen repulsion energy in various superconducting compounds. The observed oxygen desorption from the linear Cu-O chains in the high T_c superconductors ($\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{LaBa}_2\text{Cu}_3\text{O}_7$, $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$) is not present in the low T_c superconductors (La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$). Above 800°C all samples show sharp oxygen evolution peaks.

1. INTRODUCTION

There is a strong correlation between the oxygen content, the structural phase and T_c in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound. Neutron and x-ray diffraction experiments [1,2] as well as TEM studies [3] clearly showed a structural phase transition near 750°C, together with a decrease in oxygen stoichiometry. The oxygen content, in equilibrium conditions, has been measured in those samples by various techniques [1,4,5]. Up to now, these measurements show considerable scattering in the oxygen content necessary for high T_c superconductivity. The onset of superconductivity has been associated with the presence of the orthorhombic phase for an oxygen content of 6.5 [1,2,6]. However several groups reported a higher [7] or a lower [8] oxygen content necessary for the appearance of the orthorhombic structure, and the onset of superconductivity. This discrepancy is in part due to the different sample preparation techniques used by the various groups (quenching versus equilibrium conditions). In this paper we report on oxygen evolution experiments, and determine the activation energy for desorption for two classes of superconducting materials.

2. EXPERIMENTAL METHOD

Stoichiometric samples were prepared using standard powder metallurgical techniques [2,6,9,11]. The oxygen evolution experiments [9] are performed by furnace annealing the samples, placed on a sapphire holder, in the tip of a vacuum pumped closed quartz tube (volume: 10^{-4}m^3). During annealing, the pressure and temperature is continuously recorded by fast computer-aided sampling in order to calculate the time-derivative. A mass spectrometer analyses the amount and the nature of the evolved gases.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the measured oxygen evolution (with a heating rate of 10°C/min) from sample a (7,980 mg $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta x}$), sample b (11,570 mg $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta x}$), and sample c (15.160 mg $\text{Pr}_2\text{Y}_{.8}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta x}$). The two upper

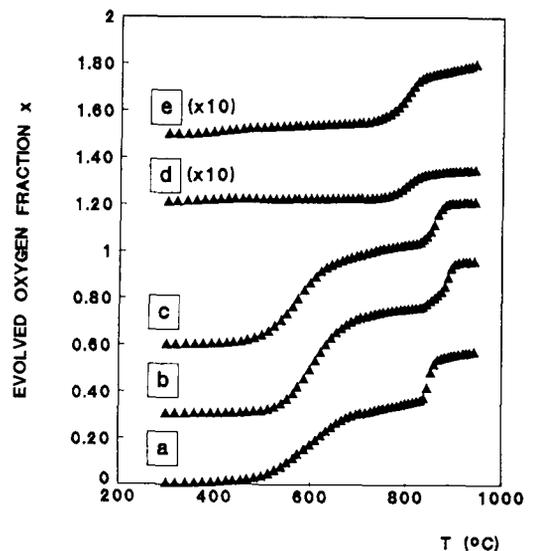


Fig. 1 Evolved Oxygen fraction vs temperature for samples a-e. The curves are shifted upward for clarity.

curves of Fig.1 show the measured oxygen evolution from respectively sample d (42,305 mg La_2CuO_4) and sample e (75,830 mg $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$). The evolved fraction x was calculated from the measured oxygen pressure, using the ideal gas law and the sample mass.

The evolved amount of oxygen is considerably larger in the high T_c samples (a,b,c) and reaches a maximum at approximately 600°C. In all samples the evolved oxygen amount reaches a saturation value at approximately 800°C, while at higher temperatures an important additional oxygen loss is observed.

Fig. 2 shows the time derivative of the O_2 pressure versus temperature for all these samples, revealing the presence of different desorption processes: broad peaks at low temperatures, and sharp peaks at higher temperatures.

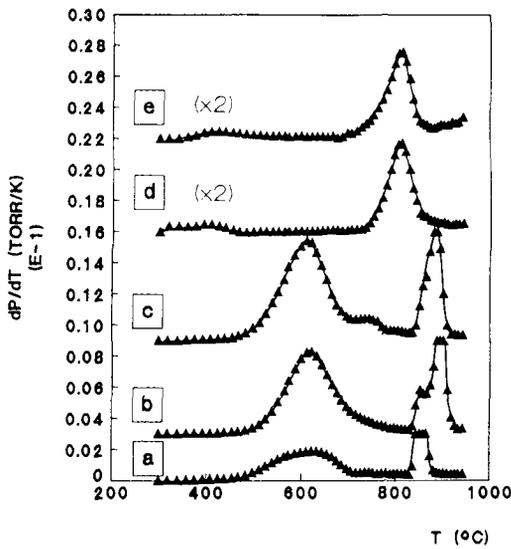


Fig. 2 Time derivative of the evolution curves of Fig. 1

Classically, first order desorption experiments from a single activation site are interpreted using the relation [10] : $dN/dt = \mu_o (N_o - N) \exp(-\Delta G/k_B T)$ where μ_o is the frequency factor, N_o the initial oxygen content in one unit cell, N the evolved content from one unit cell and ΔG a free energy barrier. This relation, extended to several desorption processes, was used to fit the evolution curves.

In a previous work [9], we calculated the desorption parameters for $YBa_2Cu_3O_{7-\delta x}$, and found for the low temperature peaks ($\leq 800^\circ C$), two desorption sites with respectively $\Delta G_1 = 0.95$ eV and $\Delta G_2 = 1.26$ eV and frequency factors $\mu_1 \simeq \mu_2 \simeq 10^4$. The first peak was associated with desorption from the orthorhombic O_1 site [1] while the second peak was associated with desorption from the tetragonal (and degenerate) $O_1 = O_5$ site. The difference in activation energy between these two peaks, was associated with the oxygen-oxygen repulsion assumed to be responsible for the formation of the linear chains.

The desorption parameters from sample c ($Pr_{2.8}Y_{0.8}Ba_{2-x}Cu_3O_{7-\delta x}$), are similar to the above mentioned results. In the $LaBa_2Cu_3O_{7-\delta x}$ sample a we can only identify one low temperature peak. It was shown that in the orthorhombic structure [11] of this material, both desorption sites are occupied (the O_1 position is fully occupied and the O_5 position is partially occupied). The desorption parameters for this peak are $\Delta G = 1.0$ eV with a frequency factor of 10^5 .

The low T_c superconductors (samples d and e) have a different desorption spectrum, mainly starting at $800^\circ C$. The activation energy $\Delta G = 2.8$ eV and the frequency factor $\mu = 10^{12}$ are much higher, although the total evolved oxygen fraction is much smaller. The frequency factor in these samples is comparable to the value for regular desorption experiments as in hydrogen evolution from a-Si:H layers [10].

The extremely small frequency factors for the high T_c superconductors clearly indicate that the oxygen incorporation in these materials is a slow process, explaining the discrepancies between quenching and equilibrium experiments as far as the oxygen content is concerned.

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References

- [1] J.D. Jorgensen, M.A. Beno, D.G. Hinks, L. Soderholm, K.J. Volin, R.L. Hitterman, J.D. Grace, Ivan K. Schuller, C.U. Segre, K. Zhang and M.S. Kleefisch, *Phys.Rev.*, **B36**, 3608 (1987)
- [2] I.K. Schuller, D.G. Hinks, M.A. Beno, D.W. Capone II, L. Soderholm, J.P. Locquet, Y. Bruynseraede, C.U. Segre and K.Zhang, *Solid State Commun.*, **63**, 385 (1987)
- [3] G. Van Tendeloo, H.W. Zandbergen and S.Amelinckx, *Solid State Commun.*, **63**, 603 (1987)
- [4] M.P.A. Vieggers, D.M. de Leeuw, C.A.H.A. Mutsaers, H.A.M. van Hal, H.C.A. Smoorenburg, J.H.T. Hengst, J.W.C. de Vries and P.C. Zalm, *J.Mater.Res.*, **2**, 743 (1987)
- [5] D.C. Harris and T.A. Hewston, *J.Solid St.Chem.*, **69**, 182 (1987)
- [6] I.K. Schuller, D.G. Hinks, J.D. Jorgensen, L. Soderholm, M. Beno, K. Zhang, C.U. Segre, Y.Bruynseraede and J.P. Locquet, *Novel Superconductivity*, S.A. Wolf and V.Z. Kresin (Eds.), Plenum Press 647 (1987)
- [7] P.K. Gallagher, *Advanced Ceramic Materials*, **2**, 632 (1987)
- [8] R. Beyers, E.M. Engler, P.M. Grant, S.S.P. Parkin, G. Lim, M.L. Ramirez, J.E. Vazquez, V.Y. Lee, R.D. Jacowitz, B.T. Ahn, T.M. Gür, and R.A. Huggins, preprint
- [9] H. Strauven, J.P. Locquet, Y. Bruynseraede, O.B. Verbeke, *Solid State Commun.*, **65**, 293 (1988)
- [10] S. Oguz, M.A. Paesler, *Phys.Rev.*, **B22**, 22 (1987)
- [11] C.U. Segre, B. Dabrowski, D.G. Hinks, K. Zhang, J.D. Jorgensen, M.A. Beno and Ivan K. Schuller, preprint