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X-ray emission spectra of vanadium atoms in a new series of (Cu,V)-based high- T_c superconductors

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Abstract

Non-resonant V $L_{2,3}$ and $OK\alpha$ X-ray emission spectra of a new series of $(\text{Cu,V})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n = 3-7$) superconductors are presented. We have found that oxygen atoms surround V-atoms in the given compounds, form a $(\text{VO}_4)^{3-}$ tetrahedrons and have a pentavalent state. This induces holes due to the substitution of divalent copper by pentavalent vanadium ions providing a hole-doping mechanism of superconductivity in this series of compounds. A spectral estimation of the oxygen concentration shows that the oxygen content under high-pressure/high-temperature synthesis conditions is not changed considerably from the start to the final product.

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1. Introduction

In $MA_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ -type high- T_c superconductors with $M-12(n-1)n$ structure, the CuO_2 planes and other metal–oxygen planes are stacked as $AO-MO-AO-CuO_2-(Ca-CuO_2)_{n-1}$, where $AO-MO-AO$ is a charge transfer reservoir and $\text{CuO}_2-(Ca-CuO_2)$ is an infinite layer block. A is an alkaline earth metal. The M site is not always occupied by one element only but it is often shared by two or more elements, usually with copper as one element and a non-metal (e.g., C, P, S) as another element [1]. Recently, it has been shown that the M-site in such structures can be shared by copper and another 3d-metal, such as Cr and V [2,3]. Chromium in the (Cu,Cr) phases is reported to be hexavalent and no holes

are created if we assume $\text{Cu}_{0.5}\text{Cr}_{0.5}\text{O}$ composition for the (Cu,Cr) plane [4]. Presence of excess oxygen and/or copper vacancies in the (Cu,Cr) plane is suggested in order to explain the occurrence of superconductivity in (Cu,Cr) phases based on the hole-doping mechanism. On the other hand, vanadium also seems to be a promising candidate for (Cu,V) type superconductors due to its ability to form a pentavalent ion (V^{5+}) with a small size similar to that of Cr^{6+} , which is susceptible of bringing the copper layers closer to each other and consequently modifying superconductivity. Such superconducting (Cu,V) phases with $M-12(n-1)n$ structures are indeed discovered recently with $T_c = 73-107$ K, with high critical current density and irreversibility fields [2,3]. It is assumed that the oxidation state of vanadium in these phases is equal to 5+ and also crystal defects such as excess oxygen should also be considered as an origin of the hole carriers. Therefore, valence state and coordination of vanadium as well as the concentration of oxygen are key factors in order to understand the

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origin of superconductivity as well as transport properties in these systems. In order to verify this supposition we have performed X-ray fluorescence measurements of vanadium and oxygen emission spectra in $(\text{Cu,V})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n = 3-7$) superconductors.

2. Experimental

V_2O_5 (99.9%), SrCuO_2 , SrO_2 , Ca_2CuO_3 and CuO (99.9%) were used to obtain nominal mixtures for high-pressure synthesis. SrCuO_2 and Ca_2CuO_3 were prepared through solid-state reaction of CuO and SrCO_3 (99.9%) or CaCO_3 (99.9%) at 1000°C for 5 days with several intermediate grinding. The mixtures were sealed in gold capsules after being well pulverized and subsequently allowed to react in a belt-type high-pressure apparatus at 6 GPa and 1300°C . After heat treatment for 1 h, the samples were quenched to room temperature, and then the pressure was released. To check possible oxygen loss, the gold capsules were weighted before and after the experiments. To determine the chemical composition of the samples, electron probe microanalysis was carried out using a JEOL JXA-8600MX analyzer. Samples with the initial composition $\text{Cu}_{0.5}\text{V}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_{7.5}$, $\text{Cu}_{0.5}\text{V}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{9.4}$, $\text{Cu}_{0.5}\text{V}_{0.5}\text{Sr}_2(\text{Ca}_{3.6}\text{Sr}_{0.4})\text{Cu}_5\text{O}_{13.5}$ and $\text{Cu}_{0.5}\text{V}_{0.5}\text{Sr}_2(\text{Ca}_{4.7}\text{Sr}_{0.3})\text{Cu}_6\text{O}_{15.3}$ were synthesized with $T_c = 98, 75, 75$ and 73 K, respectively. The compounds were confirmed to be free from impurity phases by X-ray powder diffraction measurements. The X-ray diffraction patterns of the samples displayed the presence of 1223, 1245, 1256 and 1267 phases, respectively, with no evidence for impurity phases.

The local structure and chemical state of vanadium atoms in HTSCs was studied by soft X-ray emission measurements performed with synchrotron radiation at the undulator beamline 8.0 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. Vanadium $\text{L}_{2,3}$ ($3d4s \rightarrow 2p_{3/2,1/2}$ transition) and oxygen $\text{OK}\alpha$ X-ray emission spectra (XES) were taken, employing the University of Tennessee at Knoxville's soft X-ray fluorescence (SXF) endstation [5]. The vanadium and oxygen XES were obtained with a diffraction grating of (600 lines/mm, $R = 10$ m) and energy resolution of 0.8 eV for the vanadium spectra and 0.5 eV for the oxygen in the non-resonance regime. The non-resonance regime considered here is at excitation energies far from V $2p$ and O $1s$ -thresholds (e.g., at $E_{\text{exc}} = 530-550$ eV). The vanadium and oxygen XES were calibrated with a reference sample of vanadium pure metal. For comparison, vanadium $\text{L}_{2,3}$ XES were measured in V_2O_5 and NaV_2O_5 , where the vanadium ions have a valence of (5+) and (4.5+), respectively.

3. Results and discussion

Non-resonant X-ray fluorescence can be described using a two-step model with the emission decoupled from the excitation. The first step corresponds to an electron excitation from a core level to unoccupied states in the conduction band when the sample absorbs an incoming photon. The second step is the emission of the outgoing photon when an electron undergoes a transition from the valence band to refill the core level hole created during photon absorption. Both steps are governed by the electric dipole selection rule, $\Delta l = \pm 1$, which means that the $1s$ core level holes in oxygen can only be filled by $2p$ valence electrons. For L-emission of vanadium, the $2p$ core level holes are filled by $3d$ and $4s$ valence electrons. Therefore, XES probe local partial density of states at each particular atomic site.

Fig. 1a shows V L_3 ($3d4s \rightarrow 2p_{3/2}$ transition) X-ray emission spectra of 1223, 1245, 1256 and 1267 phases. As seen, a chemical shift about -0.9 eV takes place with respect to the spectrum of pure metal which is typical for vanadium oxides with highest oxidation state of vanadium atoms (V^{5+}) (see Fig. 1b and Ref. [6]). V L_3 XES 1223, 1245, 1256 and 1267 phases consist of the main line A at 510.4 eV which is similar to that of V_2O_5 (Fig. 1b) and can be attributed to the O $2p$ -V $3d$ -like

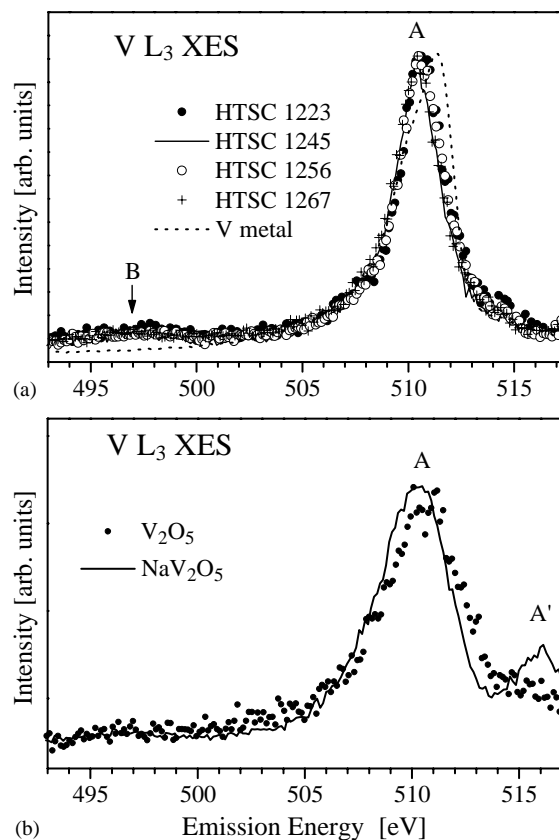


Fig. 1. (a) V L_3 XES in 1223, 1245, 1256, 1267 phases and pure metal. (b) V L_3 XES in V_2O_5 and NaV_2O_5 .

band, where vanadium gives all five electrons to the O $2p$ -band and has d^0 configuration and also a low intensive B -subband (located at 497 eV), which is due to V $3d$ -O $2s$ hybridization (see Ref. [7]). This conclusion is confirmed by comparison of V L_3 of V_2O_5 (V^{5+}) and NaV_2O_5 ($V^{4.5+}$) in Fig. 1b. In NaV_2O_5 an additional electron (compared to V_2O_5) partly fills the next d -like band (A') and as a result vanadium has a mixing valency ($4.5+$). In this case V L_3 XES shows an additional feature located at around 516 eV which is close to high-energy subband in VO_2 where vanadium has ($4+$) oxidation state and d^1 configuration [8]. Such feature is absent in V L_3 XES of (Cu,V)-based 1223, 1245, 1256 and 1267 high- T_c superconductors indicating that vanadium in these phases has an oxidation state of ($5+$). Therefore, based on these measurements we can conclude that the oxidation state of vanadium less than ($5+$) suggested in Refs. [2,3] is incorrect.

The full-width at half-maximum (FWHM) of V L_3 XES of 1223, 1245, 1256 and 1267 phases is found to be 2.6 ± 0.1 eV, which is less than in V_2O_5 (4.2 ± 0.1 eV) where the local surrounding of vanadium atoms is octahedral. Simulation of V L_3 XES in $[VO_4]^{3-}$ and $[VO_6]^{7-}$ clusters performed in MO LCAO (molecular orbitals linear combination of atomic orbitals) approach in Refs. [9,10] show that V $3d_{4s}$ -orbitals occupy a more narrow energy interval in $[VO_4]^{3-}$ cluster than in $[VO_6]^{7-}$ cluster (see Figs. 2a and b). As result, the FWHM of calculated V L_3 XES for $[VO_4]^{3-}$ (1.9 eV) is less than that of $[VO_6]^{7-}$ cluster (2.4 eV). Despite our coarse approach used for the theoretical estimation, the tendency in variation of FWHM for $[VO_4]^{3-}$ and $[VO_6]^{7-}$ clusters enables to conclude that the local

surrounding of vanadium is tetrahedral. Therefore, one can conclude that vanadium atoms form $[VO_4]^{3-}$ tetrahedrons but they are not simply substituting copper atoms in the 1223, 1245, 1256 and 1267 phases. Tetrahedral vanadium groups $(VO_4)^{3-}$ replace partly copper polyhedra in a manner similar to that which is found for (Hg,V) based 1201 superconductors [11].

The pentavalent state of vanadium in (Cu,V)-based 1223, 1245, 1256 and 1267 HTSCs indicates that the (Cu,V) plane with $(Cu_{0.5}V_{0.5})O$ composition will yield 0.5 hole per unit formula. In principle, the crystal defects such as excess oxygen in the (Cu,V) plane should also be considered as origin of hole carriers. The determination of oxygen content is one of the most difficult problems in material science, even for more simple systems. Such possibility for these compounds is discussed in Refs. [2,3]. Based on the starting oxygen content and estimations of oxygen loss during synthesis (by weighting of the gold capsules before and after the high-pressure/high-temperature treatment), the final compositions of our samples are determined as $Cu_{0.5}V_{0.5}Sr_2CaCu_2O_{7.5}$ (1223-phase), $Cu_{0.5}V_{0.5}Sr_2Ca_2Cu_3O_{9.4}$ (1245-phase), $Cu_{0.5}V_{0.5}Sr_2(Ca_{3.6}Sr_{0.4})Cu_5O_{13.5}$ (1256-phase) and $Cu_{0.5}V_{0.5}Sr_2(Ca_{4.7}Sr_{0.3})Cu_6O_{15.3}$ (1267-phase). This shows that we have excess of oxygen in all phases compared to the ideal composition, which can be considered as excess oxygen in the (Cu,V) plane giving additional hole carriers. To confirm this rather indirect determination of oxygen content in our samples, we have performed measurements of $OK\alpha$ XES for all phases. V $L_{2,3}$ and $OK\alpha$ XES have very close values of emission energies. Thus, such measurements could be realized simultaneously during one measurement with the same window of the multichannel detector. The obtained results are shown in Fig. 3. V $L_{2,3}$ XES were normalized to the same intensity and one can estimate the variation of oxygen content monitoring the intensity variation of $OK\alpha$ XES. As is seen in Fig. 3, the intensity of $OK\alpha$ XES in the 1223-phase is higher than that of 1267-phase and their ratio is close to 1.6. On the other hand, according to the chemical composition of the samples as given above, the oxygen index in the 1223-phase is 7.5 and attributing the index 2 to copper, results in a O/Cu ratio of about 3.75. For the 1267-phase the same procedure ($15.3/6$) gives a value of 2.55. Therefore, the oxygen content in the 1223 and 1267 phases varies as 3.75:2.55, which gives their ratio 1.47. In the case of phases 1245 and 1256, the $OK\alpha$ emission intensity does not follow the respective O/Cu ratio (of 3.13 and 2.7), which we estimated from the initial chemical composition. Although the estimation of oxygen concentration from the spectra demonstrates that the starting oxygen content under high-pressure/high-temperature conditions is a very coarse criterion, we find that the starting oxygen content under high-pressure/high-temperature

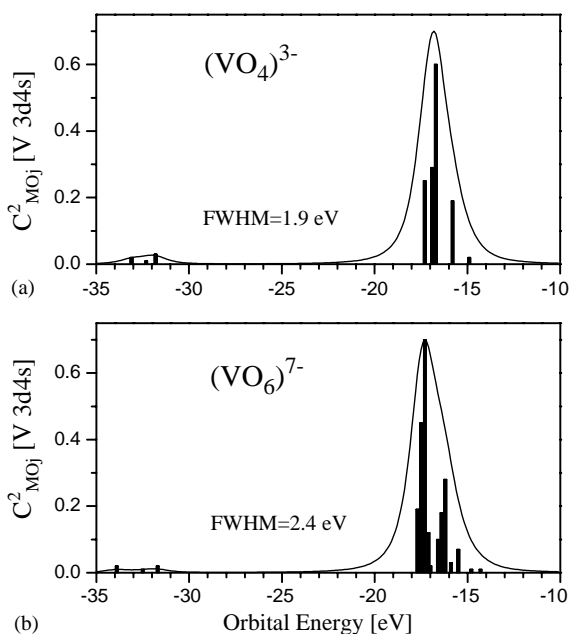


Fig. 2. Calculated V L_3 XES in $(VO_4)^{3-}$ (a) see Ref. [10] and $(VO_6)^{7-}$ (b) clusters (b), see Ref. [9].

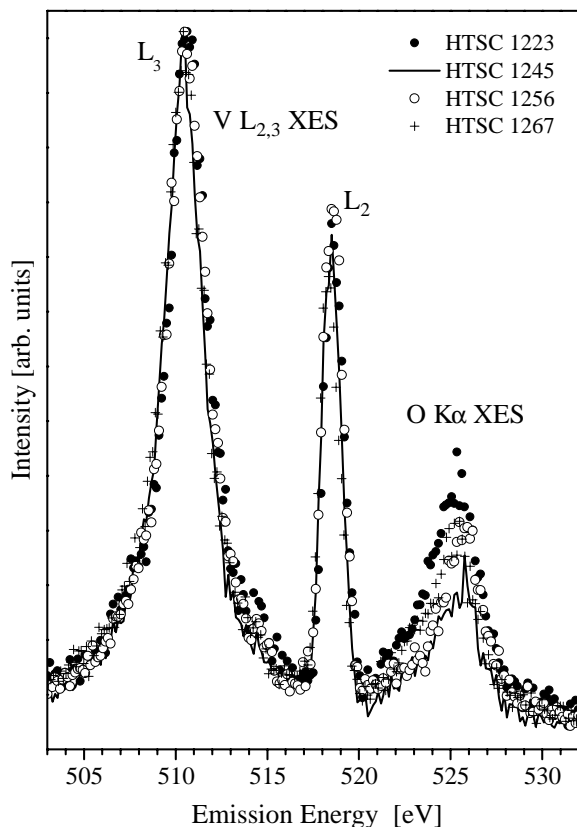


Fig. 3. V $L_{2,3}$ and O $K\alpha$ XES of samples with phases 1223, 1245, 1256 and 1267 are shown.

conditions is not changed considerably for the final product of synthesis of given compounds.

Based on our X-ray fluorescence measurements of $(\text{Cu},\text{V})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n = 3-7$) superconductors, we conclude that V-atoms substituting divalent Cu-atoms in the present compounds form $(\text{VO}_4)^{3-}$ tetrahedrons and have pentavalent (5+) state. Therefore the $\text{Cu}_{0.5}\text{V}_{0.5}$ composition will yield 0.5 holes per unit formula providing a hole-doping mechanism for superconductivity in these compounds.

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