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Influence of the Coulomb parameter U on partial densities of states of $CuGeO_3$: comparison with X-ray spectral data

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Abstract. The electronic structure of the strongly Coulomb correlated cuprate $CuGeO_3$ has been calculated by the local-density-approximation method (LDA+U). The parameter U was varied from 0 to 8 eV. The results of the band-structure calculations are compared with experimental data obtained by means of X-ray photoelectron and resonant X-ray emission spectroscopy methods (Cu Lα and O Kα X-ray emission spectra). It is established that a LDA+U calculation with $U = 4$ eV reproduces well the X-ray photoelectron and X-ray resonant emission spectral data.

PACS. 71.20.-b Electron density of states and band structure of crystalline solids – 78.70.En X-ray emission spectra and fluorescence – 79.60.-i Photoemission and photoelectron spectra

1 Introduction

$CuGeO_3$ is a layered compound with a spin-Peierls transition at ≈14 K [1] which implies the presence of strong electron-correlation effects. This transition is quite unusual for inorganic compounds. It can be viewed as a transition occurring along the Cu–O chains, from uniform antiferromagnetic spin-$\frac{1}{2}$ Heisenberg chains to a system of dimerized chains with a singlet ground state [2]. The assertion that the ground state is a spin singlet with a finite energy gap, which is responsible for the reduction of the magnetic susceptibility to zero for temperatures below 14 K [1], has been confirmed by inelastic neutron-scattering measurements [3].

Single crystals of $CuGeO_3$ are blue, clearly indicating their insulating nature. Transmission and absorption measurements with polarized light give gap values of ≈3.25−3.55 eV, depending on the polarization of the incoming light relative to the crystal axes [4,5].

Investigations of X-ray photoelectron spectra from the valence band and the core levels of $CuGeO_3$ were carried out by Terasaki et al. [6] and by Parmigiani et al. [7]. The Auger and Cu $2p \rightarrow 3d$ and Cu $3p \rightarrow 3d$ resonant photoemission spectra of $CuGeO_3$ were measured by Parmigiani et al. [7]. It was shown that $CuGeO_3$ is a *charge-transfer* insulator with $\Delta \approx 4.2$ and $U_{dd} \approx 6.7$ eV [7]. $CuGeO_3$ is found to be more ionic than superconducting cuprates and than CuO [7]. Duda et al. [8] have carried out measurements of polarized resonant O Kα spectra of $CuGeO_3$ and have observed a Zhang-Rice singlet.

Standard band-structure calculations using the LDA approach predict a metallic state for $CuGeO_3$ [9,10]. It is commonly accepted that the LDA usually gives a poor description of strongly correlated systems, as the on-site Coulomb interaction U of the localized d-electrons, that can be significant, is generally underestimated in LDA. The recently developed LDA+U approach includes the leading terms for the on-site Coulomb and exchange interactions, U and J, allowing to obtain an insulating band-structure character in transition-metal oxides and in high-temperature superconductors [11]. Recently, the LDA+U approach has been applied to band-structure calculations of $CuGeO_3$ in [12,13] with different d–d electron Coulomb and exchange-energy parameters, $U = 9.66$ eV and $J = 0.59$ eV in [12], or $U = 6.7$ eV and $J = 0.98$ eV in [13]. The calculations reproduce the insulating band structure of $CuGeO_3$ with band gaps of 3.02 eV [12] or 2.4 eV [13], and magnetic moments of 0.89 μ_B [12] or 0.76 μ_B [13].

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However, the problem is to define the U-correction for LDA+U calculations in an unambiguous manner. It is known that an overestimate of the screened Coulomb parameter U can lead to a large downward energy shift of the metal $3d$ states below the Fermi level [14,15]. This in turn leads to a poor agreement with the corresponding part of the observed spectra.

In the present paper, a combined study of the electronic structure of $CuGeO_3$ by X-ray emission and X-ray photoelectron spectroscopy is performed, which gives full information about the occupied partial and total density of states distributions, respectively. It is shown that these spectra can be directly compared with available and specially performed LDA and LDA+U calculations of $CuGeO_3$ and used as experimental criterion to determine the U parameter.

2 Calculation

The band structure calculation of $CuGeO_3$ was performed with the LDA+U approach [11]. We used a self-consistent linearized muffin-tin orbital (LMTO) method within this approximation. To show the approach [11] we employed a self-consistent tight-binding linearized muffin-tin orbital (TB-LMTO) method using the atomic sphere approach (ASA) within this approximation. To find the dependence of the calculated electronic structure on the Coulomb parameter U, a set of fixed values of U was taken instead of the calculated one. According to [12], U takes the large value 9.66 eV, obtained from the constrained density-functional calculation. Thus, we used a wide range of U-values from zero (pure LDA) to 8 eV in 2 eV steps. The exchange-parameter J was held constant at 1 eV in all calculations except for the LDA one, in which it was equal to zero. We know from our own experience that the value of J only has a relatively small influence on the results of these calculations, as opposed to the effect of U.

3 Experimental details

A single crystal of $CuGeO_3$ was grown by the self-flux method. Appropriate growth conditions were determined on the basis of the analysis of microstructure and physical properties. The crystal structure of the sample was checked by X-ray structural analysis with a DRON-3 diffractometer.

X-ray photoelectron spectra were measured using an ESCA spectrometer from Physical Electronics (PHI 5600 ci) with monochromatic Al Kα radiation. The energy resolution was approximately 0.4 eV. The pressure in the vacuum chamber during the measurements was below 5×10^{-9} mbar. The spectrometer was calibrated using the Au $4f_{7/2}$ signal from an Au-foil [$E_B(4f_{7/2}) = 84.0$ eV]. The single-crystal specimen of $CuGeO_3$ was cleaved in situ. Since the sample is an insulator, a charging effect occured. The spectra were corrected for this charging using the Ge $2p_{3/2}$ core line (with a binding energy of 1219.5 eV [7]).

The Cu Lα, β X-ray emission spectra ($3d \rightarrow 2p_{3/2,1/2}$ transition) were measured at the Advanced Light Source of the Ernest Orlando Lawrence Berkeley National Laboratory, on beamline 8.0. The fluorescent radiation emitted by the sample was analyzed with a high-resolution grating spectrometer computer-interfaced to a multichannel detector. The pressure in the sample chamber was below 10^{-8} mbar during the measurements. The Cu Lα, β X-ray emission spectra were recorded with an 10 m radius, 1500 lines/mm grating. The spectrometer resolution was about 2.5 eV.

The O Kα X-ray emission spectra ($2p \rightarrow 1s$ transition) were measured on the bulk branch line of beamline I511 at MAX II (MAX-lab National Laboratory, Sweden). The spectra were obtained using a high-resolution Rowland-mount grazing-incidence grating spectrometer with a two-dimensional detector [16]. The energy scale was calibrated using the Zn Lα and Lβ spectra in second order of diffraction from the spectrometer grating.

The X-ray emission spectra were brought to the scale of the binding energies with respect to the Fermi level using the binding energies of the O $1s$ and Cu $2p$ initial (core-level) states of the X-ray transitions as measured by XPS.

4 Results and discussion

Cu $3d$ and O $2p$ partial densities of states of $CuGeO_3$ calculated within the LDA+U scheme with $U = 0$, 2, 4, 6, and 8 eV are presented in Figure 1. One sees that, together with the increase of U from 0 to 8 eV, a gap opens up between the occupied and unoccupied states. The maximal value of this gap, which is 1.58 eV, is obtained for $U = 8$ eV. This maximum gap is below the experimental value ($\approx$3.25–3.55 eV [4,5]). As the parameter U increases, O $2p$ states move to higher energies (closer to the Fermi level) but the Cu $3d$ ones shift toward lower energies.

Information about the Cu $3d$ partial distribution in the valence state can be obtained using Cu Lα X-ray emission spectra. Cu Lα, β X-ray emission spectra originate from Cu $3d \rightarrow 2p$ electron transitions. Cu Lα X-ray emission spectra excited with high energy electrons or photons show a satellite on the high-energy side of the main peak. This satellite originates from the decay of L_2 core holes in the presence of additional $3d$ vacancies. In order to avoid this satellite, the spectra should be excited at lower energies than the L_2 ($2p_{1/2}$) ionization threshold.

In Figure 2 we present the measurements of Cu Lα, β X-ray emission spectra of $CuGeO_3$ for selected photon energies. The excitation energy was tuned from 927 to 971 eV, which includes the Cu L_3 and Cu L_2 absorption thresholds. The excitation energies are labelled by arrows. At lower exciting photon energies (up to 936 eV), the Cu Lα line is distorted by elastic peaks whose energies coincide with the excitation energies. The best approximation for valence $3d$ states is given by the spectrum obtained at an exciting photon energy of about 945 eV. This spectrum is not distorted by the satellite

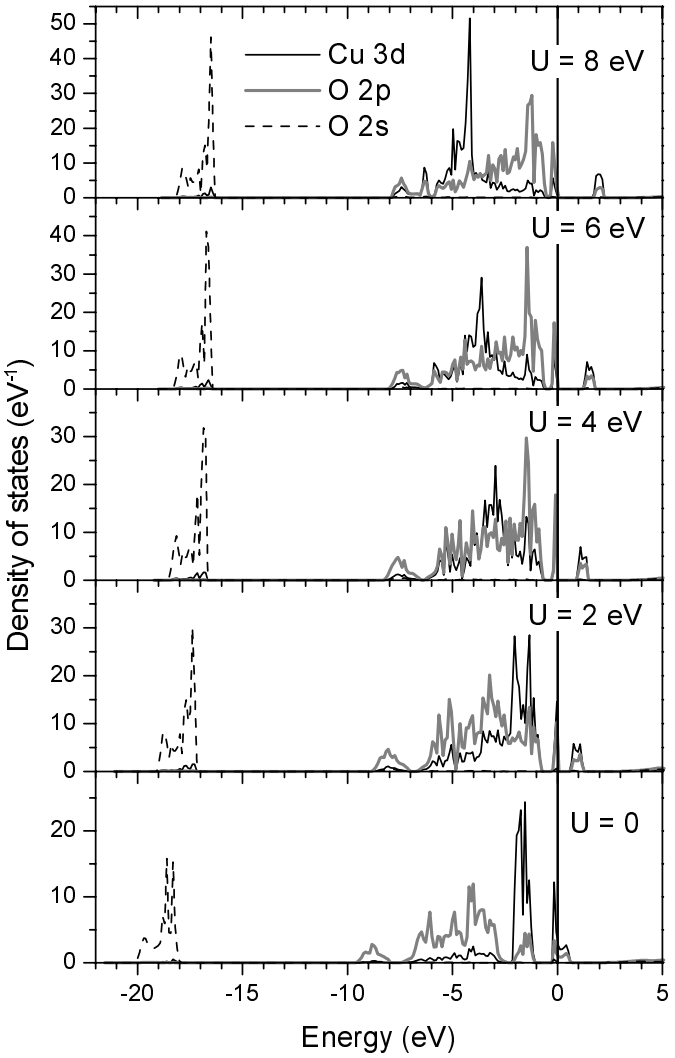

Fig. 1. Cu 3d (solid line), O 2p (shaded area), and O 2s (broken line) partial densities of states of $CuGeO_3$ calculated using the LSDA+U approximation for $U = 0$, 2, 4, 6, and 8 eV.

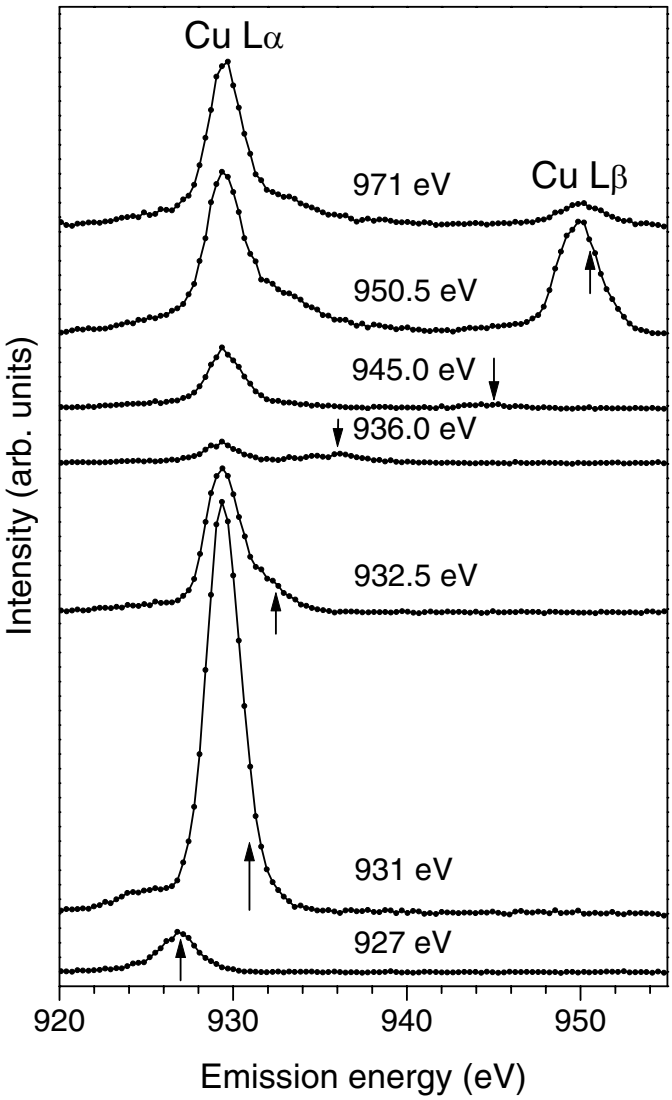

Fig. 2. Excitation-energy dependence of Cu Lα, β X-ray emission spectra of $CuGeO_3$ measured at excitation energies of 927−971 eV. Arrows indicate the excitation energies.

and has a rather high intensity. The Cu Lα spectra measured at excitation energies of 950.5 eV and 971.0 eV have satellites at about 934 eV.

O 2p states are represented by O Kα X-ray emission spectra (O 2$p \rightarrow$ 1s transition). These spectra of $CuGeO_3$ measured at excitation energies of 531.7–535.3 eV are shown in Figure 3. The spectra are in good agreement with those measured by Duda et al. [8] with the polarization vector of the incoming X-ray beam parallel to the a axis.

The vertical bars in the O 1s X-ray absorption spectrum mark the incident photon energies. The excitation energies (from 531.7 eV to 535.3 eV) for the emission spectra are shown by the solid inclined line.

O Kα resonant X-ray emission spectra of $CuGeO_3$ can be explained in terms of both band-like states (main emission band) and localized excitonic states (inelastic scattering) [8]. According to Okada and Kotani [17,18], both the Zhang-Rice singlet (ZR) and dd excitations are characterized by a Raman shift of 2–4 eV. The energy positions of these peaks in the emission energy scale are shown by the slanted line. This position is constant in the Raman-shift scale and depends on the excitation energy in the emission-energy scale. The region of the d^8 states at lower emission energies is also marked by an oblique line [17,18].

The shaded area shows the band-like part of the spectra. According to the soft O 1s X-ray absorption study of $CuGeO_3$ [19] and the calculations of O 2p empty density of states using a multiband Hubbard Hamiltonian [20], unoccupied O 2p states of in-plane oxygen atoms (O2) are located at the bottom of the empty part of the valence band (peak a at the O 1s X-ray absorption spectrum presented in Fig. 3). This means that the O Kα emission spectrum excited at 532.6 eV (which corresponds to peak a of the O 1s X-ray absorption spectrum) reveals mainly 2p states of in-plane oxygen atoms. Peak b (534.0 eV) of the O 1s X-ray absorption spectrum corresponds to

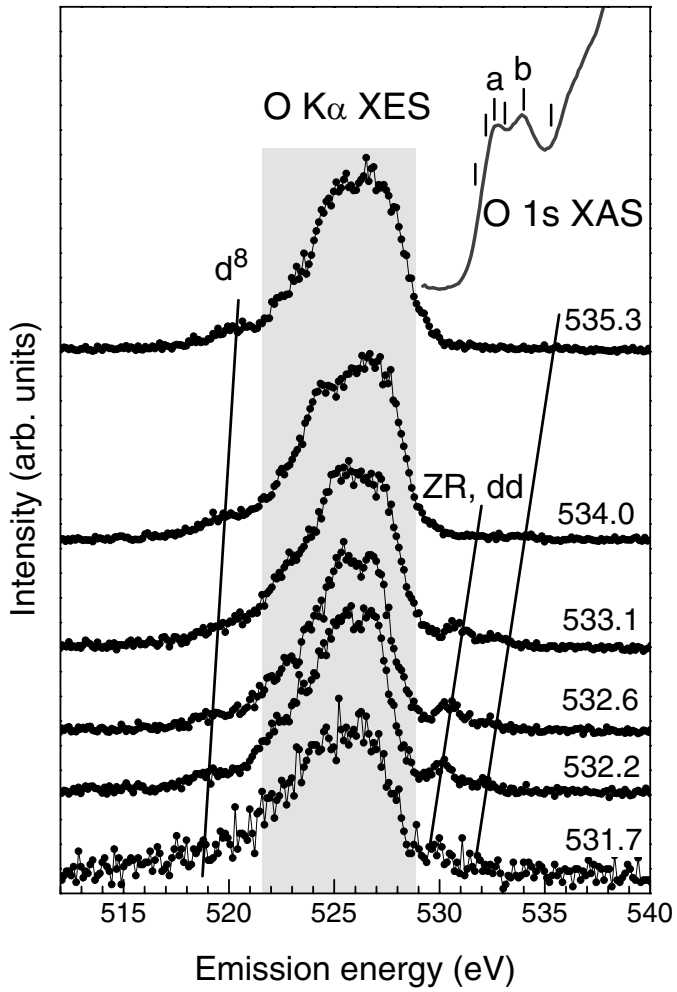

Fig. 3. O 1*s* X-ray absorption (XAS) and O Kα (XES) resonant X-ray emission spectra of $CuGeO_3$. X-ray emission spectra are measured at excitation energies of 531.7–535.3 eV shown by a slanted line. ZR and *dd* denote Zhang-Rice singlet and *dd* excitations, respectively. d^8 denotes the d^8 final state configuration. The shaded area shows the band-like part of the spectra.

a superposition of 2*p* states from both apical (O1) and in-plane oxygen atoms (O2). This means that the spectrum excited at 534 eV is produced from both sites with different weights. The main contribution to this spectrum arises from in-plane oxygen atoms (O2).

Our X-ray photoelectron data obtained for $CuGeO_3$ agree well with those obtained by Parmigiani et al. [7]. Figure 4 shows the Cu 2*p* photoelectron spectrum of $CuGeO_3$. In addition to the main lines at 934.7 and 954.7 eV, broad satellites, as expected for the Cu^{2+} cuprates, appear in the binding-energy ranges of 939–945 eV and 960–964 eV for the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ lines, respectively. The satellites show a fine structure, whose origin in cuprates is widely described in the literature [21], arising from multiplet-splitting effects owing to the interaction between the 2*p* core hole and the $3d^9$ electronic configuration in the final state of the photoemission process.

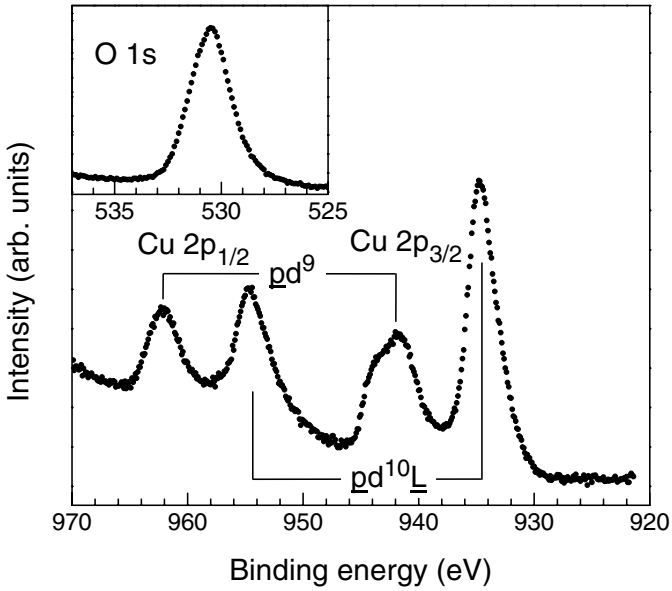

Fig. 4. Cu $2p_{3/2,1/2}$ and O 1*s* (in inset) X-ray photoelectron spectra of $CuGeO_3$.

The main peaks are described mainly by $\underline{p}d^{10}\underline{L}$ states, while the satellite structure should be primarily due to $\underline{p}d^9$ states. Here, $\underline{L}$ denotes a ligand hole arising after the transfer of an electron from a 2*p* ligand level to a metal 3*d* level and $\underline{p}$ is a metal 2*p* hole in the final state of the photoemission process.

The inset in Figure 4 presents the O 1*s* X-ray photoelectron spectrum of $CuGeO_3$. Although the crystal structure of $CuGeO_3$ is characterized by two nonequivalent oxygen atoms, the O 1*s* X-ray photoelectron spectrum of $CuGeO_3$ shows only one line. It follows that both in-plane oxygen atoms (O2) and apical oxygen atoms (O1) have equal O 1*s* binding energies, which according to our experiments are equal to 530.5 eV.

Figure 5 shows the valence-band X-ray photoemission spectrum and the Cu Lα and O Kα X-ray emission spectra of $CuGeO_3$. The X-ray emission spectra are arranged with respect to the Fermi level, taking into account the Cu $2p_{3/2}$ (E_B = 934.7 eV) and O 1*s* (E_B = 530.5 eV) core-level binding energies measured by X-ray photoelectron spectroscopy.

For the Al Kα excitation, photoelectron cross-sections σ multiplied by the atomic concentrations c, $\sigma(\mathrm{Cu}3d)c(\mathrm{Cu}) : \sigma(\mathrm{Ge}4p)c(\mathrm{Ge}) : \sigma(\mathrm{O}2p)c(\mathrm{O})$, are equal to 1 : 0.06 : 0.06 [22]. In consequence, the valence-band X-ray photoelectron spectrum results mainly from Cu 3*d* states. Based on the analysis of the X-ray photoelectron spectrum of $CuGeO_3$ done by Parmigiani et al. [7], peak *A* is assigned to $d^9\underline{L}$ final states, while components *B* and *C* could be assigned to d^8 states with a smaller contribution of $d^{10}\underline{L}^2$ states. Here, $\underline{L}$ denotes a ligand hole arising after the transfer of an electron from a 2*p* oxygen level to a copper 3*d* level, and $\underline{L}^2$ denotes two holes in a 2*p* oxygen level owing to the charge-transfer process. According to the configuration-interaction calculations [23], the shoulder *D* in the photoelectron spectrum of CuO has the sym-

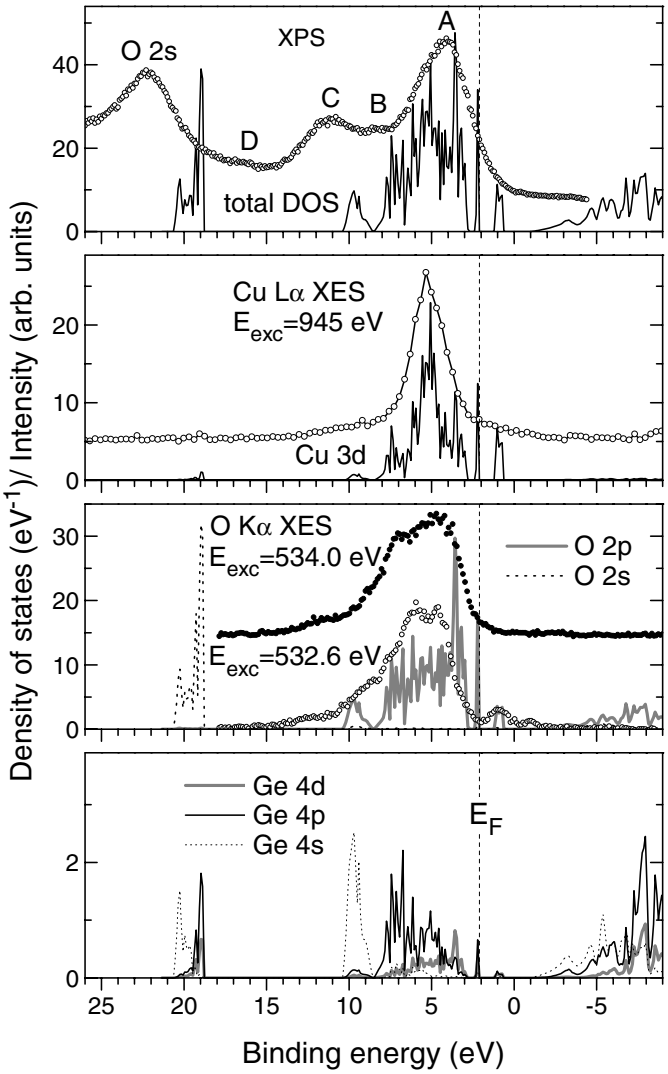

Fig. 5. X-ray photoelectron spectrum of the valence band and Cu Lα and O Kα X-ray emission spectra of $CuGeO_3$ compared with total and partial densities of states calculated using the LSDA+U approximation for $U = 4$ eV. X-ray emission spectra are brought to a common energy scale using the core-level electron binding energies. The Cu Lα emission spectrum was measured at the excitation energy of 945 eV. The O Kα emission spectra were measured at the excitation energies of 532.6 eV and 534.0 eV.

metry of a singlet $^1A_1$ derived from the free-atom ^1S state. This interpretation is confirmed by resonant Cu $2p \rightarrow 3d$ photoemission experiments [7]. We can compare the structure A ($d^9\underline{L}$ final-state configuration) with results of the band-structure calculations.

The Cu Lα spectrum coincides with the O Kα spectrum. It indicates a strong O $2p$–Cu $3d$ hybridization. According to the LDA calculation done without the correlation correction, Cu $3d$ states are located near the Fermi level, and O $2p$ states are found in a region from -3 to -7 eV (see Fig. 1). For the LDA+U calculation with $U = 8$ eV, the relative positions of O $2p$ and Cu $3d$ states are changed: O $2p$ states are located near the Fermi level while the maximum of the Cu $3d$ distribution is at about -4.5 eV.

We have compared the total and partial densities of states obtained for $U = 4$ eV with X-ray photoelectron and X-ray emission spectra in Figure 5. The calculated data are shifted by 2.15 eV with respect to the measured ones. This shift is necessary because $CuGeO_3$ is an insulator and therefore it is expected that the calculated (top of the valence band) and the experimental (in the gap) Fermi energies do not coincide (see, for example, [24]).

The relative position of O $2p$ and Cu $3d$ states are best described by an LDA+U calculation with a Coulomb energy $U = 4$ eV. However, the energy gap seems smaller than the experimental one in all these calculations, even at $U = 8$ eV. It might reach the correct value for U larger than 8 eV, however the position of the states will then be totally wrong. It cannot be excluded that the experimentally observed gap is not produced by the small peak in the density of states which is calculated near 1.5 eV. This peak is isolated from the rest of the conduction band which starts at about twice that energy. If the latter produces the experimental gap, then the agreement of our calculation with all experiments would be quite good indeed.

5 Conclusion

In summary, we present X-ray photoelectron and soft Cu Lα and O Kα X-ray resonant emission spectra of $CuGeO_3$. The Cu Lα spectrum overlaps on the binding energy scale with the O Kα spectrum indicating strong O $2p$–Cu $3d$ hybridization. From comparison of experiment and calculation, we conclude that the LDA+U calculation with $U = 4$ eV best reproduces the X-ray photoelectron and resonant emission spectra.

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