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Mechanism of Formation of Halogen-Containing High-Temperature Superconductors Based on $YBa_2Cu_3O_{7-x}$

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There are two points of view in the literature on the mechanism of formation of high-temperature superconductors (HTSC – X, where X = Cl, Br, I). One of these supposes that a topotactic redox intercalation reaction proceeds, the other assumes that the isomorphous substitution of oxygen by halogens takes place. It has been shown by tensometric measurements, the anomalous scattering effect, EXAFS, and Mössbauer spectroscopy that the interaction of halogens with the tetragonal modification of $YBa_2Cu_3O_{7-x}$ proceeds by intercalation of halogens into the anion vacant position of the Cu(1) layer. The charge transfer from the Cu(2) layers to the halogens results in the formation of electron holes in the Cu–O pyramids, which determines HTSC-properties of the intercalate compounds obtained.

Introduction

The method of modifying the properties of solids by doping, known in solid state physics and chemistry and rather widely used, has recently received widespread attention in the field of high-temperature superconductors. Here, the object is twofold: first, to create the desired change in the physical or physicochemical properties of HTSC; second, to approach an understanding of the mechanism of superconductivity by elucidating the role of different structural designs in HTSC.

There is a great number of works devoted to the doping of HTSC by isomorphous substitution of ions located in the cation sublattice. The number of works in which attempts were made to carry out the doping of the anion sublattice of HTSC is much smaller. Since fluorine and sulfur ions are similar to oxygen ions in ionic radii and chemical properties, attempts have been undertaken to substitute exactly these elements for oxygen by introducing copper and barium fluoride or the corresponding sulfides into the composition of the starting mixture in the preparation of $YBa_2Cu_3O_{7-x}$ (*1–4*). In the synthesis of fluorine-containing $YBa_2Cu_3O_{7-x}$, though the monophase product has not been obtained, a diamagnetic response has been found at temperatures of 155–168 K. Though these results are not always reproducible (*5–7*), the possibility of replacing oxygen by fluorine has itself aroused considerable interest among investigators. This interest is particularly stimulated by the fact that in a number of works the proposed mechanism of occurrence of high-temperature superconductivity in complex oxide systems involves the appearance of O^- holes in the oxygen sublattice of the oxide. From this it follows that the temperature of transition can be changed by doping

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the oxygen sublattice with other anions introduced by isomorphous substitution.

However, the possibility of such isomorphous substitution of oxygen involves certain difficulties, two being most important.

First, there is a strict limitation on size for the substituting and substituted ions; second, there are difficulties in reaching homogenization of the system, which researchers have met in attempts to conduct isomorphous substitution during the course of synthesis.

These difficulties might be overcome to a large extent if attempts were made to modify the electron structure and electrophysical properties of high-temperature superconductors by introducing the dopant ions into their lattice using intercalation—a method that is finding ever increasing applications in modern solid state chemistry (*8–10*). Indeed, it has been shown in the works of Schöllhorn (*11–13*) and Pavlukhin (*14–16*) that the presence of vacant positions in the Cu(1) layer as well as the possibility of changing the valence of the copper enable $YBa_2Cu_3O_{7-x}$ to be considered as a matrix in which intercalation processes may proceed. This enables one to consider the known process of oxygen exchange between $YBa_2Cu_3O_{7-x}$ and the environment as a redox topotactic intercalation or deintercalation, accordingly, as oxygen is absorbed or, on the contrary, is lost.

With the aim of extending further the works on the modification of the HTSC properties by intercalation we have carried out experiments on the intercalation of halogens (Cl_2, Br_2, I_2) into the $YBa_2Cu_3O_{7-x}$ lattice.

The temperature ranges of intercalations of halogens, composition and structural data on the intercalates being obtained, and data on the sites of localization of halogens in the system of bound vacant positions in the Cu(1) layer have been presented in detail in other works (17–20), and are summarized herein in Table I.

TABLE I

No.	Compound	T of synthesis	Cell parameter Å a_o	b_o	c_o	T_c^a (K)
1	$YBa_2Cu_3O_{6.3}$	—	3.83	3.83	11.74	—
2	$YBa_2Cu_3O_{6.3}I_{0.2-0.4}$	250	3.89	3.85	11.69	60
3	$YBa_2Cu_3O_{6.3}Br_{1.0-1.8}$	220	3.87	3.85	11.63	90
4	$YBa_2Cu_3O_{6.3}Cl_{1.5-1.8}$	150	3.87	3.85	11.63	86
5	$YBa_2Cu_3O_{6.94}$	—	3.89	3.83	11.67	93

Note. T_c^a is obtained from the magnetic measurements performed by A. G. Klimenkol (Institute of Inorganic Chemistry, Siberian Branch of the Academy of Science of the USSR).

Simultaneously with the publication of our results, data appeared in the literature on halogenation of yttrium–barium cuprate and the recovery of superconductivity by halogenation (*21–23*). The conditions of the synthesis of bromine- and iodine-containing $YBa_2Cu_3O_{7-x}$ reproduce those given in (*17–20*), but the results obtained are interpreted in a different way. The authors of work (*23*) have concluded that in the $YBa_2Cu_3O_{7-x}$ system, an oxygen–iodine isomorphism takes place, and the halogen entering the lattices is arranged in an ordered fashion in the interbarium planes, replacing oxygen. Thus, there are two points of view on the mechanism of halogenation of yttrium–barium cuprate. According to one of them, a redox topotactic reaction proceeds involving intercalation and localization of halogens in the system of bound vacant positions in the Cu(1) layer. From the other point of view, the formation of halogen-containing HTSC is the result of isomorphous substitution of halogen for oxygen. It is supposed that during substitution halogen atoms are arranged in an ordered fashion in the Cu(1) layer.

In order to answer the question of which of these points of view is proper, what is usually meant by the notion of isomorphism should be recalled. This term was first introduced into the science in 1819 by Mitcherlich and meant that substances with a similar chemical composition had similar external shapes of the crystals; this term was later modified by V. Goldschmit with consideration for the crystallochemical features of the structure of solids.

At present, isomorphism means the ability of chemically or geometrically similar atoms or ions to replace each other in the crystalline lattice (*24, 25*).

In the case at issue, the possibility should be considered of substituting the oxygen ion (the ionic radius of O^{2-} is 1.32 Å) by fluorine (R_{F^-} = 1.33 Å), chlorine (R_{Cl^-} = 1.78 Å), bromine (R_{BR^-} = 1.96 Å), or iodine R_{I^-} = 2.2 Å). It is easily seen that only in the halogenation of yttrium–barium cuprate by fluorine may one expect a similarity in ionic radii and chemical bond—the necessary condition for manifestation of isomorphism. In the rest of the cases, when taking into account the criterion of Goldschmidt (the difference in ionic radius between the substituted and substituting ions must be not exceed 15%), it is difficult to expect isomorphous substitution.

The Character of the Halogenation Process of $YBa_2Cu_3O_{7-x}$

How does the interaction of halogens with sold yttrium barium cuprate take place? Fig. 1 gives temperature dependencies for the vapor pressure of different halogens above the tetragonal modification of yttrium barium cuprate in the closed space of a membrane zero-manometer. Arrowed lines in this figures show what will proceed in the system if at some stages it is cooled down to the temperature of liquid nitrogen, the reacted halogen being freezed out thereby. If the halogenation reaction under study was a substitution reaction one would expect the occurrence of residual pressure due to the appearance in the system of oxygen substituted for the halogen. If an introduction of the halogen into the cuprate lattice rather than a substitution takes place, no residual pressure should be in the system during freezing.

The special care was taken to exclude the influence of impurities and water. The starting tetraphase specimen was prepared by vacuum annealing at 600°C (10^{-2} Torr) and placed in an experimental unit with dried halogen. More complicated conditions were needed to dry the starting bromine. It was dried in a column with P_2O_5 in an inert gas atmosphere or was produced by the thermal decomposition of the initially dried copper dibromide. In both cases the results were identical.

It is seen from Fig. 1 that an introduction rather than a substitution takes place, i.e., the halogenation process is one of intercalation. Of course, if the temperature is much higher than that recommended for the synthesis, the evolution of oxygen takes place, due to the substitution of it by the halogen, at the expense of the decomposition of the cuprate with the formation of complex oxyhalogenids, as shown by X-ray phase analysis.

It is well known that the lattice parameter $c/3$ is the most sensitive to oxygen content, and makes it possible to estimate the oxygen content in a $YBa_2Cu_3O_{7-x}$ specimen. A similar dependence is shown in Fig. 2. It is seen from this picture that the unit cell parameter strongly depends on the oxygen and halogen content in the sample.

Location of Halogens in the Structure of Yttrium Cuprate

To determine the location of halogens in the $YBa_2Cu_3O_{7-x}$ structure, the anomalous scattering method, EXAFS, and Mossbauer spectroscopy were used. It is known that the scattering ability of a definite sort of atom entering into the compound changes as the energy of the primary X-ray beam approximates the K-absorption edge. The effect of anomalous scattering is based on this. As a result, a change in the intensity of

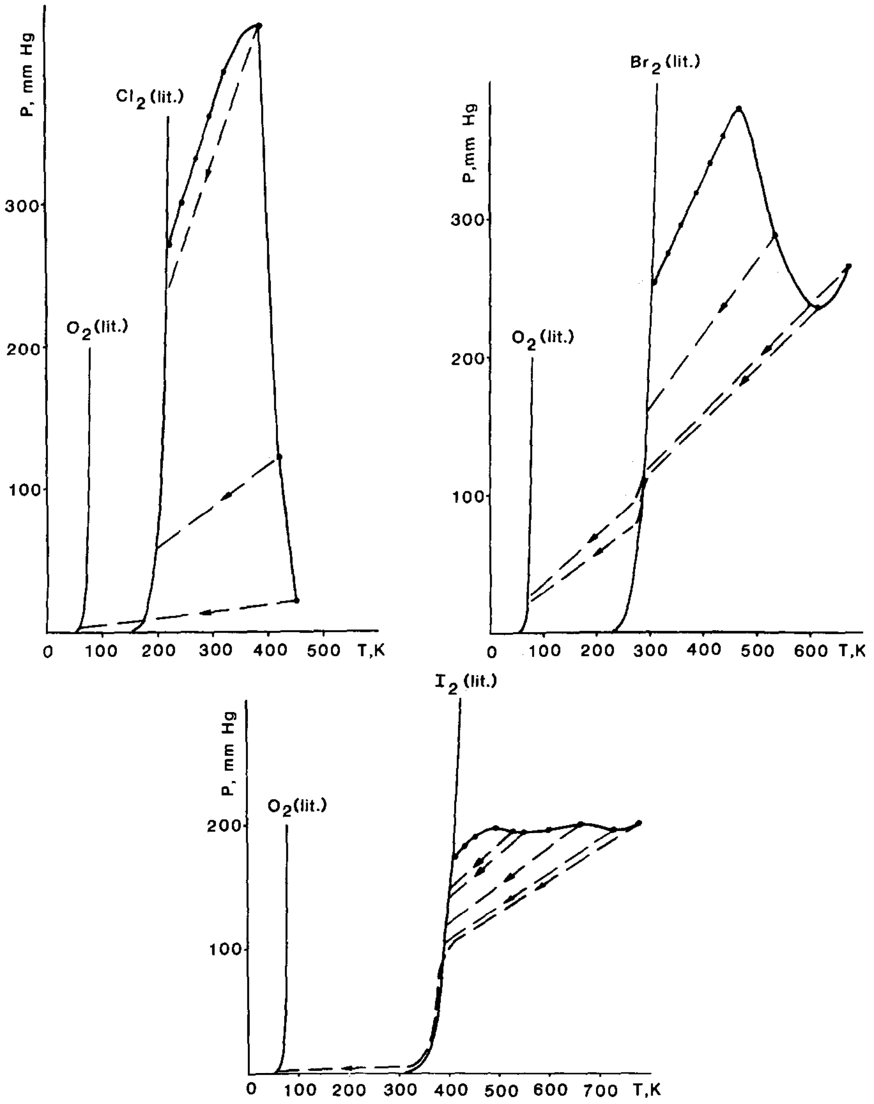

FIG. 1. Temperature dependence of quasiequilibrium pressure of Cl_2 (1) Br_2 (2) and I_2 (3) above $YBa_2Cu_3O_{6.3}$.

diffraction maximums is connected with the change in the scattering ability of a definite sort of atom in the structure.

Thus, the use of the anomalous scattering effect helps in solving the basic question of whether halogens are in the $YBa_2Cu_3O_{7-x}$ structure or whether they form an individual phase.

Figure 3 gives an X-ray diffraction pattern of bromine-containing yttrium cuprate (HTSC-Br) obtained using synchrotron radiation (SR) at the energies of a primary beam close to the K-absorption edge of bromine (E = 13,429 eV) and at energies much higher than this magnitude (E = 13,474 eV). The figures above the peaks show a relative

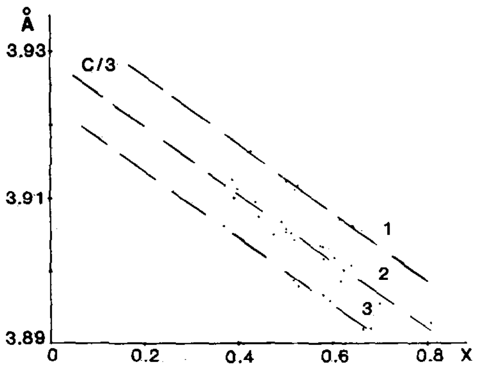

FIG. 2. The unit cell parameter $c/3$ vs initial tetraphase oxygen content and amount of intercalated halogen. 1, $YBa_2Cu_3O_{6.1}I_x$; 2, $YBa_2Cu_3O_{6.3}I_x$; 3, $YBa_2Cu_3O_{6.4}I_x$.

change in the intensity of reflections with a change in the wavelength of the primary X-ray beam.

We have calculated the probable changes in X-ray peak intensities after bromine substitution in different structural positions of $YBa_2Cu_3O_{7-x}$ and compared these results with anomalous synchrotron X-ray scattering data. The low accuracy of such calculations is connected with difficulties in the control of displacement of bromine atoms with increasing amounts of intercalated halogen. Hence under the assumption of bromine localization in the Cu(1) planes, the calculated data are in 15–20% agreement with the experimental results.

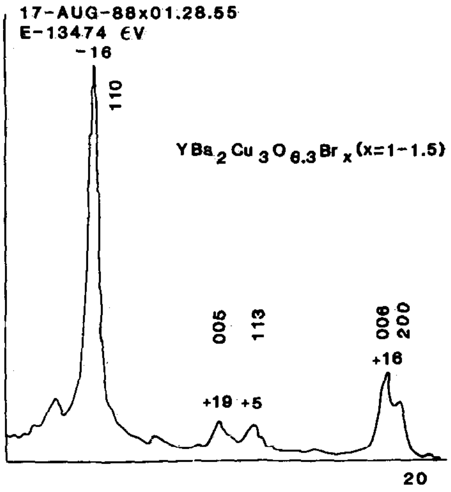

FIG. 3. X-ray diffraction pattern of $YBa_2Cu_3O_{6.3}Br_x$ recorded using the anomalous scattering effect.

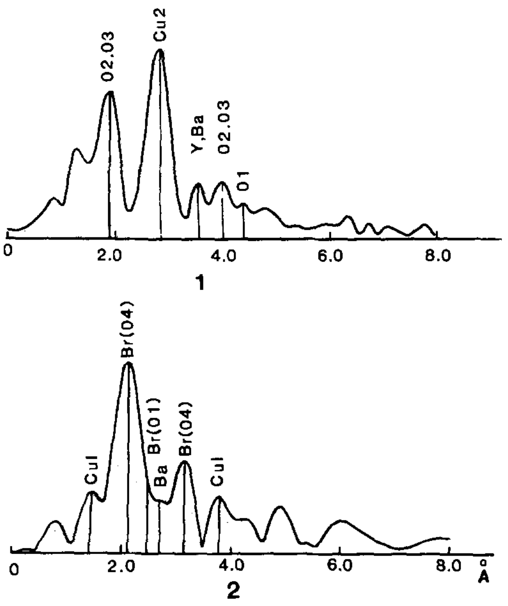

FIG. 4. EXAFS spectra of Y (1) and Br (2) K-absorption edges for $YBa_2Cu_3O_{6.7}Br_x$ and theoretical section-lined diagram.

The change in the intensity of reflections, which correspond to the orthorombic $YBa_2Cu_3O_{7-x}$ structure, is direct evidence for bromine atoms building in the HTSC structure.

This basic conclusion is confirmed by the data of EXAFS and Mossbauer spectroscopy. As known, an investigation of the extended fine structure of the K-absorption edges of the atoms composing the sample under study enables one to establish not only the presence of atoms of this sort in the structure but also the nearest surroundings.

The EXAFS spectra of Y, Br K-absorption edges for HTSC-Br are given in Fig. 4.

It should be noted that the EXAFS spectra of Y for the starting yttrium cuprate and the halogenated one are practically identical. Hence, the treatment with bromine does not change the nearest surroundings of yttrium. As to EXAFS spectra of the bromine K-absorption edge, the radial distribution functions obtained experimentally agree with the calculated ones, assuming that bromine is localized in the vacant positions of the Cu(1) layer.

Analogous results were obtained using Mössbauer spectroscopy of samples doped with ^{57}Fe. Iron cations are known to occupy the Cu(1) and Cu(2) structural positions in yttrium cuprate. It has been earlier shown (*15, 16*) that two doublets (Fe(I) and Fe(II) correspond to the iron cations located in the Cu(1) layer, which reflects the fact that ^{57}Fe has coordination numbers equal to two or more than two, respectively.

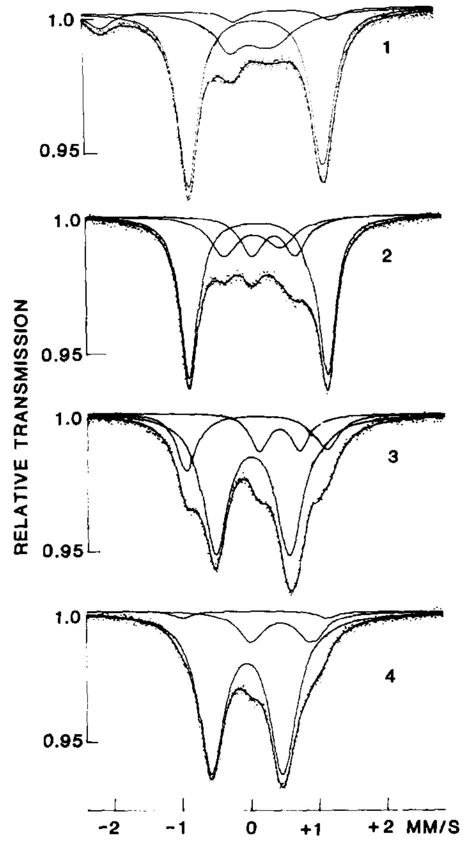

FIG. 5. Mossbauer spectra of the starting YBa$_2$(Cu$_{0.97}$Fe$^{57}_{0.03}$)$_3$O$_{7-x}$ (1) treated with I$_2$ (2), O$_2$ at 10 atm (3), and Br$_2$ (4).

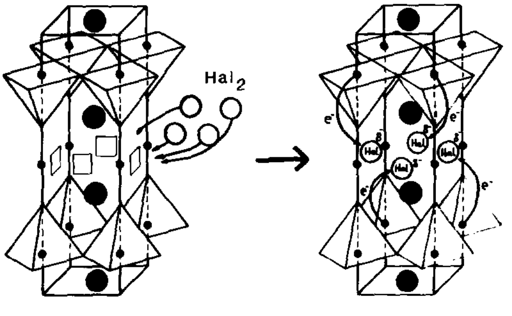

FIG. 6. A scheme of intercalation of halogens with yttrium cuprate.

The Mössbauer spectra of the starting tetragonal yttrium cuprate and of that treated with halogens are presented in Fig. 5. A sharp increase in the intensity of the Fe(II) doublet and the disappearance of the Fe(I) doublet indicate that the coordination number of cations located in the Cu(1) position increases upon the treatment of yttrium cuprate with bromine.

Thus, the data obtained suggest that the interaction of the tetragonal modification of yttrium cuprate with Cl$_2$, Br$_2$, and I$_2$ proceeds by introduction of halogens into the system of bound vacant positions of the Cu(1) layer, i.e., by a topotactic intercalation reaction (Fig. 6).

It should be expected that the intercalation of halogens, being strong electron acceptors, into yttrium cuprate is a redox reaction which involves an electron transfer from the tetragonal pyramid of the Cu(2) layer to the halogens located in the Cu(1) planes (Fig. 6).

The charge transfer results in the formation of electron holes in the Cu(2) layers, which destroy the "two-dimensional" antiferromagnetic ordering (*26*) and is detected by Mössbauer spectroscopy: the magnetic-ordering sextet associated with Fe^{3+} in the Cu(2) layers transforms into the paramagnetic doublet (Fig. 5). The degree of charge transfer appears to depend on the electron affinity of halogens and on the relationship between their radii and the sizes of vacancies in the Cu(1) layers. Thus halogens in yttrium cuprate appear to be in the $Hal^{-\delta}$ state, where $0 < \delta < 1$.

So, the interaction of halogens with yttrium cuprate is a topotactic redox intercalation reaction and can be given by the equation:

$$x\mathrm{Hal}^{-\delta} + [\mathrm{YBa_2Cu_3O_6}] = \mathrm{Hal}_x^{-\delta}\,[\mathrm{YBa_2Cu_3O_6}]^{+x\delta} + x\delta e^-$$

It should be noted that intercalates are, as a rule, metastable compounds and with time can undergo chemical transformation leading to the degradation of the matrix and to the formation of more thermodynamically stable products. Yttrium cuprate intercalated with halogens is also the metastable compound, and in the process of interaction with halogens, and then during the aging of the samples, besides intercalation, secondary processes of decomposition of the matrix proceed to give complex oxyhalogenids and halogenides, as shown by X-ray phase analysis. It is obvious that the degradation of intercalates would depend on the chemical activity of guests and increases in the series HTSC-I, HTSC-Br, HTSC-Cl. Perhaps the difficulty in obtaining monophase samples of HTSC-Cl might be attributed to this fact. The decomposition of halogen-containing HTSC beings possibly with the substitution of the oxygen ions located in the neighboring BaO layers by halogens from the Cu(1) planes.

We have emphasized (*19*) the possibility of this process in connection with a change in the Mössbauer parameters for the iron ions occuping Cu(2) positions.

Thus, all structure-sensitive methods, anomalous scattering, EXAFS, X-ray analysis, and Mössbauer spectroscopy, show halogen (iodine and bromine) localization mostly in the Cu(1) layers of the $YBa_2Cu_3O_{7-x}$ structure. Specimen decomposition for oxyhalogenids or the formation of complex multiphase mixture (chlorine, this work; fluorine, (*27*)) takes place at relatively higher temperature. Halogenated samples are sufficiently stable under these experimental conditions. However, they are thermodynamically unstable and with violation of the synthesis conditions they may decompose (iodine and bromine) or the synthesis (in the case of chlorine) by this technique may be very difficult. Probably their existence is purely kinetic effect.

In conclusion, it should be noted that topotactic redox reactions are an efficient method of affecting the electronic structure and electrophysical properties of the matrix.

Intercalation is known to affect the T_c of low-temperature superconductors, which is associated with a change in the electron state density near the Fermi surface (*28*) and also with suppression of electron instability of the matrix, which is accompanied by charge density waves and phase transitions (*29*), by introduction of donor–acceptor guests. It is not impossible that in the case of HTSC-X, guests–acceptors (O, F, Cl, Br, I etc.) play an analogous role, producing an optimal concentration of carriers (holes) and destroying antiferromagnetism (spin density waves) in the starting matrix.

Besides, intercalation compounds have been not long ago considered and intensively studied as promising subjects from the viewpoint of HTSC. It is considered that because of the specificity of the electronic and crystalline structure of intercalates the nonphonon mechanisms of pairing of charge carriers could proceed (*29*).

Note added in proof. During correction of this paper the results of H. B. Radousky *et al.* [30] have been available. This data is in agreement with ours.

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