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MICROGRAVIMETRIC INVESTIGATIONS OF HIGH-TEMPERATURE SUPERCONDUCTORS

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Abstract

It has been confirmed that, in oxide superconductors, the superconducting transition temperature T_c depends strongly on the oxygen content and oxygen ordering. The microgravimetric method is very useful in the analysis of oxide superconductors, because it allows investigations in vacuum and controlled environments in classical applications: thermogravimetric analysis, kinetics and thermodynamics of reaction, determination of oxygen contents in redox reactions, investigations of the correlation of the deviation from stoichiometry and carrier concentration and also the combined measurement of mass and additional parameters, e.g. evolved gas analysis, etc. Selected papers are reviewed.

Keywords: controlled environment, high-T_c superconductors, microgravimetric investigations, oxide superconductors

Introduction

Since the discovery of high-temperature superconductivity by Bednorz and Müller in 1986 [1], this field has received considerable attention both from scientists and from the general public. Following this first report on a resistance drop at about 30 K, hundreds or even thousands of materials have been synthesized and examined for evidence of superconductivity. Figure 1 gives an idea of the change in the transition temperature from the non-superconducting state to the superconducting state in these new materials and in some classical superconductors.

Almost without exception, the crystal structures of these cuprates are characterized by superconducting CuO_2 sheets that are separated by non-superconducting planes. This structure possesses features closely related to the perovskite ($CaTiO_3$) structure, such as vertical-sharing metal-centred octahedra, square pyramids, square chains and chains.

As these new materials are now investigated in many laboratories, simple classification based on the structural units which make up the different cuprates

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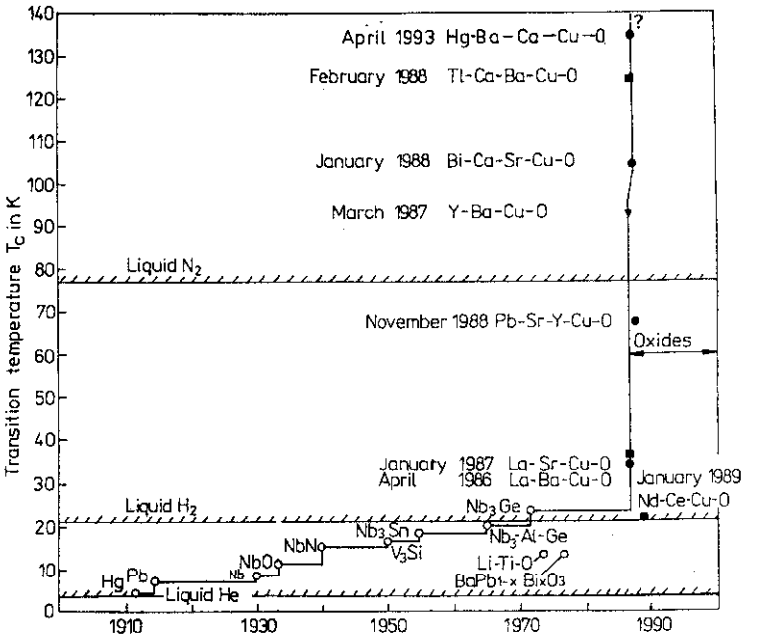

Fig. 1 The evolution of superconducting materials initially proceeded very slowly after the discovery by Kamerling Onnes in 1911. The work by Bednorz and Müller on La–Ba–Cu–O triggered a world-wide superconductivity fever, resulting in the discovery of new superconducting materials and sky-rocketing critical temperatures

are widely used as a short-hand classification. Shaked *et al.* [2] classified 26 various cuprate superconductors.

It has been confirmed that in oxide superconductors the superconducting transition temperature T_c depends strongly on the oxygen content and oxygen ordering [3, 4]. The microgravimetric method is very useful in the analysis of oxide superconductors, as it allows investigations in vacuum and controlled environments [5–22] in classical applications: thermogravimetric analysis for the study of solid-state reactions [6, 7, 9, 22], kinetics and thermodynamics of reactions [16, 19, 20], determination of oxygen contents in redox reactions [8, 10, 11, 15–18, 21], and the combined measurement of mass and additional parameters, e.g. evolved gas analysis etc. [5]. Dynamic vacuum provides protection from the readsorption of oxygen from the environment [5, 19, 20]. Hydrogen has an extremely simple electronic structure and a small mass, but is nevertheless capable of causing substantial perturbations of local electron density with a comparatively slight distortion of the lattice. The introduction of hydrogen into a superconducting oxide might therefore provide important information about the properties of the material [12–14, 17].

Investigations of the influence of oxygen isotope substitution on the properties of the high-T_c oxide superconductors [16] are very important as concerns an understanding of the mechanism of superconductivity [23]. The observation of an oxygen isotope effect provides supporting evidence that phonons play a role in the electron-pairing mechanism [24]. Selected papers are reviewed [11–13, 19, 20].

Experimental

Single-phase orthorhombic samples of composition $(RE)Ba_2Cu_3O_{7-x}$ (highest oxygen content) (*RE*=rare earth) were synthesized from stoichiometric (1:2:3) mixtures of high-purity Y_2O_3 (Nd_2O_3 or Er_2O_3), $BaCO_3$ and CuO. The original 1:2:3 mixture was prepared in a two-stage procedure. First $BaCO_3$ and CuO in a molar ratio of 2:3 were thoroughly mixed and ground in an agate mortar. Next, an appropriate quantity of $(RE)_2O_3$ was added and the whole was mixed and ground again. The mixture, in the form of a loose powder in an alumina boat, was heated at 950°C in flowing oxygen during 4 h. After slow cooling to room temperature, the sample was reground and heated under the same conditions for a further 4 h. Next, the temperature was lowered to about 400°C, which was maintained during 15 h (still in oxygen), and the sample was then slowly cooled to room temperature. X-ray examination revealed that the synthesis was essentially complete after the first heating. The *in situ* measurements of the oxygen loss were performed in a Cahn RG ultramicrobalance system that permits the decomposition to be followed in a dynamic vacuum of $\approx 10^{-6}$ torr. The samples were heated up to the temperature of the experiment at a constant rate of 10°C min^{-1}. The initial mass of the samples was ca 180 mg and the mass decrease caused by the loss of one oxygen atom per chemical formula [$(RE)Ba_2Cu_3O_7 \rightarrow (RE)Ba_2Cu_3O_6 + 1/2\ O_2\uparrow$] corresponded to ≈4 mg. In order to determine disturbances which affect the accuracy of weighing in vacuum or in a controlled atmosphere, blank runs were used to correct the data obtained during kinetic runs.

Apparent mass changes did not exceed ±40 μg. As the accuracy of the measurements was better than ±40 μg, estimation of the content in the sample was at the level of at least ±0.01 atom per chemical formula. Loose powder $(RE)Ba_2Cu_3O_7$ samples were placed in a small quartz crucible in the vicinity of a NiCr–Ni thermocouple. The system was first evacuated down to 10^{-7} torr and the sample was annealed at 120°C during 20 h to remove adsorbed gases and moisture. The samples were then heated up to the temperature of measurement at a constant rate of 10°C min^{-1}.

To ensure a constant grain size distribution, the small samples used in the measurements were always taken from a larger portion of an original $(RE)Ba_2Cu_3O_7$ preparation. In most instances, the measurement duration was long enough (sometimes up to 500 h) for equilibrium to be approached. The in-

teraction of hydrogen with La_2CuO_4, $La_{1.8}Sr_{0.2}CuO_4$ and $Sm_{1.85}Ce_{0.15}CuO_4$ was studied in the same apparatus. Pure gaseous hydrogen, produced through the decomposition of the hydride of Ti, was then admitted into the evacuated balance chamber. The hydrogen pressure was 600 torr. The samples were subsequently heated up to the temperature of the experiment at the low heating rate of $30°C\ h^{-1}$.

NMR measurements were performed with a pulse SHR-100 spectrometer at 60 MHz. The lattice parameters of all preparations were controlled, in both initial and final experiments, by the X-ray powder method (CuK_α radiation), using a Stadi P (Stoe) diffractometer with a position-sensitive detector.

Results and discussion

Measurements of oxygen loss from the chain position in the elementary cell were made for four different $(RE)Ba_2Cu_3O_{7-x}$ preparations (in the initial state $x_1=0$) heated isothermally in the range 300–470 K. Oxygen loss curves are exemplified for $ErBa_2Cu_3O_{7-x}$ in Fig. 2. Prior to further analysis, the oxygen loss data (x_t values) were normalized by considering the equilibrium state (x_{eq}) characteristic for a given temperature (e.g. for $ErBa_2Cu_3O_7$ the values of x_{eq} are equal to 0.42, 0.7, 0.8, 0.86 and 0.89 for 300, 355, 377, 400 and 425°C, respectively).

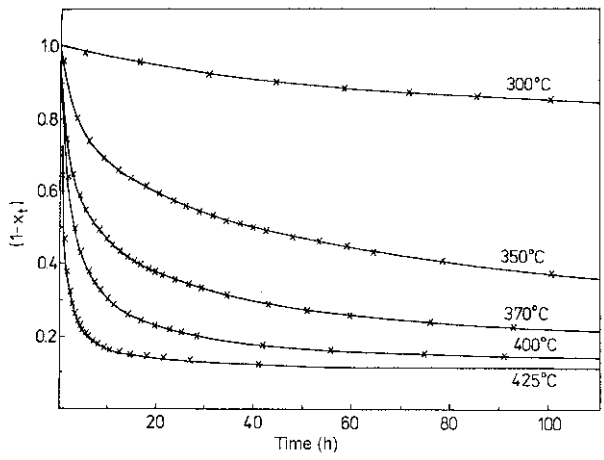

Fig. 2 Plot of $(1-x_t)$ *vs.* t for erbium preparation

Decompositions of the type $(RE)Ba_2Cu_3O_7=(RE)Ba_2Cu_3O_{7-x}+x/2O_2$ at constant temperature should follow a simple exponential relation (a first-order process) if all the grains of the preparation are of the same size. The bonding of oxygen atoms was investigated by gas evolution measurements and interpreted by means of a first-order desorption model for the evolution process [25]. The samples consisted of grains of different sizes, decomposing with different rates. It

was anticipated that the overall oxygen loss may be described by the sum of an appropriate number of exponential terms depending on the grain size distribution. It was found that, for powdered samples, the number of such exponents can be limited to the three terms, corresponding to high, medium and low decomposition rates, in which small, medium and large grains are involved:

$$\frac{x_{eq} - x_t}{x_{eq}} = Ae^{-k_1 t} + Be^{-k_2 t} + Ce^{-k_3 t}$$

where x_1 is the value reached after time t, and k_1, k_2 and k_3 are the rate constants. The solid lines in Fig. 2 were calculated by using the above equation and appropriate constants.

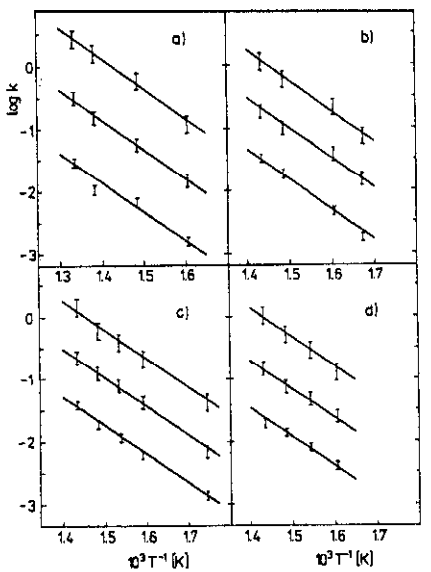

Fig. 3 Arrhenius plots for a – neodymium, b – europium, c – erbium and d – yttrium preparation

As may be seen in Fig. 3, the Arrhenius plots fully confirmed the assumption that the overall oxygen loss curves may be represented as the sum of partial curves relating to decay at different rates, but characterized by the same activation energy of 0.92±0.02 eV for all (RE)$Ba_2Cu_3O_7$ preparations.

The influence of hydrogen on the magnetic and superconducting properties of the La_2CuO_4 and $La_{1.8}Sr_{0.2}CuO_4$ systems has been studied. It was established that the interaction of hydrogen with the insulating La_2CuO_4 samples results in a reduction of oxygen [10, 11, 13, 17], while the reaction of hydrogen with $La_{1.8}Sr_{0.2}CuO_4$ can be interpreted as several parallel and follow-up reactions, as is shown in Fig. 4. The mass loss corresponds to an oxygen loss (reduction from cuprate to Cu_2O), and a mass gain is due to the dissolution of hydrogen. The mass

can also increase, however, if the water vapour formed by reduction of the oxygen content does not evaporate, but reacts with La_2O_3 to yield $La(OH)_3$ [17]. The latter decomposes as the temperature is further increased. The final step occurs with the formation of metallic copper Cu^o under equilibrium conditions.

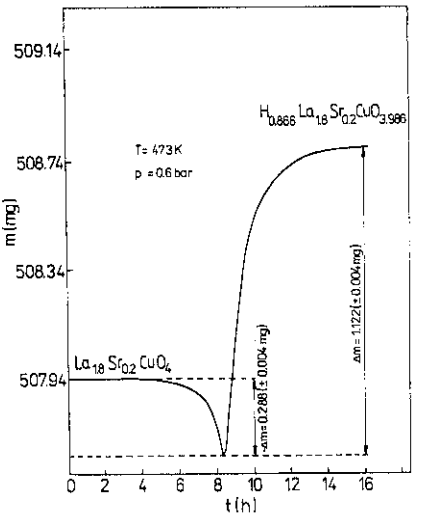

Fig. 4 Gravimetric kinetic curve for the process of interaction of hydrogen with $La_{1.8}Sr_{0.2}CuO_4$

Studies of the hydrogenated samples by X-ray structural analysis revealed that the reflections characteristic of the tetragonal structure of the original sample persist, but their intensity decreases with increasing hydrogen concentration, and the noise increases. This 'amorphization' of the X-ray diffraction patterns apparently results from the grinding of the samples to dimensions smaller than a certain critical dimension in the region ≤0.1 μm. No secondary phases were present in the diffraction patterns. In addition, an analysis of the X-ray diffraction patterns demonstrated that the lattice constant along the tetragonal axis increases systematically with increasing hydrogen concentration (Table 1). In this manner, samples of $H_xLa_{1.8}Sr_{0.2}CuO_{4-y}$ with x=0, 0.02, 0.1, 0.3 and 0.866 were produced.

Table 1 Lattice constants and unit-cell volume of $H_xLa_{1.8}Sr_{0.2}CuO_{4-y}$

$H_xLa_{1.8}Sr_{0.2}CuO_{4-y}$	H content x	Lattice constant		Cell volume/ Å^3
		a/Å	c/Å	
$La_{1.8}Sr_{0.2}CuO_4$	0.00	3.774	13.232	188.43
$La_{1.8}Sr_{0.2}CuO_{3.99}$	0.02	3.776	13.237	188.74
$La_{1.8}Sr_{0.2}CuO_{3.98}$	0.10	3.774	13.267	188.94
$La_{1.8}Sr_{0.2}CuO_{3.99}$	0.30	3.774	13.322	189.72

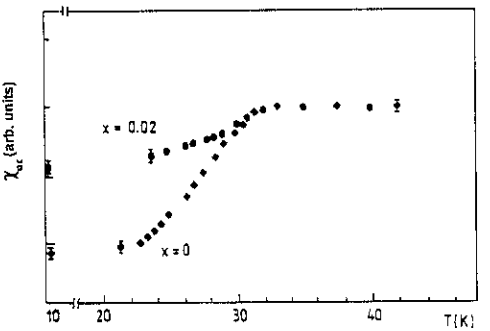

Fig. 5 Temperature dependence of the magnetic susceptibility of $H_xLa_{1.8}Sr_{0.2}CuO_{4-y}$

To determine the superconducting transition temperature, the *rf* magnetic susceptibility was measured. In samples with $x \geq 0.1$, the superconductivity was suppressed essentially completely. In the sample with $x=0.02$, on the other hand (Fig. 5), the transition onset temperature T_c, corresponding to the slope change in χ, remained the same as that of the original sample. The amount of superconducting phase, however, decreased by a factor of 1.5. The absorption of hydrogen therefore results in a decrease in the amount of superconducting phase in the cuprate. In other words, the superconductivity is suppressed in certain parts of the cuprate (phase separation). The hydrogen concentration in the sample with $x=0.1$, at which the superconductivity is suppressed, is approximately equal to the concentration of the Sr dopant atoms in this ceramic. At this concentration, the mechanism for the suppression of the superconductivity by hydrogen in the lanthanum-strontium ceramic is probably associated with a neutralization of holes as hydrogen is localized in a copper-oxygen plane. The fact that hydrogen can be localized in this plane, at the positions with the coordinates (1/2, 1/2, 0) and (0, 0, 1/2), is confirmed by an analysis of the sizes of the interstices on the basis of the crystallographic data and the ionic radii of the elements. These positions are equivalent, and each has four O^{2-} (with an ionic radius of 1.40 Å) in its neighbourhood. These oxygen ions form interstices with a size of about 1 Å, the optimum size for being filled by a hydrogen atom. Along the tetragonal axis, these positions lie between two La^{3+}, whose interactions with the hydrogen cation (proton) are apparently the reason for the increase in the lattice constant c (Fig. 6).

NMR measurements at a frequency of 60 MHz for a sample with $x=0.866$ showed that the proton-resonance signal is a single symmetric line of Gaussian shape with a width of 63 kHz, which is essentially independent of the temperature. An estimate was made of the width of the NMR line caused by the dipole interactions of the proton with the nearest La and Cu nuclei and protons, with oxygen occupying the positions under consideration.

From appropriate formulas [12], the linewidth was estimated to be ≈30 kHz, or comparable to the width found experimentally. Finally, there is yet another circumstance: if hydrogen does occupy these positions, the composition of the resulting samples will be $H_{1.0}La_{1.8}Sr_{0.2}CuO_4$. This composition is close to the

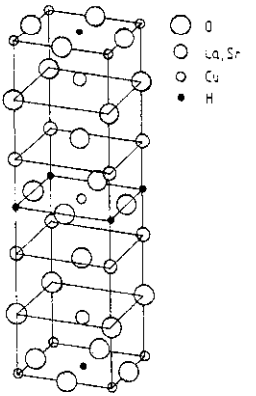

Fig. 6 Localization of hydrogen atoms in the unit cell of $La_{1.8}Sr_{0.2}CuO_4$

composition with the maximum hydrogen content found experimentally from the saturation of the lanthanum-strontium ceramic with hydrogen. It follows from the results that hydrogen occupies a position in the centre of the Cu–O planes of the unit cell. This position is in a region of distribution of the electron density of oxygen. The results obtained indicate that quantum chemistry calculations are extremely necessary for the mechanism and theory of high-T_c superconductivity.

Fig. 7 Photographs showing experts in the topics presented at the 27th IVMT (IUPAC) Conference during their meeting in Brussels. The picture was taken from Chemistry International Vol. 17, No 1 (1995) 4

In Poland, oxide superconductors have been investigated in the pioneering works by Damm *et al.* [26].

Figure 7 shows experts in the topics presented at the 27th IVMT (IUPAC) conference during their meeting in Brussels.

Conclusions

These fundamental studies are invariably time-consuming and require careful experimental procedures.

Clearly, more experiments on well-characterized samples are required for further clues to the mechanism of superconductivity in high-T_c materials. The considerable early promise of these fascinating compounds has yet to be realized, largely as a consequence of serious issues relating to the properties and processing of these complex materials.

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