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HTSCs with apical oxygen replaced by halogens

N V Anshukova, A I Golovashkin, L I Ivanova, A P Rusakov

Abstract. The fundamental structural unity of familiar oxide HTSCs and their oxyhalide counterparts, with apical oxygen ions replaced by halogen ions, is demonstrated and discussed. As a consequence of this unity, major physical phenomena are expected to be common for both classes, such as doping effects, concentration-driven insulator–metal transitions, the unusual pair superconductivity, and the temperature dependence anomalies in the critical magnetic field, linear expansion coefficient, and heat capacity jumps. New experimental results are discussed, accounted for by the exciton mechanism of superconductivity with the local nature of excitations taken into account.

The crystal structure of the known high- T_c superconductors (HTSCs) is presently well-understood [1]. Oxide HTSCs are primarily cuprate layered systems containing CuO_2 planes and either oxygen octahedrons (e.g., in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) or oxygen pyramids (as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) around copper ions. There are also noncuprate oxide HTSCs, based on $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, in which oxygen octahedrons are formed around Bi ions. Such octahedrons or pyramids and, consequently, apical oxygen ions are thought to be the key elements of HTSC structure. Superconductivity in such systems is believed to be due to superconducting CuO_2 planes. Some models consider the interaction of free charge carriers with oscillations of apical oxygen ions to be mainly responsible for high critical temperatures T_c [2]. In some HTSC compounds, such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, the oxygen octahedron is distorted; nevertheless, it is still possible to identify oxygen ions in their structure acting as apical ones [3]. Between apical oxygen ions (i.e., between octahedrons or pyramids), additional atomic layers (for example, BiO in $\text{BiSr}_2\text{CuO}_5$ or TlO in $\text{TlBa}_2\text{CuO}_5$) or chains (of CuO in $\text{YBa}_2\text{Cu}_3\text{O}_7$) may be located. This is the conventional view on the basic structure of oxide HTSCs. The physical concepts of the role of various structural elements of oxide HTSCs developed in recent literature also seem to be quite reasonable and keep in line with the main experimental facts.

In recent years, some new classes of oxide HTSC have been found, whose structure differs dramatically from the structure of the above-mentioned cuprate oxides. First,

mention should be made of HTSCs with a ‘an infinite-layer’ structure, such as SrCuO_2 , $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ and their analogs, in which strontium is partly replaced by barium, lanthanum, neodymium, or praseodymium [1]. Oxygen ions in these HTSCs occur only in CuO_2 planes, and apical oxygen ions, as they are generally understood, are absent. Another class is oxyhalide HTSCs, in which apical oxygen is replaced by chlorine or fluorine. These HTSC compounds attract particular interest, because the replacement of apical oxygen by heavier elements (chlorine, fluorine) must significantly change the phonon spectrum of these compounds, especially in the high-frequency range. The substitution of a halogen for oxygen must also affect the electronic parameters of the compounds, such as the concentration of charge carriers, the density of electron states at the Fermi level, etc., and thus (given the decisive role of the usual phonon mechanism of superconductivity) change their superconducting properties.

By now, a number of HTSC compounds containing halogen atoms have already been found. Some of them are listed in Table 1, where the maximal values of the critical temperatures are also indicated.

In principle, halogen atoms can be located at interstices of the initial oxide compounds. These nonstoichiometric halogen atoms can serve as an additional source of holes (possibly, increasing T_c), but are not an essential structural element. We will only deal with oxyhalides in which halogen atoms replace apical oxygen ions, i.e., serve as structural elements, rather than merely impurities, sources of free charge carriers. To the first approximation, we will not take into account the presence of some amounts of interstitial halogens.

Table 1. Oxyhalide HTSC compounds.

Compound	T_c , K	Reference	Note
$\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{O},\text{F})_{4+\delta}$	55	[4, 5]	Highest critical temperature T_c obtained in $\text{La}_{0.7}\text{Sr}_{1.3}\text{Cu}(\text{O},\text{F})_{4+\delta}$
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$	92	[6]	
$\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}\text{F}_z$	83	[6]	
$\text{YSr}_2\text{Cu}_3\text{O}_{4-x}\text{F}_y$	63	[7]	
$\text{Nd}_2\text{CuO}_{4-x}\text{F}_y$	27	[8–12]	
$\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x-y}\text{F}_y$	27	[13]	
$\text{Sr}_2\text{CuO}_2\text{F}_2$	47	[14, 15]	
$\text{Sr}_2\text{CuO}_{3-x}\text{F}_x$	70	[16]	
$\text{Sr}_{2-x}\text{A}_x\text{CuO}_2\text{F}_{2+\delta}$ ($\text{A} = \text{Ca}, \text{Ba}$)	64	[17]	Highest critical temperature T_c obtained in $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$
$(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$	80	[18]	Highest critical temperature T_c obtained in $\text{Sr}_{2.3}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{1.3}$
$(\text{Ca},\text{Na})_2\text{CuO}_2\text{Cl}_2$	26	[19, 20]	
$(\text{Ca},\text{K})_2\text{CuO}_2\text{Cl}_2$	24	[21]	
$\text{Ca}_{2-x}\text{Na}_x\text{CaCu}_2\text{O}_4\text{Cl}_2$	49	[22]	

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Upon the replacement of oxygen ions located at lattice sites in compounds such as Sr_2CuO_3 , the first ions to be replaced are apical oxygens. It was shown, for example, that in the superconducting compound $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ apical oxygen ions are completely replaced by fluorine ions, and oxygen ions only take up positions in CuO_2 planes [14, 17]. Similarly, in $(\text{Ca}, \text{Na})_2\text{CuO}_2\text{Cl}_2$ [19, 20], all the positions of apical oxygen are replaced by chlorine. The authors of these papers emphasize the absence of chlorine atoms at the interstices. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$, the content of oxygen decreases on doping with fluorine [6]. The process of replacement of oxygen by halogens is most vividly illustrated by the compound $(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-y}$, in which chlorine also replaces apical oxygen [18]. This compound is isostructural with $(\text{La}, \text{Sr})_2\text{CaCu}_2\text{O}_6$. Taking a divalent element (Sr, Ca) instead of the trivalent lanthanum, O^{2-} can be replaced by F^{-1} without changing the crystal structure. Note also that since the size of Cl^{-1} ions (1.81 Å) exceeds the size of O^{2-} ions (1.40 Å), Cl^{-1} is incorporated into the interstices of oxyhalides only with difficulty. The fact that it is apical oxygen ions that are most readily replaced by halogens suggests their reduced valence and lower potential energy compared to oxygen ions in the CuO_2 plane. There is also some experimental evidence in favor of this conclusion. Thus, when HTSC samples are heated, it is the oxygen atoms from CuO chains (in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) and apical oxygens that are the first to escape. The CuO_2 planes are most stable to heating, losing little or no oxygen [1].

The key role of the crystal structure of oxide HTSCs in increasing critical temperatures, emphasized in many theoretical models of HTSC, brings up a question of whether the above-mentioned new classes of HTSCs are quite different, each having a peculiar relation between critical temperature and structure, or have they something in common? It was shown that there is a fundamental feature common to all these classes, which enables a unified treatment of superconductivity of these compounds.

To begin, let us consider the structural features of oxide and oxyhalide HTSCs. All of them have a basic structural element, namely, an ‘apical pair’ (Fig. 1a) consisting of two ions of either oxygen or fluorine or chlorine (X_1 , X_2) with different valences. Between these apical ions, there are Cu or Bi ions (one or more than one). The covalent bond between the central ion M (or one of several central ions) and an apical ion X_1 with reduced valence in an apical pair is equivalent to a

heavy hole localized on the M–X bond. This hole bond M– X_1 is shown in Fig. 1a as a dashed line with a heavy hole localized on it. In the perpendicular plane passing through the ion or ions M, there are some other oxygen ions which together with the apical pair form a ‘structural unit’, i.e., an octahedron (in La_2CuO_4 , Fig. 1b), or a polyhedron (in $\text{YBa}_2\text{Cu}_3\text{O}_7$, Fig. 1c) in the three-dimensional (3D) case, and a rhombohedron (SrCuO_2 , Fig. 1b) in the two-dimensional (2D) case. The octahedron can be distorted, as in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. Each structural unit has only one hole bond, as is shown in Fig. 1. Note that the state of the ion M bound to the apical ion X_1 differs slightly from the states of other ions M in the structural unit (if there are several). In principle, some other elements (chalcogens, nitrogen, hydrogen) could also serve as apical ions, although such HTSCs have not yet been found.

The formation of such apical pairs and hole bonds in oxide and oxyhalide compounds is caused by energy degeneration of the d or s levels of ion M and the p level of ion X (for example, the Cu d or Bi s and O p levels). This resonance degeneracy is energetically disadvantageous; therefore, the degeneracy is eliminated by the interaction with the crystal field by elastic deformation, when the distance between the apical ion M and the ion X (we take it to be X_1) is slightly reduced. This may be the decrease in the distance between the Cu (or Bi) ion and one of oxygen ion (in oxides) or halogen ions (in oxyhalides). The energy of the rest of the oxygen ions diminishes, so the total energy of the system decreases. This effect is well-known in solid-state physics for compounds with Cu ions (the Jahn–Teller effect; sometimes, the noncentral ion effect; etc.). The decreased distance between the M ion and the apical ion X_1 leads to a greater overlap of their wave functions; as a result, the covalent bond strengthens and the electron charge of the X_1 ion is partially transferred to the M ion. In other words, the valence of the X_1 ion decreases, which can be regarded as a localization of a hole in the vicinity of this apical ion on the M– X_1 bond.

The hole bonds of structural units formed in the crystal tend to ordering (see Fig. 2). The ordering leads to doubling of the lattice parameter and the appearance of an energy gap E_g at the Fermi level. In other words, a charge density wave (CDW) arises in the system, giving the electron spectrum dielectric features.

The ordering occurs because this decreases the potential (electrical) energy (Wigner crystallization) [23, 24]. It is known that even quasi-free heavy holes can form an ordered structure, i.e., a hole lattice [23–25] if the amplitude of zero-point oscillations of these holes is substantially less than the lattice parameter. The kinetic energy increases further upon ordering due to the formation of the energy gap $E_g \simeq 1–2$ eV upon doubling of the lattice parameter.

One more structural aspect is worth noting. The hole bonds considered above tend to combine into pairs. This is most clearly demonstrated for BKBO or SrCuO_2 (Fig. 2a), although can readily be seen for other compounds. It is this type of ordering that leads to the doubling of the lattice parameter, the formation of the energy gap E_g , and the maximal increase in the energy of the system.

Thus, all the oxide and oxyhalide HTSCs are basically similar in structure, which must determine similar physical properties of these compounds.

Formerly, we developed a model of the so-called ‘local’ (short-range) bosons for oxide HTSCs [3, 26], which

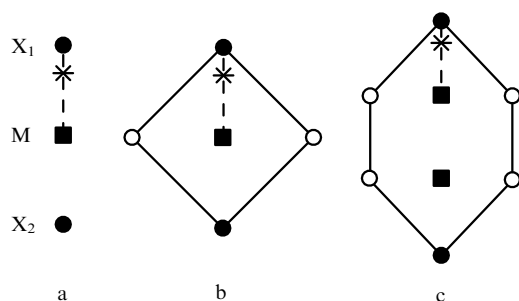


Figure 1. (a) Apical pair M–ion Cu or Bi; X_1 , X_2 are the apical ions of oxygen, fluorine or chlorine with different valences, * is the heavy localized hole. (b), (c) Projections of the structural unit for the cases of (b) octahedron or rhombohedron and (c) polyhedron: (■) ion M, (●) ions of the apical pair, (○) oxygen ions, and (*) localized hole.

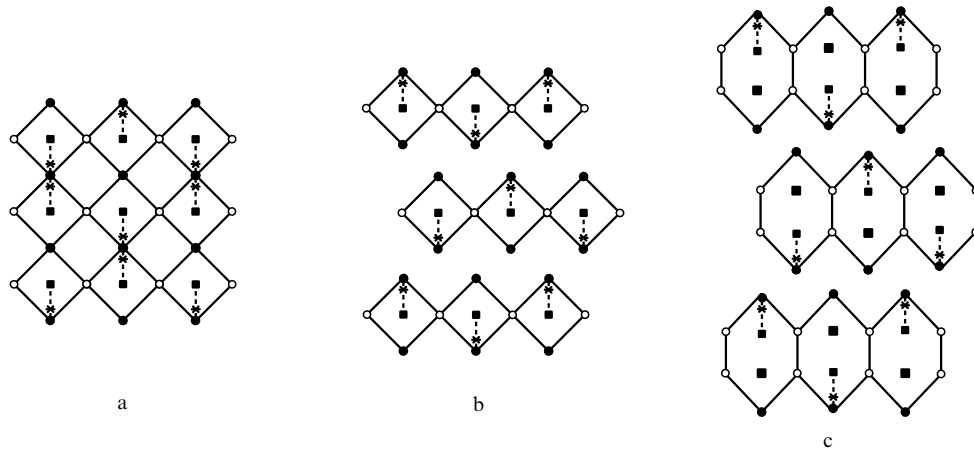


Figure 2. Examples of the ordering of hole bonds in crystals: (a) BKBO (3D) or SrCuO_2 (2D), (b) $\text{Sr}_2\text{CuO}_2\text{F}_2$, (c) $\text{Ca}_{2-x}\text{Na}_x\text{CaCu}_2\text{O}_4\text{Cl}_2$. Designations as in Fig. 1. For the sake of simplicity, the rest of the lattice ions are not shown.

explained their abnormal properties and high critical temperatures. Actually, this is a particular case of the well-known Ginzburg exciton model for superconductivity [27], where local excitations of heavy holes are considered as excitons. The model can be extended to oxyhalide HTSCs.

The presence of a hole on the halogen–ion (X–M) bond reduces the effective charge of the X ion. In this case, the ground state of $\text{Sr}_2\text{CuO}_2\text{F}_2$, for example, can be presented as $\text{Sr}_2^{+2}\text{Cu}^{+1+\delta}\text{O}_2^{-2}\text{F}^{-1}\text{F}^{-\delta}$, where $0 < \delta < 1$. The valence $1 + \delta$ arising in the ions of Cu must impart these compounds antiferromagnetic properties with a magnetic moment of the order of $\mu_B\delta$, where μ_B is the Bohr magneton. A spin density wave (SDW) must arise in the system in addition to the charge density wave.

The ordering of heavy holes not only changes the symmetry of the crystal structure, but also leads to a rearrangement of both phonon and electron spectra of oxyhalide compounds. These changes are considered in [3, 26] for the case of HTSCs.

The ground state of the heavy hole pair discussed above is most likely singlet. At the same time, a triplet excited state must also exist. In response to a magnetic field, the corresponding energy level would split into three sublevels, which could be observed by the EPR method, as was done for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [28] and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ [29, 30].

Certain differences in the properties of oxyhalide HTSCs and oxide HTSCs are due to the specific local polarization and deformation of their lattices, which result from different parameters of oxygen and halogens. However, the structural similarity of these two classes of HTSCs suggests a local instability of the lattice of oxyhalide HTSCs, as is the case in oxide HTSCs. This instability is determined by the structural degeneracy of two charge density waves arising from two possible ways of ordering of heavy holes, as is seen in Fig. 2. The elimination of this degeneracy upon tunneling gives rise to an energy gap W , which describes jumps (tunneling) of heavy holes between neighboring apical bonds. It also leads to anomalies in the elastic properties and thermal expansion coefficient for oxyhalide HTSCs as for oxide HTSCs. Like oxide HTSCs, oxyhalides must exhibit an insulator–metal concentrational phase transition [3, 26].

The above-mentioned local instability of the oxyhalide lattice is mainly responsible for the high-temperature super-

conductivity arising in these compounds. Excitations through the energy gap W in the system of localized holes correspond to their jumps (tunneling) in real space. Consequently, these excitations are local exciton-type excitations in the system of localized holes through the gap W , i.e., local (short-range) bosons. The interaction of free charge carriers arising upon doping with these local bosons leads to a superconducting coupling of free charge carriers. These pairs have a short coherence length due to boson localization. The critical temperature in such a system can be estimated as $T_c \sim W \exp(-1/\lambda)$. The constant of electron–boson (electron–exciton) interaction is $\lambda \sim 1$, since this interaction cannot be weak due to the great local polarizability associated with the excitation of heavy holes. The energy W is not less than the energy of high-frequency phonons at the edge of the Brillouin zone, i.e., 0.05–0.1 eV. In this case $T_c \simeq 50$ –100 K, which is actually observed in oxyhalide HTSCs [4–7, 14–18, 22].

Below, we present some experimental data, in particular, on the heat-capacity jump at T_c , which provide support for the above theoretical considerations. The λ shape of the $\Delta C(T)$ dependence cannot be explained in the framework of the usual phonon superconductivity mechanism, but is readily accounted for within the exciton mechanism with allowance for the local nature of excitons. Undoubtedly, the coupling of free carriers via phonons also makes a certain contribution to T_c . Noteworthy is an additional increase in T_c if two interaction mechanisms operate [2].

One of the most characteristic features of the model is the presence of a tunneling gap equal to $W \simeq 0.05$ –0.1 eV. This should be observed in various spectral studies. Actually, a number of optical experiments with HTSC systems revealed absorption bands and other features in this spectrum range [31–38]. This gap was, probably, also observed at 100 meV in the tunneling experiments with YBaCuO films [39].

The small coherence length caused by the local character of paired bosons must lead to an abnormal temperature dependence (with a positive curvature) of the upper critical magnetic field $H_{c2}(T)$, since this result is independent of the nature of electron coupling [40, 41]. All the oxide HTSC systems for which high-quality samples have recently been produced exhibited abnormal $H_{c2}(T)$ dependences over a wide range of temperatures. Some examples of such depen-

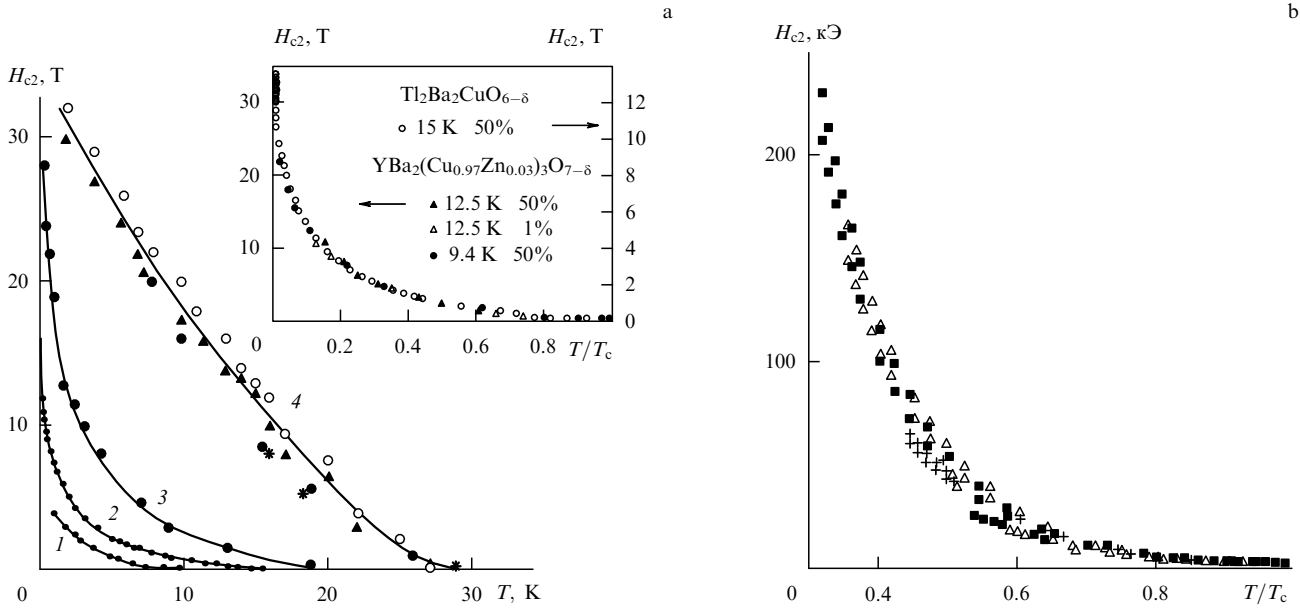


Figure 3. (a) Temperature dependences of the upper critical magnetic field for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$ [42] (curve 1), $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ [43] (2), $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ [44] (3), and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (4): (●) heat capacity data [45]; (*) susceptibility data [46]; (○) resistivity data [47]; and (▲) resistivity data [48]. Shown in the inset are the results for $\text{YBa}_2(\text{Cu}_{0.97}\text{Zn}_{0.03})\text{O}_{7-\delta}$ [49] (left-hand scale) and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (right-hand scale). (b) $H_{c2}(T)$ dependence obtained by the scaling method for single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [50].

dences [42–49] are shown in Fig. 3. The $H_{c2}(T)$ curves were obtained by various methods, such as resistive, magnetic, and heat-capacity measurements. Note that the measurements were carried out on samples with critical temperatures less than the highest temperature T_c , i.e., on samples that were not optimally doped for a given HTSC system (the only exception was the BKBO system), in order to obtain the $H_{c2}(T)$ curves down to the lowest temperatures.

Figure 3b shows the $H_{c2}(T)$ dependence for single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [50]. Using the scaling method, the authors of [50] showed that the $H_{c2}(T)$ dependence for this HTSC compound was abnormal up to fields exceeding 200 T.

Abnormal (with reduced curvature) $H_{c2}(T)$ dependences were also observed for some other HTSC systems, for example, $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ [51], $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_4$, $\text{Nd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_4$ [52], and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [53].

In some papers [45–48] the influence of the sample quality on the shape of the $H_{c2}(T)$ dependence was studied examining BKBO. It was shown in [47, 48] that the higher was the sample quality, the more abnormal was the $H_{c2}(T)$ dependence. In [45, 46] special high-quality samples were selected for the experiments on heat capacity and magnetic susceptibility, in which the width of the diamagnetic transition was no more than a few Kelvins and the value of the Meissner effect did not change with temperature down to the lowest temperatures. Thus, the observed abnormal positive curvature of the $H_{c2}(T)$ dependence cannot be explained by the existence of various superconducting phases in the sample. The fact that the abnormal $H_{c2}(T)$ dependence can be detected not only by the resistive method, but also by the calorimetric method, suggests its fundamental character. Unfortunately, no measurements of $H_{c2}(T)$ in oxyhalide HTSCs have yet come to our notice.

Being similar to oxide HTSCs in the electron spectrum and some other parameters, oxyhalide HTSCs should share other abnormal dependences exhibited by oxide HTSCs [54].

Of particular interest is the abnormal shape (of λ type) of the heat capacity jump in oxide HTSCs (Fig. 4). Such λ -type jumps were observed for single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [55–59], $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [58, 59], and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ [60]. The shape and magnitude of the heat capacity jump are extremely sensitive to the presence of structural defects. For example, the magnitude of the jump in a twin-free crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is nearly twice the jump in the same crystal with twin boundaries [57]. The λ shape of the jump (as in ^4He) suggests the local nature of superconducting pairs [40] and cannot be described by the usual phonon superconductivity mechanism. This result can be understood within the above model of local bosons [3, 26]. Note that in earlier experiments, which were made on imperfect samples, these anomalies were not clearly observed. Therefore, one of the most important problems in the current studies of HTSCs is to obtain high-quality samples.

Thus, very different HTSCs — oxyhalides, infinite-layer and three-dimensional oxide HTSCs — all can be given a unified treatment accounting for their structural and physical properties. They all contain apical bonds with heavy holes localized on them. The ordering of these bonds (appearance of charge density waves) leads to the doubling of the lattice parameter and imparts the electron spectrum dielectric properties. The appearance of free charge carriers upon doping gives rise to an insulator–metal concentration phase transition. Jumps (tunneling) of heavy holes between neighboring apical bonds (excitations through the tunneling gap W) induce a local boson field, which leads to pairing of free carriers and produces a superconducting state with high T_c . This superconductivity mechanism can be identified as the mechanism of ‘coupling local bosons’ or an exciton mechanism with small-radius excitons.

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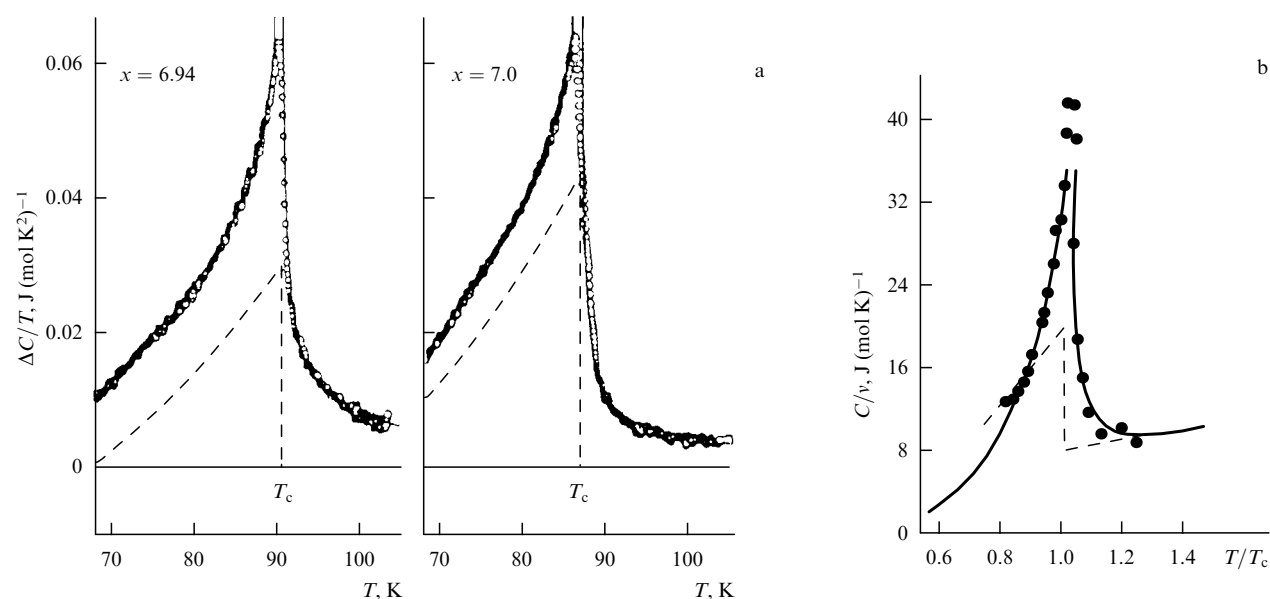


Figure 4. Temperature dependences of heat capacities of some HTSCs near T_c : (a) $\text{YBa}_2\text{Cu}_3\text{O}_x$ [56] for $x = 6.94$ and $x = 7.0$; dashed line represents the heat capacity jump in the mean-field approximation; (b) temperature dependences of heat capacities of ^4He (solid line) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (solid circles) [40]; coefficient $v = 1$ for ^4He , $v = 0.06$ for $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$; dashed line indicates the heat capacity jump in the BCS model.

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