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OXYGEN SOLUBILITY IN THE SUPERCONDUCTING COMPOUND $YBa_2Cu_3O_x$ ($6 \leqslant x \leqslant 7$), STUDIED BY TG AND BAROMETRIC MEASUREMENTS

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Thermogravimetry in controlled oxygen atmospheres and barometric measurements between 300 and 1200 K were performed on the $YBa_2Cu_3O_x$ superconducting phase. The complete reversibility of the exchange of a certain part of the oxygen, as found even at 250 °C, and the observed relationship between oxygen partial pressure, oxygen content and temperature, can be explained by the dissolution of oxygen in $YBa_2Cu_3O_x$. It is concluded that samples with high x values (≈ 7), as necessary for good superconducting properties, can be obtained at high temperatures only at high oxygen pressures, but they were obtained by annealing at normal pressure between 250 and 350 °C.

Since the first announcement of high-T_c superconductivity, many papers have been published on the preparation, physical properties, identification and structure of the superconducting phases in the Ln–(Ba/Sr)–Cu–O system (e.g. [1, 2]).

The orthorhombic structure of $YBa_2Cu_3O_x$ (with $x \approx 7$) has ordered oxygen vacancies (Fig. 1) [3]. A temperature-dependent transition to a tetragonal cell has been observed, which is accompanied by a change in the site occupancy in the quadratic surrounding of the copper [4]. A weight loss has been reported [5] to occur when a $YBA_2Cu_3O_x$ sample is heated in different gas atmospheres.

As the tetragonal phase ($x \approx 6$) is not superconducting, it must be concluded that there is a strong relationship between the temperature of preparation and heat treatment, the partial pressure of oxygen and the superconducting properties.

We now report on attempts to correlate basic structural information with the thermodynamic behaviour, as studied by thermoanalytical and related methods.

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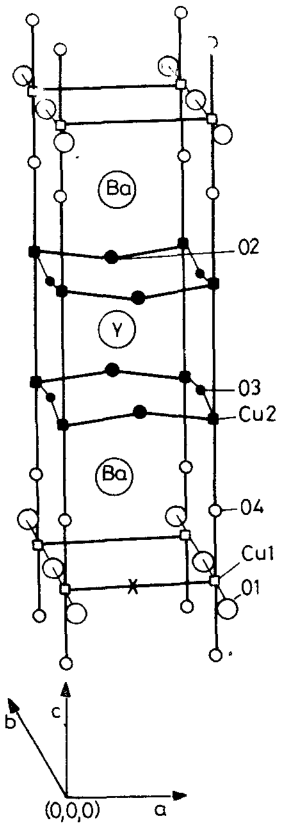

Fig. 1 Structure of the orthorhombic $YBa_2Cu_3O_x$ phase [8]. (x: $\left(\frac{1}{2}, 0, 0\right)$ position unoccupied in the ideal structure. In the tetragonal phase the position 01 becomes unoccupied)

Experiments

$YBa_2Cu_3O_x$ samples were prepared from Y_2O_3, $BaCO_3$ and CuO in a solid-state reaction at 950° in air for 24 h. The powder was reground, heated in oxygen at 800° for 16 h, and then slowly cooled, as described in [3].

Isochoric equilibrium measurements were made with a quartz-glass Bourdon manometer. Thermogravimetric investigations were carried out at different oxygen partial pressures which were controlled by emf measurements.

Results

The results of thermogravimetric investigations (Fig. 2) on a sample treated in oxygen at constant partial pressure revealed reversibility between the heating and cooling curves. Furthermore, a stepwise temperature increase caused sharp mass loss steps. Between 298 K and 1173 K, a total mass loss of 1.10 wt-% oxygen in $1 \cdot 10^5$ Pa O_2, and of 1.41 wt-% oxygen in $1.86 \cdot 10^4$ Pa O_2, was observed, indicating a clear relation between the oxygen potential and x in $YBa_2Cu_3O_x$.

The same behaviour was found by barometric measurements of the solid-gas equilibrium under isochoric conditions (Fig. 3). Different curves were obtained for different mass/volume ration (curves 1, 2 and 3) and it was impossible to prevent the oxygen loss by applying a compensating oxygen pressure to the barometric cell (curves 1a, 1b, 2a, 2b and 2c).

Since the absolute value of x is not known exactly, all values of Δx were related to the sample denoted by θ, which was heated in $8 \cdot 10^4$ Pa O_3 at 300°, and for which x is of the order of 6.8–6.9.

From Fig. 3 it can be concluded that, constant oxygen partial pressure, the oxygen content of the solid depends considerably on the temperature.

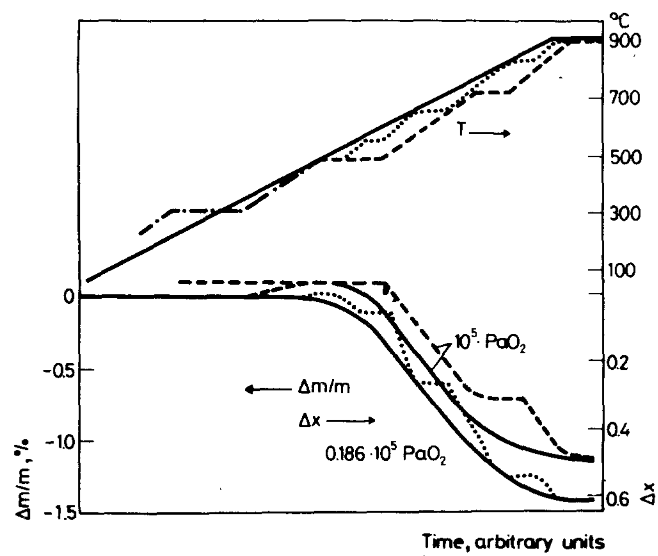

Fig. 2 Dependence of the mass loss (expressed as $\frac{\Delta m}{m}$ and Δx, respectively) on the temperaturg in $1 \cdot 10^5$ Pa and $1.86 \cdot 10^4$ Pa O_2, respectively. The same types of lines are used for the corresponding temperature curves (upper part) and mass loss curves (lower part)

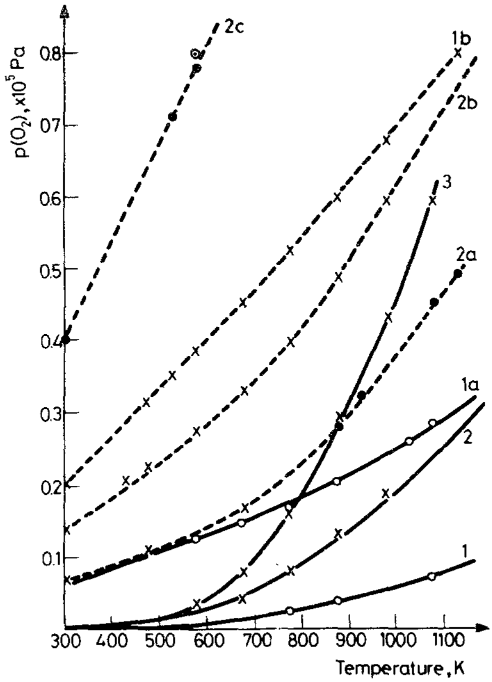

Fig. 3 Oxygen pressure in equilibrium with $YBa_2Cu_3O_x$. Run 1: 50 mg, a) $+6.67 \cdot 10^3$ Pa O_2, b) $+ 2 \cdot 10^4$ Pa O_2. Run 2: 200 mg, a) $+6.67 \cdot 10^3$ Pa O_2, b) $+1.27 \cdot 10^4$ Pa O_2, c) $+4 \cdot 10^4$ Pa O_2. Run 3: 500 mg

Discussion

TG and equilibrium measurements show that the results cannot be explained by an equilibrium between two phases (e.g. orthorhombic and tetragonal) in a quasibinary system, for in this case there should be only one well-defined decomposition pressure at a given temperature. The results can be explained either by a quasibinary solid solution of oxygen in $YBa_2Cu_3O_x$, or by the presence of at least two compounds with homogeneity ranges. Although the phase diagram in the Y–Ba–Cu–O system contains various ternary and at least two quaternary compounds at 900° (as shown for a rough orientation in Fig. 4), the latter explanation seems not to be favoured. This may be concluded from the fact that equilibrium is established very quickly even at the rather low temperature of 250°.

This high mobility of oxygen in the $YBa_2Cu_3O_x$ lattice is indicated by an equilibrium between the occupation numbers of oxygen in the $\left(0, \frac{1}{2}, 0\right)$ and $\left(\frac{1}{2}, 0\right.$

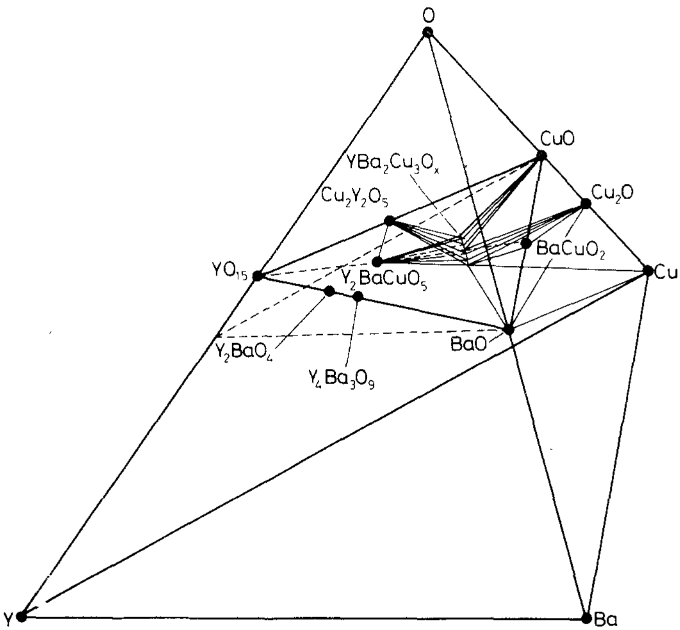

Fig. 4 Phases so far identified in the Y–Ba–Cu–O system. Only so ne of the possibly coexisting regions are shown

0) positions, as found from neutron diffraction experiments [6], whereas the variable oxygen content accords with the temperature-dependent ccupation of the $\left(0, \frac{1}{2}, 0\right)$ site [4]. Thus, the quadratic planar surrounding of the Cu in (0, 0, 0) is heavily disturbed. This seems to be the reason for the observed decrease in the

Table 1 Influence of the annealing temperature in oxygen T_a on the midpoint temperature T_c^m and the width of the transition ΔT_c

T_a, °C	T_c^m, K	ΔT_c, K
250	92	1
380	92	0.5
600	90, 80	17*
600	78	18
650	68	16
850	semiconducting	

* two transitions

superconducting transition temperature T_c and an increase in the width of the transition ΔT_c (Table 1) [7].

Even a comparatively small change (of the order of 0.1) in Δx causes a marked decrease in T_c, whereas the unit cell remains orthorhombic.

Furthermore, it must be concluded that optimal concentrations x are expected to be obtained at high temperatures only at very high oxygen pressures. Fortunately, there is also a steep dependence of $\log p(O_2)$ on temperature, and suitable kinetic behaviour. Consequently, high-quality samples can be obtained by normal pressure annealing between 250° and 350° [7].

These preliminary results must be complemented by further investigations on the thermodynamic behaviour in the Y–Ba–Cu–O system, and also on the nature of the o-t phase transition.

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Zusammenfassung — Die supraleitende Phase $YBa_2Cu_3O_x$ wurde mit Hilfe von Thermogrametrie und barometrischen Messungen im Bereich 300 bis 1200 K untersucht. Die sogar bei 250 °C beobachtete Reversibilität des Austausches von einem Teil des Sauerstoffs sowie die gefundenen Beziehungen zwischen Sauerstoffaktivität (Partialdruck), Sauerstoffgehalt und Temperatur können durch eine Lösung von Sauerstoff in $YBa_2Cu_3O_x$ erklärt werden. Aus den Ergebnissen kann gefolgert werden, daß Proben mit hohem x (≈ 7), die gute Supraleitungseigenschaften zeigen, bei hohen Temperaturen nőr unter hohem Sauerstoffdruck hergestellt werden können. Sie werden jedoch auch durch Tempern bei Normaldruck bei 250 bis 350 °C erhalten.

Резюме — Проведены термогравиметрические и барометрические измерения сверхпроводника $YBa_2Cu_3O_x$ в контролируемой атмосфере кислорода и в интервале температур 300–1200 K. Полная обратимость обмена определенной части кислорода, найденная даже при 250°, и наблюдаемая взаимосвязь между парциальным давлением кислорода, его содержанием и температурой, могут быть объяснены растворением кислорода в $YBa_2Cu_3O_x$. Сделано заключение, что образцы с высоким значением x (≈ 7), являющимся необходимым для хороших сверхпроводящих свойств, могут быть получены при высоких температурах только при ввсоких давлениях кислорода. Вместе с тем, такие образцы могут быть получены путем отжига при нормальном давлении кислорода и при температурах между 250 и 350°.