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INTERCALATION OF HALOGENS INTO THE LATTICE OF $YBa_2Cu_3O_{7-x}$ PHASES AND SUBSTITUTION OF HALOGENS FOR OXYGEN ATOMS

A.G. KLIMENKO and V.Ye. FEDOROV

Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the U.S.S.R., Novosibirsk 630090 (U.S.S.R.)

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ABSTRACT

The results of studies of halogen-containing yttrium–barium cuprates are reviewed. Different methods for the synthesis of $YBa_2Cu_3O_{7-x}Hal_y$ phases are discussed and the structural features and physical properties of the phases are analysed. Attention is given mainly to the low-temperature methods which allow preparation of single-phase samples. Mechanisms of halogen insertion into the $YBa_2Cu_3O_{7-x}$ lattice are discussed, as well as the role of different structural fragments in the high-temperature superconductivity phenomenon.

INTRODUCTION

The first reports [1–3] of the high critical temperature ($T_c \approx 155$ K) of fluorine-containing cuprates, using $YBa_2Cu_3O_{7-x}$ as a starting point, have stimulated further investigations of the synthesis of fluorine derivatives. Although the original observations of high T_c values of fluorine-containing phases have not been confirmed in these studies the work in this direction is being continued [4–24]. Recently, there have also been attempts to obtain materials containing other halogens [25–31].

Generally, halogen derivatives of the type $YBa_2Cu_3O_{7-x}Hal_y$ are obtainable by two mechanisms of interaction of $YBa_2Cu_3O_{7-x}$ with halogens, these being intercalation of halogens into the $YBa_2Cu_3O_{7-x}$ matrix lattice and substitution of a halogen for oxygen atoms.

Intercalation of various atoms or molecules (electron donors or electron acceptors) into compounds with a low-dimensional character of the crystal lattice is one of the well-known methods of chemical modification of electrophysical properties of inorganic materials. This mechanism usually involves intercalation of atoms or molecules which are electron donors, e.g. intercalation by alkali metals or other strongly electropositive metals. Such an intercalation involves matrix reduction: the atoms of the metal become ionized and their electrons move to the conduction band, thereby changing the electronic state density at the Fermi level. In the intercalation by acceptors, i.e. when there is oxidation of the matrix, a part of the electronic density on the host lattice migrates to the guests, causing a reduction in the conduction band occupancy.

Thus, intercalation of compounds by atoms or molecules that are electron donors or electron acceptors is accompanied by a change in the electronic properties of these compounds and may be used for modification of the properties of materials, including superconducting ones, in the desired direction.

Yttrium–barium cuprates have a crystal lattice that has a layered character but in these materials there are no van der Waals spaces between the layers similar to those exhibited by other inorganic layered compounds having a structure of the type $CdCl_2$, MoS_2, etc., so that the classical intercalation into the interlayer space is here impossible.

When considering halogen-containing phases of the type $YBa_2Cu_3O_{7-x}Hal_y$ from the point of view of substitution of oxygen in the anionic sublattice by halogens, the following may be pointed out. Comparing the crystallochemical para-meters of oxygen and halogens one notes that whereas the ionic radii of the oxygen ion O^{2-} and the fluoride ion F^- are very similar, the ionic radii of other halogen ions (Cl^-, Br^-, and especially I^-) are considerably greater. Therefore, it is generally believed that, at least for crystallochemical reasons, it is in the oxo–fluoride systems where substitution of halogen ions for oxygen ions must be expected to occur first, such a possibility being smaller for oxo–chloride and unlikely for bromide and iodide derivatives. It should also be noted that if halogenation occurs by the intercalation mechanism and is accompanied by filling of the vacant sites of the type O5 (for $YBa_2Cu_3O_7$) or O5 and O1 (for $YBa_2Cu_3O_6$) then in this case also it is the fluoride ions that may be preferred since the geometrical dimensions of these vacancies are similar to the O^{2-} and F^- ionic radii.

The experimental evidence shows, however, that halogen derivatives are formed not only in the systems with fluorine but also with chlorine, bromine and even iodine. The possibility of intercalation and substitution in the anionic sublattice with the aim of modifying the properties of $YBa_2Cu_3O_{7-x}$ has been studied both theoretically and experimentally.

The theoretical studies consisted of calculating the electron band structure of fluorine-containing phases and comparing the results with the characteristics of the orthorhombic phase $YBa_2Cu_3O_7$.

Band structure calculations for the equilibrium orthorhombic phase $YBa_2Cu_3O_{7-x}$ show [32–35] that three top bands of the *d* block localized near the Fermi level are represented by two nearly half-filled x^2–y^2 bands originating only from the layers (CuO_2) and one almost empty z^2–y^2 band originating only from the chains (CuO_3) (Fig. 1). The energy position of the chain z^2–y^2 band with respect to the other bands and the Fermi level depends on the nature of the interatomic interactions in the chain (CuO_3)

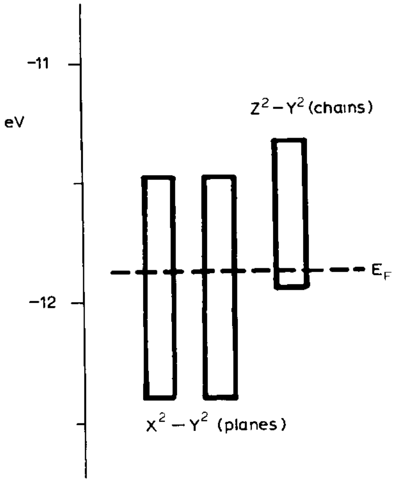

Fig. 1. Three top bands of the *d* block for the orthorhombic phase $YBa_2Cu_3O_7$ [35].

and first of all on the interatomic Cu–O distances. When the chain band bottom falls below the Fermi level (which is mainly determined by the Cu1–O4 distance) is very important for the electronic properties of these phases. When the z^2–y^2 band bottom is below the Fermi level some electrons from the layers (CuO_2) will flow over to the chains (CuO_3), reducing the x^2–y^2 occupancy. Thus, the z^2–y^2 band formed by the electronic states of the chain atoms acts as a kind of electronic reservoir governing the occupancies of the bands crossing the Fermi level.

The electronic structure of fluorine-containing compounds $YBa_2Cu_3O_{7-x}F_y$ has been studied theoretically [36–38]. It has been shown [37] that in the case of the F atoms filling the vacant O5 sites between adjacent chains (CuO_3) the chains retain the same one-dimensional band features characteristic of the pure $YBa_2Cu_3O_7$ phase; when the F atoms substitute for oxygens in the chain itself the one-dimensional band features will disappear. From these results it has been concluded that if it is the one-dimensional band features that are critical for the high T_c superconductivity phenomenon then the effect of fluorine insertion into the vacant sites of the structure on the T_c values must be small, whereas substitution of fluorine for oxygen belonging to the chains will cause a dramatic drop in T_c or a complete disappearance of superconductivity.

Xu et al. [38] have shown that for the $YBa_2Cu_3O_{7-x}$ compounds in which fluorine substitutes for oxygen in the CuO_2 planes or for type O1 atoms in the Cu1 chains the band structure remains similar to that in $YBa_2Cu_3O_7$. However, when fluorine substitutes for type O4 oxygen atoms coordinated to Cu1 along the *c* axis the band structure is markedly changed because of the very strong interaction (of antibonding character) of the Cu1 atoms with F causing substantial upward displacement of the chain band. From this the authors conclude that fluorine is more likely to substitute for oxygen atoms in the planes or chains (type O1) than for type O4 atoms in the chains.

The experimental results on the synthesis and properties of fluorine-containing $YBa_2Cu_3O_{7-x}F_y$ phases obtained by different authors are rather contradictory. Thus, the use of a high-temperature solid-state synthesis ($\sim 950\,^\circ C$) as a source of fluorine in such solid state salts as BaF_2 [1–3,7–9,14,15,20], CuF_2 [7], YF_3 [7,10,22], YOF [5,22], KHF_2 [5], NH_4HF_2 [6] results in the formation of multiphase reaction products always containing, along with other phases, some BaF_2. The superconducting phases obtained in such reactions show T_c values close to that of the initial $YBa_2Cu_3O_7$ phase, either slightly below or slightly exceeding it. The extent of fluorination by this method is small. For example, the composition of the fluorinated phases obtained by Vanderah et al. [22] is described by the formula $LnBa_2Cu_3O_xF_{0.2-0.4}$ Low-temperature fluorination ($\leq 300\,^\circ C$) of $YBa_2Cu_3O_7$ using ZnF_2 [13] produced a phase with the composition $YBa_2Cu_3O_{6.6}F_{0.4}$ showing semiconducting properties.

Low-temperature ($\leq 450\,^\circ C$) fluorination of $YBa_2Cu_3O_{7-x}$ using gaseous fluorine leads, as a rule, to multiphase products, both superconducting and semiconducting [4,7,11,12,16,19]. In the fluorination of the orthorhombic phase $YBa_2Cu_3O_{7-x}$ using gaseous fluoride at $400\,^\circ C$ a semiconducting phase with the composition $YBa_2Cu_3O_{4.5}F_{3.5}$ [12] has been obtained. The method gives, however, poorly reproducible results. Better results are obtained with the use of gaseous NF_3 at $300\,^\circ C$. In this way $YBa_2Cu_3O_{7-x}F_y$ phases ($y = 0.08–1.11$) have been synthesized [21]. There have also been reports of other methods for fluorination of high T_c materials, such as microwave plasma treatment [23], sol–gel technique [24] and ion implantation [2].

Similar results have been obtained with other halogens [20,25–32]. Thus, treatment of the tetragonal phases $YBa_2Cu_3O_{6+x}$ ($x \lesssim 0.3$) 2with gaseous halogens (Cl_2, Br_2, I_2) at particular temperatures ($\sim$ 250, 220 and $120\,^\circ C$, respectively) [25] results in the formation of halogen-containing superconductors with high critical temperatures: $T_c \gtrsim 78$ K for $YBa_2Cu_3O_{7-x}Cl_y$, $T_c \approx 90$ K for $YBa_2Cu_3O_{6.3}Br_{1.0-1.5}$ and $T_c \approx 60$ K for $YBa_2Cu_3O_{6.3}Cl_x$ [25]. Chlorine-containing phases $YBa_2Cu_3O_{7-x}Cl_y$ ($0.3 \leqslant y \leqslant 0.6$) have been synthesized at $150–170\,^\circ C$ by interaction of the orthorhombic phase $YBa_2Cu_3O_{7-x}$ with PCl_5 [30]. The samples obtained in this way were pure, with a T_c coinciding with that of the starting orthorhombic phase ($T_c \approx 92$ K). [30,31].

In most of the works devoted to the synthesis of halogenated materials the authors note formation of side products, sometimes X-ray amorphous, which could not be isolated and in some cases were not even identified. For these reasons, the compositions cited are apparently not always authentic and should be treated with caution.

Thus, experimental evidence is presently available on all halogen-containing systems; this gives us some general ideas about the possibilities of halogen introduction into the $YBa_2Cu_3O_{7-x}$ phases by different methods and allows first suggestions to be made concerning the role of the halogen atoms in such phases.

In considering the different approaches to the preparation of halogen-containing compounds using $YBa_2Cu_3O_{7-x}$ as a starting point it should be noted that the high-temperature solid-state syntheses always produce multiphase products containing some BaF_2 (or $BaCl_2$ in the case of chlorine derivatives) which indicates their high thermal stability in the systems studied. For this reason, it is difficult to determine with sufficient accuracy the amount of halogen that has inserted into the $YBa_2Cu_3O_{7-x}Hal_y$. In addition, high-temperature reactions appear to lead to a statistical distribution of the halogen atoms in the oxygen sites and are therefore not suitable for the synthesis of phases in which the halogens could be ordered in particular sites in the crystal lattice.

Another approach to the synthesis of halogen-containing materials consists of employing lower temperatures and more active halogen-containing reagents. It has been found convenient here to use gaseous F_2, NF_3, Cl_2, Br_2) or readily volatile liquid or solid reagents (NH_4HF_2, I_2, PCl_5) in which case purer reaction products are obtained. In this connection, a low-temperature method for the synthesis of high purity $YBa_2Cu_3O_{7-x}Cl_y$ phases, employing PCl_5 as a chlorinating agent [30,31], is of great interest. It is known that PCl_5 is thermally unstable, dissociating into PCl_3 and Cl_2 upon heating. The evolving chlorine is an active chlorinating agent. There is one more important point connected with the use of PCl_5 for chlorinating $YBa_2Cu_3O_{7-x}$; this is associated with the fact that PCl_3 formed in the thermal dissociation of PCl_5, easily oxidizes to $OPCl_3$ and may act as an excellent acceptor of oxygen. All the reaction side products can be easily removed by washing in organic solvents, for example acetonitrile. The advantage of the low-temperature methods is that milder synthesis conditions often allow the formation of phases which do not form, or are unstable in, high-temperature experiments. Therefore, the low-temperature reactions are undoubtedly of interest in the synthesis of complex halogen-containing cuprates using $YBa_2Cu_3O_{7-x}$ as a basis. Expectations of the existence of 'unusual' phases in the systems under consideration are explained by the peculiar structural features of these materials containing crystallochemical fragments — layers and chains — with sharply differing properties. The presence in the $YBa_2Cu_3O_{7-x}$ structure of several crystallochemically non-equivalent types of oxygen atoms (including type O5 oxygen vacancy) opens the possibility of the synthesis of halogen-containing phases with an order in the anionic sublattice, for example when the halogens are localized only in the chains.

THE STRUCTURE AND PROPERTIES OF HALOGEN-CONTAINING YTTRIUM-BARIUM CUPRATES

In discussing the properties of halogen-containing materials of the type $YBa_2Cu_3O_{7-x}Hal_y$ it is necessary to consider their structure, i.e. to answer the question of the sites of localization of the halogen atoms. Of course, an accurate answer to this question can be obtained only after direct X-ray studies of these materials. Unfortunately, no sufficiently reliable structural data are available at present since all of the studies have been performed only on powdered polycrystalline samples.

There has been only a very limited number of attempts to answer these questions using different methods. It appears that authors are inclined to think that the halogen atoms are localized mainly in the planes of the Cu1 chains in the case of low-temperature syntheses. Halogen-containing phases obtained in high-temperature reactions have not been isolated in pure form and were therefore not studied with respect to their structure. The results of a neutron diffraction study on powders [21] of the fluorine-containing phases with the composition $YBa_2Cu_3O_{7-x}F_y$ ($0.08 \leqslant x \leqslant 1.11$) obtained in a 300 °C fluorination of the orthorhombic phases $YBa_2Cu_3O_{7-x}$ by gaseous NF_3 show that the fluorine atoms are located mainly in the vacant O5 sites (Fig. 2). The extent of filling of these sites increases with increasing y, with the a parameter increasing linearly and the b parameter decreasing linearly, i.e. there is a gradual change from the orthorhombic to a tetragonal phase.

On the basis of this evidence it is possible to consider such a process as

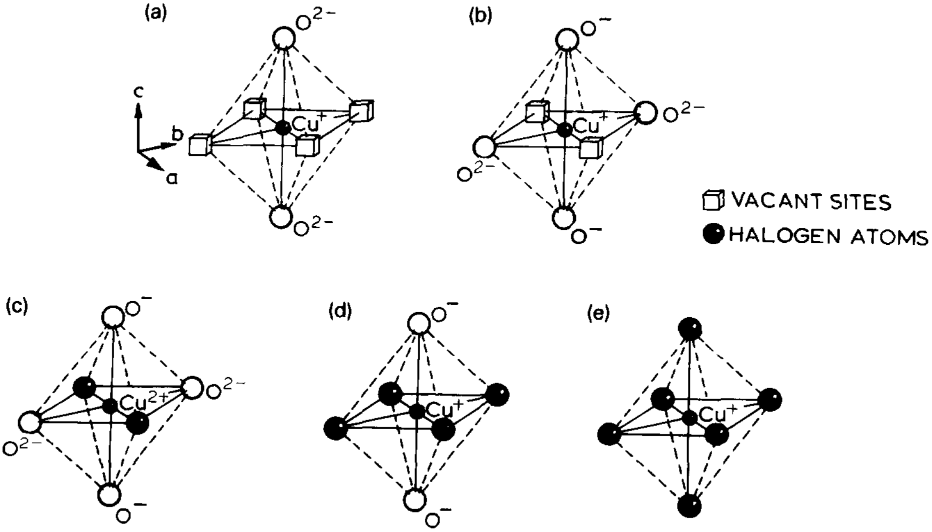

Fig. 2. Coordination of ligands around the Cu1 atoms in different phases: a, $YBa_2Cu_3O_6$; b, $YBa_2Cu_3O_7$; c, $YBa_2Cu_3O_7Hal$; d, $YBa_2Cu_3O_6Hal_2$; e, $YBa_2Cu_3O_4Hal_4$.

intercalation, i.e. filling by the fluorine atoms of the vacant O5 sites. The composition of the phases with completely filled O5 sites will be described by the formula $YBa_2Cu_3O_7F$.

A tetragonal phase with the composition $YBa_2Cu_3O_{4.5}F_{3.5}$ (according to neutron activation analysis) has been obtained in the fluorination of the orthorhombic phase $YBa_2Cu_3O_{7-x}$ with gaseous fluorine at 400 °C [12]. Neutron diffraction studies on powders showed the O5 sites to be completely filled. The other fluorine atoms could not be located because of the similarity of the crystallochemical parameters of the fluorine and oxygen ions. On the basis of an analysis of the interatomic distances the authors suggest them to be localized mainly in the O1 sites and probably in the O4 sites. When all of the O5 and O1 sites are filled by fluorine the composition of such a phase is described by the formula $YBa_2Cu_3O_6F_2$; when all O4 sites are also occupied then the limiting composition will be $YBa_2Cu_3O_4F_4$.

On the basis of an analysis of the Mössbauer spectra (with a ^{57}Fe label) [25], it was concluded that the halogens in the $(Cu_{1-z}Fe_z)_3O_{7-x}Hal_y$ phases occupy the sites of the oxygen-deficient Cu1 layers.

Thus, the results obtained allow us to suggest that in the low-temperature halogenations of the $YBa_2Cu_3O_{7-x}$ phases localization of the halogens occurs in the chains around the copper atoms. It appears that it is the vacant O5 sites that are filled first (to form a $YBa_2Cu_3O_7Hal$ phase) and with increasing halogenation the halogen atoms begin to substitute for the O1 oxygens in the chains, leading to a phase with the composition $YBa_2Cu_3O_6Hal_2$. (This is in accordance with the two-step oxygen intake observed by means of emanation thermal analysis (ETA) [40] using the standard $YBa_2Cu_3O_6$ and radon as a probe.) Under more extreme conditions substitution for the O4 atoms occurs, with the resulting phase having the limiting composition $YBa_2Cu_3O_4Hal_4$.

It can be easily noted that these transformations involving changes only around Cu1 lead to a change not only in the coordination of Cu1 but also in the charge state of the copper atoms. Thus, whereas in the $YBa_2Cu_3O_6$ phases the coordination number of Cu1 is 2 (dimer) and in $YBa_2Cu_3O_7$ it is 4 (rhomb), in the halogen-containing phases it is 6 (octahedron). If we assume the Cu1 atoms in the $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ phases have a charge state of +1 (a conclusion that follows from the analysis of structural, voltammetric and other physical properties [39]) then in the course of halogenation oxidation of Cu1 to +2 (in the $YBa_2Cu_3O_7Hal$ phase) appears to occur first; with the non-isocharge substitution $O^{2-} \rightarrow Hal^-$ the Cu1 atoms are again reduced to Cu^{1+} ($YBa_2Cu_3O_6Hal_2$) and further isocharge substitution of the type $O^- \rightarrow F^-$ does not lead to further change in the state of the copper atoms (Fig. 2).

It is known that the superconducting properties of the $YBa_2Cu_3O_{7-x}$ phases are determined primarily by the electronic properties of the Cu1 chains since essential changes in going from the superconducting $YBa_2Cu_3O_7$

and $YBa_2Cu_3O_{6.5}$ to the dielectric $YBa_2Cu_3O_6$ phase occur only in these structural fragments. Since it is these chains that are involved in the halogenation processes it is of interest to elucidate the role of different atoms of these fragments in superconductivity.

In considering the effect of the nature of the Cul chains on the superconducting properties the following may be pointed out. It appears that it is the charge state of O4 oxygens bridging the Cu2 and Cul chains that are most essential here. Based on the sum of crystallochemical and electronic properties these oxygen atoms may be assigned in different phases a charge state of O^{2-} or O^-.

The charge state O^- plays a key role in the electronic properties of these materials [39]. Such atoms are capable of accepting electrons according to the scheme $O^- + e^- \rightarrow O^{2-}$ and can thus act as electronic reservoirs to accept the surplus electronic density from the Cu2 planes. Transfer of electronic density from the Cu2 planes (probably by the mechanism of resonating valence bonds) appears to be an indispensable element for involving them in conduction. Otherwise, these two-dimensional structural fragments with a half-filled conduction band will tend to dielectrization of the electronic spectrum either because of strong Mott–Hubbard electronic correlations or because of Peierls instability.

It appears that in the superconducting phase $YBa_2Cu_3O_7$ the O4 atoms have a charge state of O^-. In the dielectric phase $YBa_2Cu_3O_6$ the O4 atoms are in the O^{2-} state; they are not capable of accepting electrons and hence cannot act as an electron reservoir to accept the electronic density from the Cu2 layers.

It can be assumed that in the superconducting halogen-containing phases of the type $YBa_2Cu_3O_7Hal$ and $YBa_2Cu_3O_6Hal_2$ the O4 atoms are in the O^- state (Fig. 2). This ensures the required electronic conditions for electron density transfer from the Cu2 chains and results in the superconductivity of such phases. When, however, substitution of the O4 atoms by isocharge halogen ions occurs (as may be the case with the $YBa_2Cu_3O_4F_4$ phase) such phases become dielectric because the F^- atoms cannot act as electron acceptors.

Thus it appears that it is the electronic nature of the bridging atoms in the O4 sites connecting the Cu2 layers with the Cul layer that is critical for the superconductivity of halogen-containing phases.

In spite of the fact that there have been many studies of halogen-containing yttrium–barium cuprates the available information on the physical properties of these phases is rather fragmentary and contradictory. This results from the fact that most of the studies involved multiphase samples, the physical properties, and composition in many cases, of which did not reflect the true parameters of pure halogen-containing phases. It applies first of all to samples obtained by a high-temperature synthesis. For this reason, we shall discuss below the physical properties of halogen-containing phases which were obtained at low temperatures in a sufficiently pure form [25,26,30,31], i.e. of bromine- and iodine-containing phases obtained by treatment of the tetragonal phase $YBa_2Cu_3O_{7-x}$ with gaseous halogens [25,26] and chlorine-containing phases obtained in the interaction of $YBa_2Cu_3O_{7-x}$ with PCl_5 [30,31].

The superconducting characteristics of the samples were determined by studying their low-field properties with the help of a SQUID magnetometer. The diamagnetic effect and Meissner effect measurements were obtained according to the standard procedure [25].

In the initial orthorhombic samples $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$) the appearance of diamagnetic moment was registered at $T_{co} = 92$ K [25,26] and $T_{co} = 93$ K [30,31]. Prior to the treatment by gaseous halogens the tetragonal samples showed no superconductivity up to 1.5 K whereas after treatment superconductivity was observed (Fig. 3) [25,26].

The results of analogous measurements for a number of single-phase samples with different chlorine contents are shown in Fig. 4 [30,31]. In refs. 25 and 30 the superconducting transition was characterized by T_{co} and T_c (the temperature of the superconducting transition determined from the maximum of the dM_{ZFC}/dT derivative). These characteristic temperatures, together with the structural parameters of some halogen-containing samples, are given in Table 1. It has been noted that for the bromine- and chlorine-containing phases the temperature of the superconducting transition coincides with T_c for $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$). For the iodine-containing samples obtained from the tetragonal phase $YBa_2Cu_3O_{6.3}$ the value of T_c was substantially lower; this was related by Klimenko et al. [25,26] to the steric limitations of iodine insertion into the structure of $YBa_2Cu_3O_{7-x}$.

Comparison of the magnetic properties of $YBa_2Cu_3O_{7-x}Hal_y$ with those of ceramic samples and $YBa_2Cu_3O_{7-x}$ crystals indicates a substantial de-

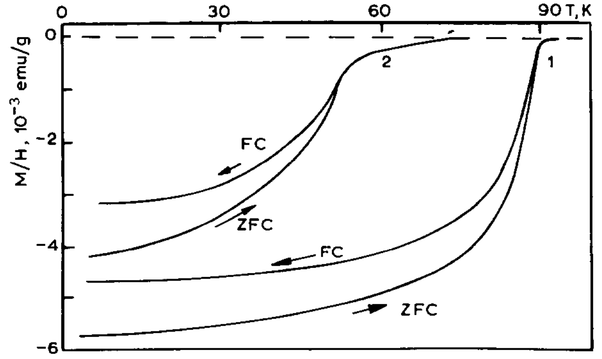

Fig. 3. Temperature dependence of the magnetic susceptibility of brominated and iodinated samples: 1, $YBa_2Cu_3O_{6.3}Br_{1.0+1.5}$; 2, $YBa_2Cu_3O_{6.3}I_{0.2+0.4}$. ZFC and FC are the curves corresponding to the diamagnetic and Meissner effect measurements. Magnetic field $H = 1.3$ Oe [25].

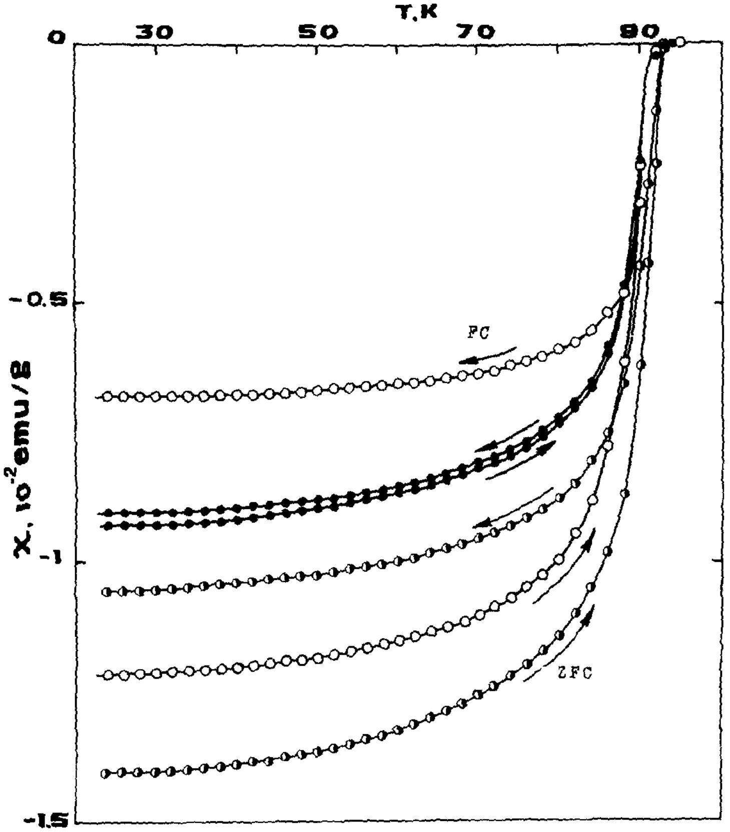

Fig. 4. Temperature dependence of the magnetic susceptibility of $YBa_2Cu_3O_{7-x}Cl_y$ samples: ○, $y=0.3$; ●, $y=0.35$; ◑, $y=0.6$. Magnetic field $H=0.4$ Oe [30,31].

crease in the difference between the Meissner effect and the diamagnetic effect. This fact has been related [25,30] to the use of finely dispersed powders for halogenation. The intergranular contacts forming a multiply connected network in ceramic samples are destroyed in such powders,

TABLE 1

Structural parameters and superconducting temperatures of samples of yttrium-barium cuprates [25,30]

Sample	Unit cell parameters (Å)			T_{co} (K)	T_c (K)	Reference
	a	*b*	*c*			
$YBa_2Cu_3O_{6.3}$	3.83	3.83	11.74	1.5		[25]
$YBa_2Cu_3O_{6.3}I_{0.2+0.4}$	3.89	3.85	11.69	78	52	[25]
$YBa_2Cu_3O_{6.3}Br_{1.0+1.5}$	3.87	3.85	11.63	92	90	[25]
$YBa_2Cu_3O_{7-x}$	3.823	3.886	11.685	93	91	[30,31]
$YBa_2Cu_3O_{7-x}Cl_{0.3}$	3.824	3.889	11.687	92.5	90	[30,31]
$YBa_2Cu_3O_{7-x}Cl_{0.6}$	3.827	3.894	11.684	92.5	90	[30,31]
$YBa_2Cu_3O_{7-x}Cl_{0.35}$	3.822	3.887	11.682	93	91	[30,31]

leading to a substantial reduction in the magnetic flux trapping in the intergrain space. It should be noted that restoring the integrain contacts in $YBa_2Cu_3O_{7-x}$ by a high-temperature annealing of pressed samples is not applicable in the case of halogen-containing compounds. For this reason no resistivity measurements have been performed for the single-phase $YBa_2Cu_3O_{7-x}Hal_y$ samples.

The samples of halogen-containing yttrium cuprates represent a collection of separate aggregates, with the observed divergence of the FC and ZFC curves (Figs. 3 and 4) being attributable to the existence of an intercrystallite Josephson structure and pinning centres (for example at twin boundaries). The role of the twin boundaries as effective pinning centres may be seen from a comparison of the magnetic properties of the orthorhombic $YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7-x}$ and tetragonal $YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7-x}Br_y$ (T_c = 88 K) sample (Fig. 5) [25]. In the bromine-containing sample at low fields there is complete coincidence of the diamagnetic effect and the Meissner effect and no flux trapping; this we think [25] is related to the absence of twinning in the tetragonal phase.

CONCLUDING REMARKS

An important result of the studies on the magnetic properties of single-phase halogen-containing Y–Ba cuprates $YBa_2Cu_3O_{7-x}Hal_y$ is the conclu-

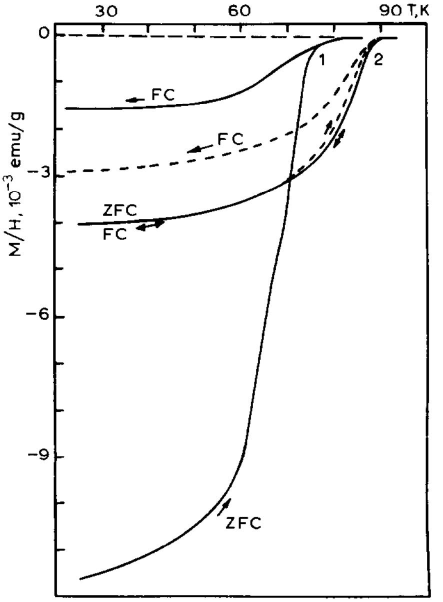

Fig. 5. Temperature dependence of the magnetic susceptibility of superconducting samples with orthorhombic and tetragonal structure: 1, $YBa_2(Cu_{0.97}Fe_{0.03})O_{6.98}$ (dense ceramic); 2, $YBa_2(Cu_{0.97}Fe_{0.03})_3O_{6.3}Br_y$ (powder). Magnetic field: solid lines, 1.3 Oe; dashed line, 26 Oe.

sion about the coincidence of the limiting superconducting temperatures ($T_c \approx 90$ K) for all types of acceptor atoms introduced into the O1 and O5 sites of the Cu1 planes [25,26,30,31]. In the case of monovalent acceptors the condition for achieving the limiting superconducting temperature (according to the scheme discussed above) is approximately described by the ratio $y \approx 2x$. Strictly speaking, this conclusion is at present only a hypothesis requiring further detailed experimental substantiation. In particular, it is necessary to study the structure and physical properties of $YBa_2Cu_3O_{7-x}Hal_y$ samples at different concentrations of oxygen and halogens which will allow determination of the range of stability of halogen-containing phases as well as of the range of applicability of the models discussed above. To elucidate the role of different structural fragments in the high T_c superconductivity phenomenon it would be extremely interesting to perform detailed structural studies by means of neutron diffraction techniques and a comparative analysis of the phonon spectra of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-x}Hal_y$.

Summing up the first results on the properties of halogen-containing yttrium–barium cuprates, it can be pointed out that this direction seems to be very promising for elucidation of the nature and mechanisms of high T_c superconductivity.

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REFERENCES

1 S.R. Ovshinsky, R.T. Young, D.D. Allred, G. DeMaggio and G.A. Van der Leeden, Phys. Rev. Lett., 58 (1987) 2579.

2 M. Xian-Ren, R. Yan-Ru, L. Ming-Zhu, Qing-Yunt et al. Solid State Commun. 64 (1987) 325.

3 R.N. Bhargava, S.P. Herko and W.N. Osborn, Phys. Rev. Lett., 59 (1987) 1468.

4 P.K. Davies, J.A. Stuart, D. White, C. Lee et al., Solid State Commun., 64 (1987) 1441.

5 A.K. Tyagi, S.J. Patwe, U.R.K. Rao and R.M. Iyer, Solid State Commun., 67 (1988) 385.

6 U.R.K. Rao, A.K. Tyagi, S.J. Patwe, R.M. Iyer et al., Solid State Commun., 67 (1988) 385.

7 H.H. Wang, A.M. Kini, H.-C.I. Kao, E.H. Appelman et al., Inorg. Chem., 27 (1988) 5.

8 D. Cheng, L. Jingkui, C. Guangcan, X. Sishen et al., Kexue tongbao, 33 (1988) 2023.

9 R. Hermann, N. Kubicki, H.U. Mueller, H. Dwelk et al., Phys. Status Solidi B, 146 (1988) K25.

10 N.R. Bansal, A.L. Sandkuhl and D.E. Farrell, Appl. Phys. Lett., 52 (1988) 838.

11 N.N. Sauer, E. Garsia, J.A. Martin, R.R. Ryan et al., J. Mater. Res., 3 (1988) 813.

12 E. Garsia, N.N. Sauer, R.R. Ryan, A. Williams et al., J. Mater. Res., 3 (1988) 819.
13 J.C. Kim, J.S. Swinnea, A. Manthiram and M. Steinfink, Solid State Commun. 68 (1988) 287.
14 Z.Z. Sheng, W. Kiehl, D. Marsh, D. Mooney et al., Appl. Phys. Commun., 8 (1988) 127.
15 S.-G. Eriksson, L.-G. Johansson and V.C. Olsson, Physica C, 153–155 (1988) 902.
16 B.M. Tissue, K.M. Civillo, J.C. Wright et al., Solid State Commun., 65 (1988) 51.
17 K.M. Civillo, Solid State Commun., 66 (1988) 1237.
18 F. Sumiyoshi, T. Hamaga and S. Kawabata, Cryogenics, 28 (1988) 3.
19 Y. Hakuraki, F. Sumiyoshi and T. Ogushi, Appl. Phys. Lett., 52 (1988) 1528.
20 M.F. Yan, G. Sageev Grader, W.W. Rhodes and H.C. Ling, J. Mater. Sci., 24 (1989) 703.
21 J.R. La Graff, E.C. Behrman, J.A.T. Taylor, F.J. Rotella et al., Phys. Rev. B., 39 (1989) 347.
22 T.A. Vanderah, D.L. Decker, D.C. Harris and B.L. Chamberland, Mater. Res. Bull., 24 (1989) 121.
23 R.T. Young, S.R. Ovshinsky, B.S. Chao et al., Mater. Res. Soc. Symp. Proc., 99 (1988) 549.
24 P.T. Wu, R.S. Liu, H.M. Sung, and J.H. Kung, Mater. Res. Soc. Symp. Proc., 99 (1988) 623.
25 A.G. Klimenko, V.I. Kuznetsov and Ya.Ya. Medikov et al., Superconductivity: Phys., Chem., Eng., 2 (1989) 5.
26 A.G. Klimenko, V.I. Kuznetsov, Ya.Ya. Medikov et al., Preprint 88-24, Institute of Inorganic Chemistry, Novosibirsk, 1988 (in Russian).
27 Yu.A. Osipyan, O.V. Zharikov, N.S. Sidorov et al., Pis'ma Zh. Eksp. Teor. Fiz., 48 (1988) 225.
28 Yu.A. Osipyan, O.V. Zharikov, G.V. Novikov et al., Pis'ma Zh. Eksp. Teor. Fiz., 49 (1989) 61.
29 B.A. Tallerchik, A.O. Olesk, T.N. Egorova et al., J. Less-Common Met., 150 (1989) 311.
30 V.P. Fedin, M. Sheer, Yu.I. Mironov, A.G. Klimenko et al., Izv. Sib. Otd. SSSR (1989), to be published.
31 A.G. Klimenko, S.M. Ishikaev, Yu.I. Mironov, V.P. Fedin et al., Superconductivity: Phys., Chem., Eng., 2 (1989) to be published.
32 D.W. Bullett and W.G. Dawson, J. Phys. C, 20 (1987) L853.
33 A.J. Freeman, J. Yu, S. Massidda and D.D. Koelling, Physica B., 148 (1987) 212.
34 J.K. Burdett, G.V. Kulkarni and K. Levin, Inorg. Chem., 26 (1987) 3650.
35 J.M. Williams, M.A. Beno, K.D. Carlson et al., Acc. Chem. Res., 21 (1988) 1.
36 W.M. Temmerman, Z. Szotek, P.J. Durham et al., J. Phys. F 17 (1987) L319.
37 W.Y. Hsu, R.V. Kasowski and F. Herman, Phys. Rev. B., 37 (1988) 5224.
38 Y. Xu, W.Y. Ching and K.W. Wong, Phys. Rev. B., 37 (1988) 9773.
39 N.F. Zakharchuk, V.S. Kravchenko, V.Ye. Fedorov et al., Preprint 89-17, Institute of Inorganic Chemistry, Novosibirsk, 1989.
40 V. Balek and J. Šesták, Thermochim. Acta, 148 (1989) 229.