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The exchange of oxygen isotopes in high-temperature superconductors

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Abstract

The following paper presents a new method of characterizing the exchange of oxygen in oxygen-containing solids. High-temperature superconductors of Y–Ba–Cu–O systems display a unique exchange process which is determined to a great extent by stoichiometric compositions and structure.

A preliminary characterization of the exchange may be stated as follows: the greater the oxygen affinity, the smaller the tendency towards isotope exchange. As the oxygen affinity decreases, the initial temperature required for diffusion and exchange processes to the site increases, the initial temperature required for diffusion and exchange processes to the site increases, and the temperature at which emission and absorption of oxygen are equal decreases. The extent of the relative accumulation of ^{18}O in the gas phase bears a correlation to the transition temperature in the superconducting Y–Ba–Cu–O phase.

A very similar mechanism for the diffusion of oxygen in solid phases can be inferred from the alteration of the ^{18}O content in the $^{34}O_2$ in the gas phase.

Qualitative conclusions regarding isotope exchange processes, surface conditions, and the movement of oxygen may be drawn from the time- and temperature-dependent changes in various formulated coefficients.

In addition, the method presented allows opposing processes within a solid to be distinguished and recorded separately.

INTRODUCTION

Since the discovery of the phenomenon of high-temperature superconductivity in lanthancuprat (La_2CuO_4) by Bendnorz and Müller [1], a number of ceramic high-temperature superconductors have been found [2–4]. All high-temperature superconductors presently known contain,

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without exception, the elements copper and oxygen as well as other interchangeable metals. These two elements form a common sub-lattice, the structure of which has a decisive significance for the superconducting properties of the ceramic. The oxygen stoichiometry, in addition to that of other cations, plays an important role in adjusting the Cu–O sub-lattice to an appropriate degree, a precondition for the superconducting ability. There have been a number of attempts to achieve similar results by partially substituting other anions (F^- [5–8], Cl^- [7–10]) for O^{2-}. The present authors have also undertaken experiments on the influence of halogenide in ceramic high-temperature superconductors [11–15]. In such work, particularly relevant methods were involved which helped to produce noteworthy findings regarding oxygen stoichiometry, the movement of oxygen, and the surface conditions of the high-temperature superconductor, and to define the type of interaction between solid and gas phases (both O_2 and halogen-containing doping gases). As a result, valuable knowledge was gained regarding the preparation of high-temperature superconducting ceramics.

Information of this sort is principally attained through the measurement of oxygen isotope exchange. The interaction of ^{18}O-marked gas and oxygen-containing solids is normally observed by detecting the change in isotope content in the gas phase by using a spectrometer.

GENERAL

Three different isotope exchange processes between a ^{16}O-oxidic solid and a ^{18}O-containing gas phase may be distinguished:

(a) Homogeneous oxygen exchange within the gas phase through gaps in the surface

$$O_2(g) + {}^*O_2(g) \rightleftharpoons 2O^*O(g) \tag{1}$$

(b) Partially heterogeneous oxygen exchange of a molecule from the gas phase with the solid

$${}^*O_2(g) + O(s) \rightleftharpoons O^*O(g) + {}^*O(s) \tag{2}$$

(c) Completely heterogeneous oxygen exchange of a molecule from the gas phase with the solid

$${}^*O_2(g) + 2O(s) \rightleftharpoons O_2(g) + 2{}^*O(s) \tag{3}$$

These three equations represent in general all possible kinds of oxygen exchange reactions between the gas phase ($^{32}O_2$, $^{34}O_2$, $^{36}O_2$) and the solid ($^{16}O(s)$, $^{18}O(s)$).

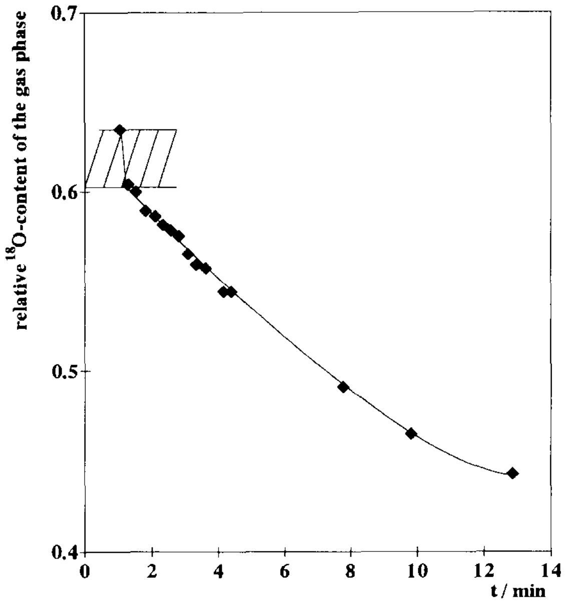


Fig. 1. Oxygen isotopic exchange between orthorhombic $YBa_2Cu_3O_{7-x}$ and ^{18}O-containing gas under isothermic conditions.

All three exchange processes then approach a limit if additional ^{16}O is not supplied as a result of auto-diffusion from the solid (observations of the auto-diffusion in the solid are attainable from the course of the isotope exchange process). It must also be noted that the homogeneous exchange proceeds only by means of the surface of the solid, and therefore allows no observation of the solid itself.

Isotope exchanges are generally measured isothermically. A typical plot of an isothermic measurement of isotope exchange between an ^{18}O gas phase and $YBa_2Cu_3O_{6.95}$ is presented in Fig. 1. The process is typically rapid within the exchange layer immediately after the addition of the gas (marked by shading), followed by a clear reduction of exchange due to the diffusion process in the solid. The problem with such measurements appears to be that they can only be calculated integrally if corresponding limiting conditions are defined. Thus, the absolute values attainable depend on the quality of the applied model. The expected anisotropy of the diffusion, in particular, can only be observed with great difficulty. Hence, the value of such measurements is found in the comparative examination of that which perfectly agrees with the final position. The time required for isothermic measurements is unjustifiably high, especially if comparative observations are to occur. Here there is great uncertainty about how to assign unambiguously the various possible processes (eqns. (1)–(3)) to the experimentally ascertained curve forms.

Because temperature ranges of initially high oxygen mobility, in particular, are involved in high-temperature superconductors, the normal experimental procedure was changed to include a dynamic-thermal measuring apparatus. In contrast to the generally used dynamic-thermal experiment procedures, the method used was a particular form of evolved gas analysis in which, as in emanation analysis, no stoichiometric change in the solid is needed to obtain measurable effects.

The advantage of this method over thermal emanation analysis is that it avoids isotopes that are foreign to the system. Nor is it necessary, as before, to dope with radioactive elements or to use radiation-sensitive equipment for detection. In contrast to thermal gas analysis, information about the diffusion process in the solid (absorption and emission) is also accessible.

The fundamental aim of the dynamic-thermal experiment documented here was a greater distinction between the possible stages of the process corresponding to eqns. (1)–(3). This distinction is possible if, in addition to the coefficients c and y proposed by Musikantov et al. [16], other coefficients are formulated. The coefficients applicable to this experiment and their definitions may be briefly outlined as follows:

(i) The coefficient c defined in eqn. (4) [4] expresses the proportion of ^{18}O relative to the total oxygen content in the gas phase. The value of c diminishes when, as a result of isotope exchange within the solid, the ^{18}O content in the gas phase decreases. Both the exchange and diffusion processes may be followed with the help of this coefficient.

$$c = \frac{(^{34}O_2)/2 + (^{36}O_2)}{(^{32}O_2) + (^{34}O_2) + (^{36}O_2)} \tag{4}$$

(ii) Coefficient y describes the deviation of the ^{18}O-containing atmosphere from its isotopic balance. The relative content of the $^{34}O_2$ within a defined ratio of $^{32}O_2(g)$ and $^{36}O_2(g)$ is important for the isotopic distribution. The deviation of the isotopic composition from the statistically-derived isotopic balance can be represented by the difference between the $^{34}O_2$ content in the gas phase at isotopic equilibrium and the $^{34}O_2$ content in the gas as actually attained at time $t = i$. Coefficient y equals zero at equilibrium.

$$y = (^{34}O_2)_{eq} - (^{34}O_2)_{t=i} = 2c(1-c) - \left[\frac{(^{34}O_2)/2}{(^{32}O_2) + (^{34}O_2) + (^{36}O_2)}\right] \tag{5}$$

(iii) Coefficient s corresponds to the partial pressure of oxygen on the solid. A standardization of each reading to the initial partial pressure is suggested to enable closer comparison.

$$s = \frac{[(^{32}O_2) + (^{34}O_2) + (^{36}O_2)]_{t=i}}{[(^{32}O_2) + (^{34}O_2) + (^{36}O_2)]_{t=0}} = \frac{p_i}{p_0} \tag{6}$$

An increase in s shows that the release of oxygen (emission) from the solid combines with a possible intake of oxygen (absorption), whereby the partial pressure of the oxygen increases during the experiment. The relationship reverses when the value of s decreases.

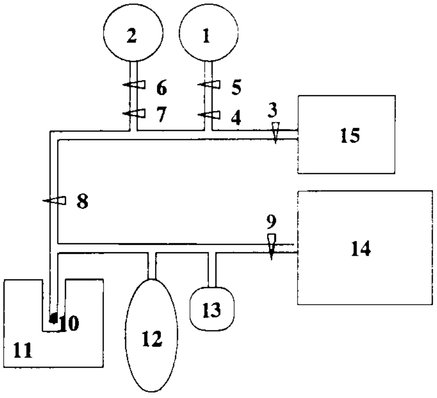
(iv) Coefficient v records the proportion of ^{18}O in the gas phase contained at the ^{34}O peak. This quotient is standardized at the ascertained initial value.

$$v = \left\{\frac{(^{34}O_2)/2}{[(^{34}O_2)/2] + (^{36}O_2)}\right\}_{t=i} \left\{\frac{[(^{34}O_2)/2 + (^{36}O_2)]}{(^{34}O_2)/2}\right\}_{t=0} \qquad (7)$$

The determination of the coefficient v is therefore quite important, because it enables exchange processes to be recorded independently of $^{34}O_2$, thereby also making accessible data concerning oxygen exchange in regions of dominating oxygen emission from the solid. If homogeneous and heterogeneous exchange processes expire at the same time, the ratio changes, and v increases as a result.

EXPERIMENTAL

The main arrangement of the measuring devices used in the experiment is given in Fig. 2. All measurements were carried out with Finnigan



1, 2	**gas reservoir**
3–9	**on/off valves**
10	**sample holder**
11	**furnace**
12	**gas pocket for defining the initial gas volume**
13	**capacity pressure gauge and interface with exit for the recorder**
14	**mass spectrometer**
15	**vacuum pump**

Fig. 2. Scheme of the measuring unit.

quadrupole mass spectrometer, model 400. In order to keep the matrix effect of the gas phase as small as possible, the volume of the apparatus was constructed to attain an optimal balance between low gas volume and sufficiently large measuring results. Accordingly, this optimization ought to occur by decreasing the pressure while maintaining the volume. As a result, the average free path of the molecule increases, allowing an even distribution to be achieved faster in the gas phase. To increase the sensitivity of the mass spectrometer, a pipe of precious metal was placed at the valve opening, directing the specified gas directly into the ionic source of the measuring equipment.

Preliminary tests with the equipment empty at a gas pressure of up to 40 Pa and at a temperature of 713 K showed no evidence for exchange of $^{36}O_2$ with the gas equipment; therefore, distortions of the measuring results due to such secondary reactions may be discounted. To determine how long the lag between an effect and its detection would be, $^{32}O_2$ was added to a gas phase at a pressure of 133.32 Pa, together with a short pulse of ^{40}Ar, and the time required until a constant ^{40}Ar peak was achieved and measured. Under these conditions, the average lag lasted approximately 26 s, which corresponds to about 4 K at a heat rate of 10 K min^{-1}. Considering that a scan area corresponds to 4–5 s under these conditions, the margin of error is within limits tolerable for dynamic-thermal measurements.

Preliminary tests on various high-temperature superconductors showed that water and carbon dioxide could be bound in varying amounts to the surface of the solid. Both compounds contain oxygen and could therefore influence the isotope ratio during the measuring. In various tests of $YBa_2Cu_3O_{7-x}$ over 2 hours at a pressure of 0.01 Pa and a temperature of 573 K, the evolution of H_2O and O_2 and, partially, of small amounts of CO_2, could be observed. Water and carbon dioxide were absorbed on the surface. In contrast, the detected oxygen is apparently emitted directly from the surface of the solid. The amount released is so small, however, that the change of integral stoichiometry in the tests concerned is negligible. As a result of this type of thermal pre-treatment of the solid samples, a mild oxygen gradient in the surface is created alongside the necessary removal of H_2O and CO_2, and a potential diffusion-inhibiting layer (skin effect) is reduced [17].

Therefore, all test materials were prepared under the same conditions (2 h at 573 K) before the measurements were taken. The degree to which the partial pressure of oxygen depends on the temperature was as expected for various stoichiometries in the Y–Ba–Cu–O system (Fig. 3). This proves that the necessary pre-treatment of test materials has no influence on comparative observations and the conclusions subsequently reached.

The exact conditions of measurement were as follows (Fig. 2). Before the beginning of each measuring period the temperature was brought to 308 K and the pressure to at least 0.133 Pa. All measurements were taken with a

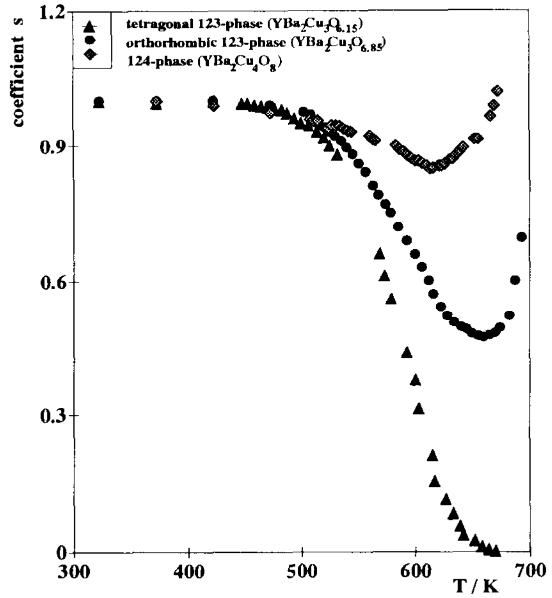


Fig. 3. Change of oxygen partial pressure (coefficient *s*) of different oxocuprates with increasing temperature.

heating rate of 10 K min^{-1}. Valve 13 was adjusted so as to assure that the pressure drop would not surpass 15% during the complete measuring period. Valves 2 and 6, and 3 and 7 were set to the desired gas composition. Valve 8 was adjusted to allow the isotope gas a maximum pressure of 40 Pa. The actual measuring begins after the start of the temperature program in the heater. The deviation of the calculated isotope ratio was in all cases within the range of ±0.7%. For further details, see Stöcker's work [18].

RESULTS

On the method

The results of dynamic-thermal measurements are influenced to such a degree by the exact measuring conditions that they ought to be closely defined. The influence of the heating rate on the results is shown in Fig. 4. The change in the oxygen partial pressure, represented by the coefficient *s*, due to temperature can consequently be inferred. It ought to be noted that in contrast to previous dynamic-thermal methods, e.g. DTA/TG, the initial temperature in this method is independent of the heating rate, and only the size of the measured effects decreases with increased heating rates. The

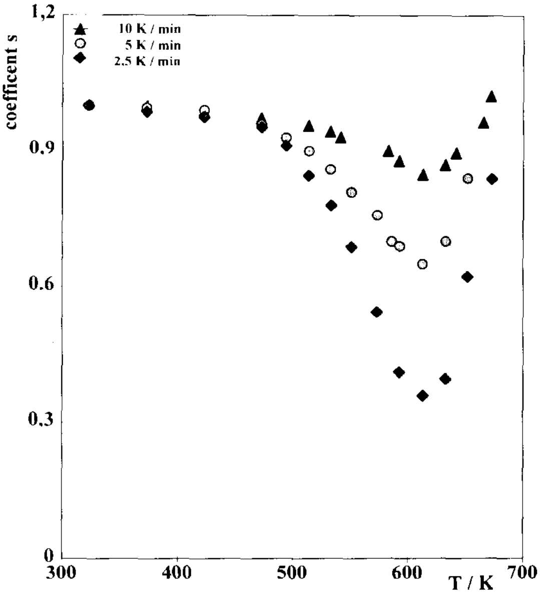


Fig. 4. Oxygen pressure (coefficient *s*) of the sample in relation to the heating rate for $YBa_2Cu_4O_8$.

most favourable heating rate, however, limits the pressure loss in the measuring equipment. This loss ought not to surpass 15% whenever possible. The heating rate must therefore be chosen so that the pressure change during the entire measuring period does not exceed this value.

Work at higher partial pressure fulfils the condition that the pressure loss be kept to a minimum. As shown in Fig. 5, exchange processes take place earlier at higher O_2 pressures. This may be explained by the higher covering of isotope gases on the surface of the solid and, consequently, the greater number of collisions. In contrast, oxygen emission processes are altered to greater extents at higher partial pressure. The change in coefficient *c*, signifying the greater differentiation of homogeneous and heterogeneous exchange processes, begins at the same initial temperature, though with greater sensitivity at lower partial pressures (Fig. 5(b)).

The isotope distribution in the gas phase is another important influence in this method. Various scenarios may be discussed:

(a) When isotope distribution in the gas phase is in equilibrium, only changes in the coefficient *c* can be assessed.

(b) An only partially disturbed isotope distribution is best monitored by the counting technique, as all measuring components are of the same order of magnitude. Under these conditions, both changes in coefficient *c* as well as observations concerning isotope exchange processes are possible.

(c) The same statements made in (b) above apply to a more disturbed isotope distribution. However, because in this case $^{34}O_2$ is present in only

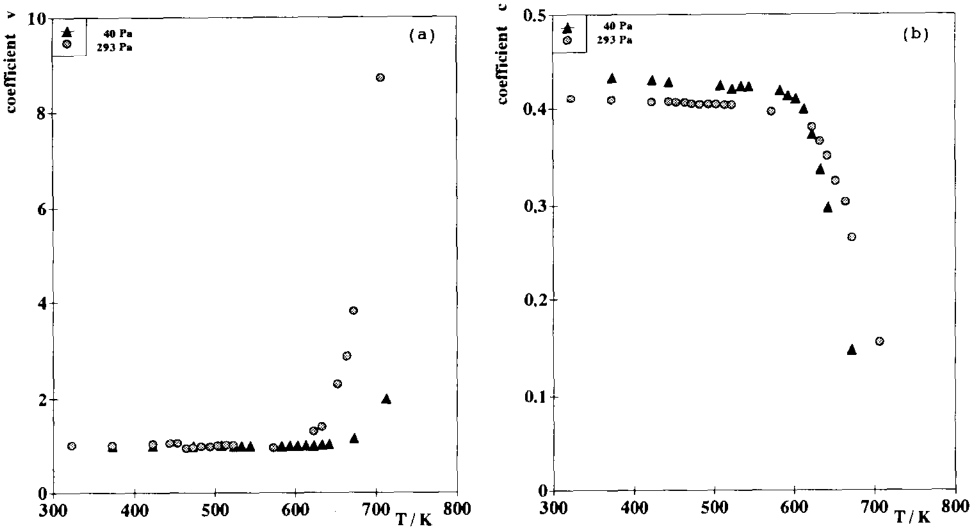


Fig. 5. Dependence of results on the vapour pressure used: (a) isotopic exchange (coefficient v); (b) ^{18}O-content of the gas phase (coefficient c).

very small concentrations, calculating coefficients y and v places a great demand on the precision of the measuring.

A gas with only slight deviation from isotopic equilibrium proved to be most suitable for the conditions chosen.

Characterization of various oxocuprates

After the most favourable measurement conditions were determined and the reproducibility of the method was ascertained, a series of various oxocuprates was tested extensively. The compounds tested and the resultant data are summarized in Table 1.

As may be seen from Figs. 6–11, various cuprate phases show unique curves for the particular coefficients in response to various temperatures. The curves formed here may be reproduced and allow the various phases to be characterized and distinguished from one another. Continuous exchange processes and auto-diffusion are generally able to be distinguished from the changes in the coefficients c, y and v. It can therefore be established in all tests that an increasing exchange activity accompanies decreasing oxygen activity in the solid. With increasing oxygen activity, the oxygen intake rises (coefficient s decreases) and the equilibrium temperature between oxygen intake and emission also rises.

Such a distinction is not possible simply by determining the change in the oxygen partial pressure.

TABLE 1

Data of investigated Y–Ba–Cu–O ceramics

Solids used in the experiments	Stoichiometric composition	X-ray analysis	Transition temperature T_c/K
Tetragonal 123-phase	$YBa_2Cu_3O_{6.15}$	Tetragonal	Semi-conducting
Orthorhombic 123-phase	$YBa_2Cu_3O_{6.95}$	Orthorhombic	92
124-Phase	$YBa_2Cu_4O_8$	Orthorhombic	75
Chlorinated 123-phase	$YBa_2Cu_3O_{6.1}Cl_{0.95}$	Orthorhombic/ tetragonal	90
Ozonated 123-phase	$YBa_2Cu_3O_{6.5}$	Diffuse orthorhombic	88
Orthorhombic deficient 123-phase	$YBa_2Cu_3O_{6.65}$	Orthorhombic	71

DISCUSSION

Taking the example of the chlorinated tetragonal 123-phase (Fig. 9) over various temperature ranges, these statement above are discussed and clarified below. It is worth mentioning that this is an originally non-superconducting 123-phase which became superconducting as a result of oxidizing chlorination by the "stirring" of oxygen, although it is largely regarded as a test of oxygen deficiency.

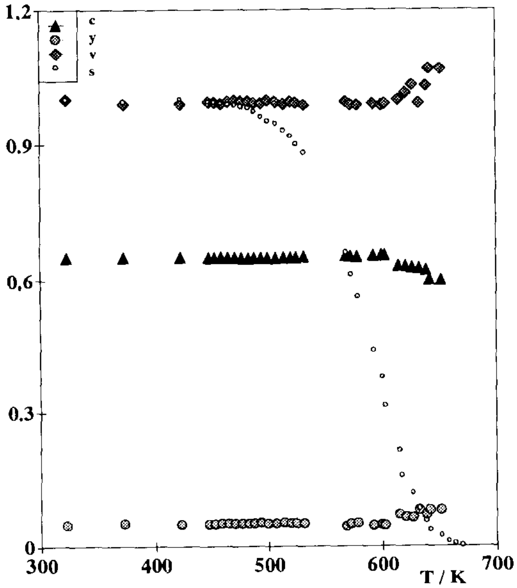


Fig. 6. Change of all coefficients for the tetragonal 123-phase ($YBa_2Cu_3O_{6.85}$) with increasing temperature.

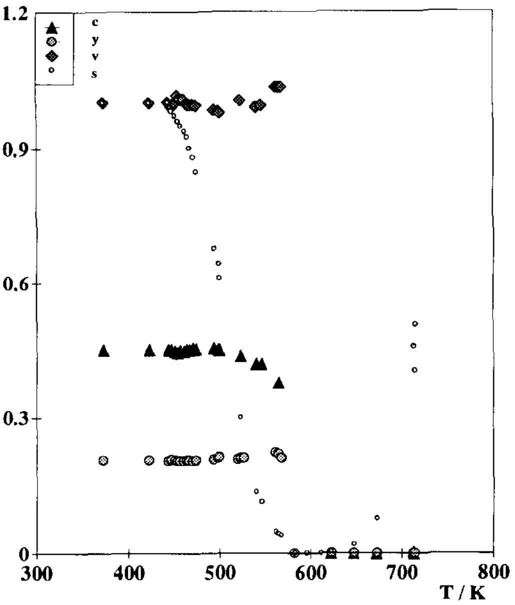


Fig. 7. Change of all coefficients for the orthorhombic oxygen-deficient phase $YBa_2Cu_3O_{6.65}$ with increasing temperature.

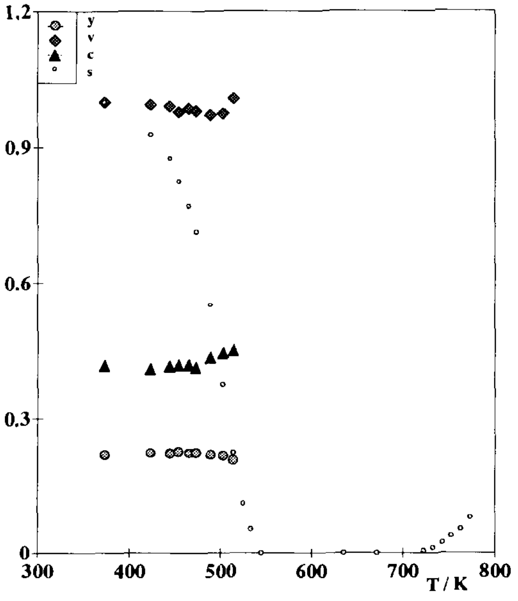


Fig. 8. Change of all coefficients for the ozonated tetragonal 123-phase ($YBa_2Cu_3O_{6.5}$) with increasing temperature.

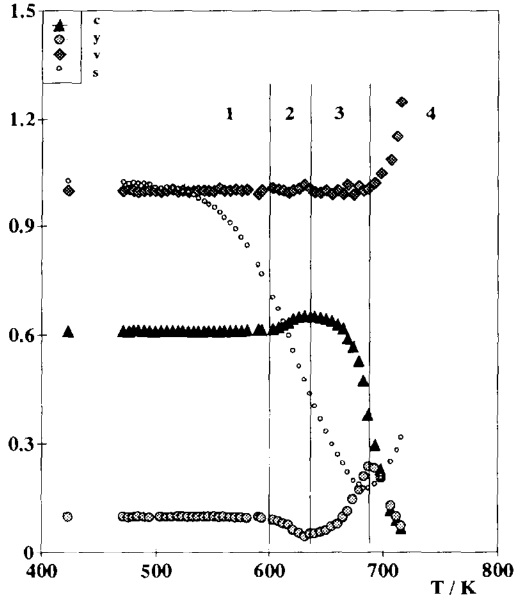


Fig. 9. Change of all coefficients for the chlorinated tetragonal 123-phase ($YBa_2Cu_3O_{6.1}Cl_{0.95}$) with increasing temperature.

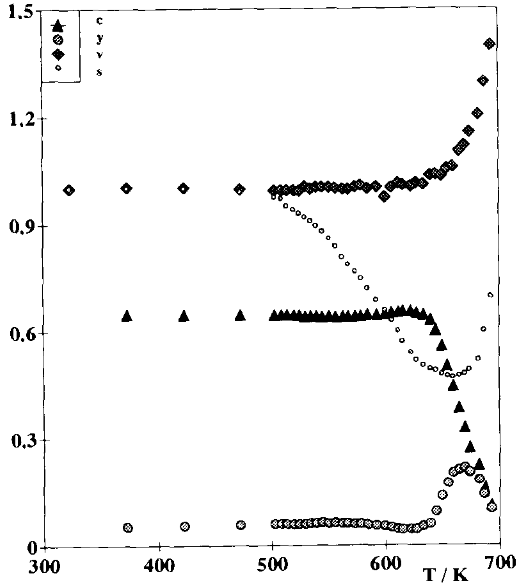


Fig. 10. Change of all coefficients for the oxygen-saturated orthorhombic 123-phase ($YBa_2Cu_3O_{6.95}$) with increasing temperature.

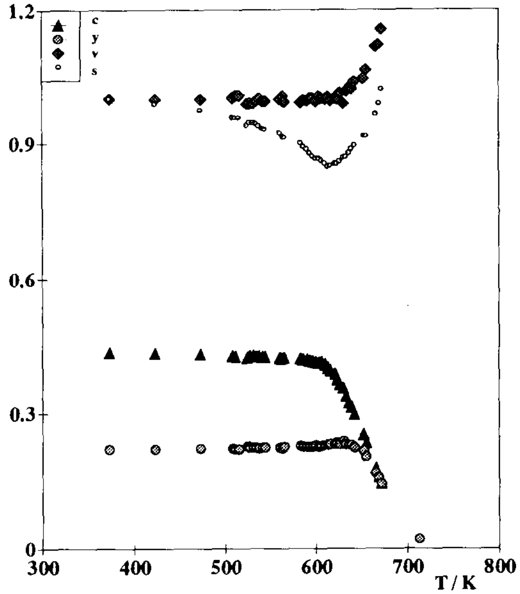


Fig. 11. Change of all coefficients for the 124-phase ($YBa_2Cu_3O_8$) with increasing temperature.

First range

The absorption of oxygen through the solid (seen as the decrease of coefficient s) is first apparent. At the same time, ^{18}O gathers and concentrates on the surface of the solid. All other coefficients remain constant. There is no evidence for any isotope exchange processes taking place. In the comparative discussion of oxygen absorption, the type of pre-treatment for the test substance should be considered.

Second range

In this range, a temperature is reached at which the isotope exchange processes begin. The speed at which oxygen is incorporated decreases. As this process slows down, the probability of absorbed gas molecules desorbing is increased. Therefore, within this stage, both homogeneous and heterogeneous isotope exchange processes may take place. This is manifested by the increasing concentration of $^{34}O_2$ and the decrease in coefficient y. An isotope separation during the incorporation of oxygen within the surface of the solid is fairly unlikely. The relative ^{18}O concentration can be explained by partial heterogeneous isotope exchange reactions as defined in eqn. (2). Through the reaction of $^{32}O_2(g)$ with the $^{18}O(s)$ accumulated on the surface resulting on $^{34}O_2(g)$, the ^{18}O already bound in the solid is again mobilized. This occurs during the simultaneous decrease in the total oxygen concentration in the gas phase (coefficient s fall), with the relative increase in c. By attributing the increase in c and the decrease in y to the greater concentration of $^{34}O_2$, it becomes understandable that the minimum y and maximum c occur at the same temperature.

The relative increase in the ^{18}O concentration in this temperature range is related to certain pre-conditions, however, and can be limited or prevented by two circumstances: a small incorporation of ^{18}O in the solid during an oxygen-saturated phase, e.g. the orthorhombic 123-phase, results in the formation of a smaller amount of ^{18}O isotope-containing oxygen molecules; and, too great an oxygen diffusion deep within the solid (typical in oxygen-deficient phases) leads to an amount of $^{18}O(s)$ at the surface that, as a result of partial heterogeneous exchange, is insufficient to form $^{32}O(g)$.

Third range

As the temperature is further increased, the oxygen absorption is superimposed on the initial oxygen emission (dynamic equilibrium). The increase in coefficient y proves that heterogeneous oxygen isotope exchange corresponding to eqn. (3) prevails over the homogeneous (eqn. (1)) and partially heterogeneous (eqn. (2)) isotope exchange. The processes which came to an end in the second temperature range are, as a result, overcompensated. While coefficient v fluctuates only slightly, c falls again. The counter processes typical in this temperature range can be noticed by contrasting the course of the coefficients s, c and y.

Fourth range

The auto-diffusion of oxygen becomes dominant in this temperature range. This is clear from the drastic decrease of coefficient c and the increase of v. A certain oxygen status in the solid (in terms of absorption/emission) is therefore necessary. Statements about the course of auto-diffusion are possible from the change in c and v (average oxygen auto-diffusion coefficient) with time. Coefficient v has the advantage of being independent of the emission of oxygen from the solid, thus making a comparison of various tests easier. Surprisingly, the course of v is nearly congruent in the tests undertaken; the diffusion mechanism is therefore very similar. This is made understandable by the knowledge that a certain oxygen status must be attained for the initiation of auto-diffusion, leading to the levelling of the structural differences among the investigated compounds in the surface area. The single exception is with the chlorinated material in which the temperature at the start of this process is noticeably higher with the same increase of v, which may be explained by a blocking effect of the Cl^- ions. Due to the auto-diffusion recorded in this temperature range, deeper-lying parts of the solid also contain ^{18}O. In contrast with what was observed in the third temperature range, the partial process of emission no longer influences the result of the isotope exchange—the isotope distribution in the gas phase tends towards the ideal distribution and y tends to zero.

A comparable discussion of the curves of various stoichiometries of the superconductors used permits interesting correlations to be drawn.

The general oxygen affinity in the test of a solid is expressed by coefficient s. In contrast to the unmodified tetragonal 123-phase ($YBa_2Cu_3O_{6.16}$), the orthorhombic 123-phase ($YBa_2Cu_3O_{6.95}$) and the 124-phase ($YBa_2Cu_4O_8$), the oxygen affinity in this series generally increases (Fig. 3, and see also Figs. 6, 10, 11). Both the initial temperature and the degree of oxygen absorption correspond completely to expectations: with decreasing oxygen affinity, the initial temperature moves to a higher value and the amount of absorbed oxygen becomes smaller. If one includes the modified phases in this comparison, they can also be readily explained. As a result of ozonization and chlorination, some superconducting orthorhombic phase is formed in this test. Amorphous by-product phases also develop alongside still-unchanged and pre-existing tetragonal phases. The early initial temperatures of oxygen absorption in these tests are consequently due to the portion of oxygen-deficient phase, as well as to amorphous by-products. The renewed oxygen emission ascertained at higher temperatures is, however, caused by the previously formed orthorhombic phase. Characteristically, the pure tetragonal phase gives off no oxygen at 700 K, the highest temperature reached in this experiment (s stays at zero).

Concerning the integral oxygen stoichiometry, both the chlorinated and the ozonated phases undergo only a slight modification, such that the similarlity to the original tetragonal phase is evident.

The temperature-dependent change of coefficient c as the integral measure of the ^{18}O-content in the gas phase permits an interesting correlation to be made with the transition-temperature of the superconducting phases investigated (Fig. 12, compare with Figs. 6, 7 and 11). It is striking that phases with a transition temperature of 90 K first show a slight increase in the value of c before the expected decrease takes place as a result of the onset of the isotope exchange. The fairly close results of these three tests suggests that these superconducting phases of the chlorinated and ozonated test materials are extremely similar, chemically and physically, to a pure orthorhombic 123-phase. This is supported by radiological and Raman experiments [13].

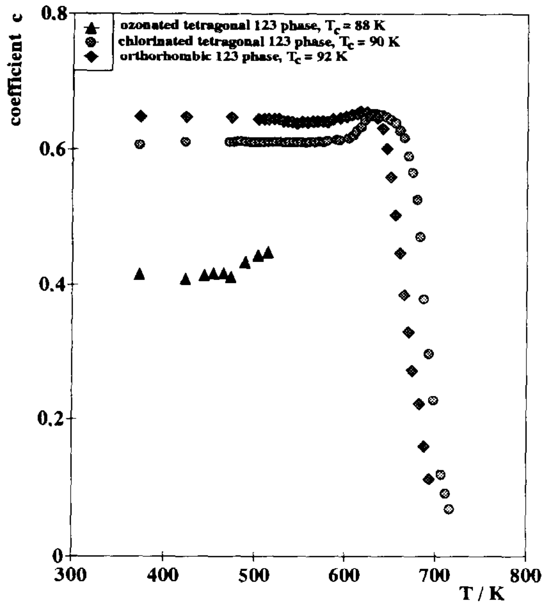


Fig. 12. Change of coefficient *c* with increasing temperature for the 90 K samples.

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