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Cu $2p$ chemical shifts for $YBa_2Cu_3O_{6.5}$: Valence of the Cu atoms

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We study the chemical shift of three different Cu atoms in $YBa_2Cu_3O_{6.5}$, and compare the results with the formally mono-, di-, and trivalent model compounds Cu_2O, CuO, and $NaCuO_2$. We find similar chemical shifts between Cu in the empty chains, Cu in the planes, and Cu in the intact chains as between the Cu atoms in the model compounds. This suggests that the different Cu atoms in $YBa_2Cu_3O_{6.5}$ have formal valences of approximately 1, 2, and 3.

Core-level x-ray photoemission spectroscopy (XPS) can provide important information about the chemical state of an atom by measuring the chemical shift of a core level,[1,2] i.e., how the binding energy of the level changes with the environment. In particular, information about the valence can be obtained. If the electronic charge on an atom is reduced, the electrostatic potential is lowered and the binding energy of the core electron is increased. However, the interpretation of the results for solids is often not straightforward.[3] Previously[4] we studied the valence of Cu in Cu_2O, CuO, and $NaCuO_2$, which are formally monovalent, divalent, and trivalent, respectively. For these model systems we found that the valence concept could explain fairly well experimental Cu $2p$ core binding energies as well as the shape of the photoemission spectra.[5,6] Since the discovery of the high-T_c compounds one central question is the formal valence of Cu in these systems. $YBa_2Cu_3O_{7-x}$ is particularly interesting, since the Cu atoms have different coordinations due to the presence of both Cu-O planes and Cu-O chains. We have chosen to study $YBa_2Cu_3O_{6.5}$, for which there are reasons to believe that the different Cu atoms have the approximate valences +1, +2, and +3. The structure of $YBa_2Cu_3O_{6.5}$ is obtained from that of $YBa_2Cu_3O_7$ by doubling the unit cell in the a direction (perpendicular to the chains) and removing all O atoms in every second chain (empty chain). The structure remains orthorhombic.[7] $YBa_2Cu_3O_{6.5}$ contains locally approximately the same Cu coordination as in the model systems. The plane Cu [hereafter referred to as Cu(2) for the Cu above the intact chain and Cu(4) for the Cu above the empty chain] have locally a coordination [four nearest O neighbors at the distances 1.94 and 1.95 Å (Ref. 7)] which is similar to the coordination (four O neighbors at distances 1.95 and 1.96 Å) for CuO, and it is therefore believed that the planes contain approximately divalent Cu. The empty-chain Cu [Cu(3)] has two O neighbors at a distance of about 1.8 Å. Since Cu_2O have two nearest neighbors at 1.84 Å it has been argued that the empty chains contain approximately monovalent Cu. Cu in the intact chain [Cu(1)] has two O nearest neighbors at a distance of about 1.8 Å and two neighbors at 1.94 Å. In the reference compounds $NaCuO_2$ and CuO the four nearest O atoms are located at 1.85 Å and 1.95–1.96 Å, respectively. This has been used as an argument for the valence of Cu in the intact chain to be between two and three. In the following we will denote Cu(3), Cu(2), and Cu(1) as $Cu^{“1+”}$, $Cu^{“2+”}$, and $Cu^{“3+”}$, respectively, to roughly indicate the expected valence.

We have performed self-consistent local density functional (LDA) calculations using the linear muffin-tin orbital (LMTO) method.[8] As for the model systems we find that the number of $3d$ electrons is similar for $Cu^{“1+”}$, $Cu^{“2+”}$, and $Cu^{“3+”}$, with the trivalent $Cu^{“3+”}$ having about 0.2 $3d$ electrons less than the other Cu atoms. For the formally monovalent $Cu^{“1+”}$ we find the *largest* net positive charge due to much fewer $4p$ electrons than in the other cases. Nevertheless, the initial-state shift follows chemical intuition and the $2p$ level is highest for $Cu^{“1+”}$ and lowest for $Cu^{“3+”}$. These shifts show a similar behavior as for the model compounds. We have not tried to determine the deviations in the valence of $Cu^{“1+”}$, $Cu^{“2+”}$, and $Cu^{“3+”}$ from +1, +2, and +3, respectively. Such deviations are particularly interesting for the Cu atoms in the plane, since the number of holes in the plane is important for the transport properties.[9] We have also calculated the relaxation energy for $Cu^{“2+”}$ and $Cu^{“3+”}$ and find that the binding energy is 0.5 eV larger for $Cu^{“3+”}$. Some experimental photoemission results[10] have been interpreted in terms of two structures (at the separation 1.4 eV) corresponding to Cu^{2+} and Cu^{3+}, while other experiments have only observed one structure in this energy range.[11]

We want to calculate the $2p$ core-level binding energy, using the highest occupied state, ε_v, as the reference level. This energy can be expressed as

$$\Delta E_c \equiv \varepsilon_v - [E(N, n_c = 6) - E(N, n_c = 5)], \tag{1}$$

where $E(N, n_c)$ is the ground-state energy with N valence electrons and n_c electrons in the $2p$ core level. By using the theorem[12]

$$\frac{dE(N, n_c)}{dn_c} = \varepsilon_c(n_c), \tag{2}$$

where ε_c is the $2p$ eigenvalue, we obtain to a good ap-

TABLE I. Theoretical (LDA) Cu $2p$ core-level binding energies. All energies are in eV and measured relative to the highest occupied level.

	LDA ΔE_{2p}		LDA ΔE_{2p}
		$\mathrm{Cu_2O}$	930.8
Cu$^{\text{"2+"}}$	930.9	CuO	931.7
Cu$^{\text{"3+"}}$	931.4	$\mathrm{NaCuO_2}$	932.3

proximation

$$\Delta E_{2p} = [\varepsilon_v - \varepsilon_c(6)] + \tfrac{1}{2}[\varepsilon_c(6) - \varepsilon_c(5)]. \tag{3}$$

We apply the frozen core approximation, using different cores for the $n_c = 6$ and $n_c = 5$ calculations. The core-level position is obtained in perturbation theory

$$\varepsilon_c(n_c) = \varepsilon_c^0(n_c) + \Delta V(n_c), \tag{4}$$

where $\varepsilon_c^0(n_c)$ is the core-level energy of a free atom with n_c core electrons and

$$\Delta V(n_c) = \int d^3r[V(\mathbf{r}, n_c) - V^0(\mathbf{r}, n_c)]\rho_c(\mathbf{r}, n_c), \tag{5}$$

with $V^0(\mathbf{r}, n_c)$ and $V(\mathbf{r}, n_c)$ being the potentials of the free atom and the atom in its solid-state environment, respectively. The density corresponding to the $2p$ level is given by $\rho_c(\mathbf{r}, n_c)$. The binding energy can then be written as

$$\begin{aligned}\Delta E_{2p} = {} & [\varepsilon_v - \Delta V(6)] + \tfrac{1}{2}[\Delta V(6) - \Delta V(5)] \\ & -\tfrac{1}{2}[\varepsilon_c^0(6) + \varepsilon_c^0(5)],\end{aligned} \tag{6}$$

where the first term contains the initial-state shift of the $2p$ level relative to the highest occupied level. The changes of this term give the shifts of the initial-state position of the $2p$ level between different Cu atoms in $\mathrm{YBa_2Cu_3O_{6.5}}$. We refer to these changes as the chemical shift. The second term corrects for final-state effects, and we refer to this as the relaxation energy. The last bracket only depends on atomic quantities. It gives the main contribution to the $2p$ binding energy, but it is independent of the compound. We therefore focus on the first two terms in the following discussion.

To calculate the binding energy for Cu$^{\text{"3+"}}$ we have to perform a self-consistent calculation with one core hole created at Cu$^{\text{"3+"}}$. One extra screening electron is added to ensure charge neutrality for the unit cell. The highest occupied state changes only slightly in energy, which indicates that the unit cell is sufficiently large. For the plane Cu, Cu$^{\text{"2+"}}$, there are two Cu(2) atoms and if we want to preserve the symmetry we must put two core holes in the unit cell. The distance between the core holes is $6.4a_0$, which is so large that the interaction between them should not be very important.

All calculations are based on the LDA.[13] The one-particle equations were solved using the LMTO method in the atomic sphere approximation, which has been described in detail elsewhere.[8] In order to compare the charges in $\mathrm{YBa_2Cu_3O_{6.5}}$ with the model systems we have chosen the same Cu and O sphere radii as earlier, i.e., $R_{\mathrm{Cu}} = 2.5a_0$ and $R_{\mathrm{O}} = 2.0a_0$.[4] The charge on one atom is of course arbitrary because it depends on the sphere radius chosen, but changes between different atoms become a relevant quantity if the same sphere radii are used. For an atomic $3d$ orbital, between 96 and 97% of the charge falls inside the Cu sphere, suggesting that our $3d$ charges may be slightly too low. We used 30 points in the irreducible Brillouin zone, two energy panels, and s, p, and d orbitals on all atoms, plus f orbitals on Ba. For R_{Y} and R_{Ba} we took the sphere radii $3.61a_0$ and $3.89a_0$, respectively. The interstitial spheres in the Cu layers and in the Y layers had radii $2.0a_0$ and $1.44a_0$, respectively.

The calculated binding energy of the Cu $2p$ core level for Cu$^{\text{"2+"}}$ and Cu$^{\text{"3+"}}$ are shown in Table I. Adler, Buchkremer-Hermanns, and Simon[11] performed photoemission measurements on the $\mathrm{YBa_2Cu_3O_{6.95}}$ compound where from the stoichiometry one expects 30% $\mathrm{Cu^{3+}}$. Such a large amount of trivalent Cu should be seen as a structure at the high-energy side of the main line if $\mathrm{NaCuO_2}$ is taken as a reference compound for the $\mathrm{Cu^{3+}}$ compound. Adler, Buchkremer-Hermanns, and Simon concluded that the line shape cannot account for that large $\mathrm{Cu^{3+}}$ content, even if the main line is slightly broader than for other $\mathrm{Cu^{2+}}$ compounds, which might reflect some amount of trivalent Cu. On the other hand, Steiner *et al.*[10] found a small component $\mathrm{Cu^{3+}}$ in the main peak, assuming that the $\mathrm{Cu^{3+}}$ component is at 1.4 eV higher binding energy than the almost degenerated $\mathrm{Cu^{1+}}$ and $\mathrm{Cu^{2+}}$ signals. With an O content corresponding roughly to $\mathrm{YBa_2Cu_3O_{6.5}}$ the $\mathrm{Cu^{3+}}$ peak was not observed anymore. According to our calculations the binding energy is 0.5 eV larger for Cu$^{\text{"3+"}}$ than for Cu$^{\text{"2+"}}$. This small separation between the peaks is probably the reason for the difficulties of seeing a Cu$^{\text{"3+"}}$ component,

TABLE II. The $4s$ (n_{4s}), $4p$ (n_{4p}), $3d$ (n_{3d}), and total (n_{Cu}) Cu electronic charge in the ground state. $\Delta V(6)$ is the shift of the core level relative to a free Cu atom, and V_{Mad} is the Madelung potential on the Cu site. The initial-state contribution in Eq. (6) to the binding energy is $\varepsilon_v - \Delta V$, where ε_v is the highest occupied state. All energies are in Ry.

	n_{4s}	n_{4p}	n_{3d}	n_{Cu}	$\Delta V(6)$	V_{Mad}	$\Delta V - V_{\mathrm{Mad}}$	ε_v	$\varepsilon_v - \Delta V$
Cu$^{\text{"1+"}}$	0.59	0.47	9.28	10.34	0.040	0.543	−0.583	−0.277	−0.237
Cu$^{\text{"2+"}}$	0.53	0.64	9.30	10.47	−0.128	0.325	−0.453	−0.277	−0.149
Cu$^{\text{"3+"}}$	0.57	0.72	9.14	10.44	−0.191	0.429	−0.620	−0.277	−0.086
$\mathrm{Cu_2O}$	0.52	0.42	9.30	10.24	0.065	0.702	−0.637	−0.126	−0.191
CuO	0.45	0.55	9.13	10.13	−0.041	0.795	−0.836	−0.132	−0.091
$\mathrm{NaCuO_2}$	0.58	0.74	9.12	10.44	−0.351	0.230	−0.545	−0.376	−0.061

TABLE III. The centers of the O 2p (C_{2p}) and Cu 3d (C_{3d}) bands as well as their difference. We also show the energy (ε_v) of the highest occupied state. All energies are in Ry.

	C_{2p}	C_{3d}	$C_{3d}-C_{2p}$	ε_v
Cu_2O	−0.432	−0.291	0.141	−0.126
CuO	−0.373	−0.371	0.002	−0.132
$NaCuO_2$	−0.497	−0.644	−0.147	−0.376
Cu"1+"	−0.442	−0.383	0.060	−0.277
Cu"2+"	−0.475	−0.482	0.007	−0.277
Cu"3+"	−0.414	−0.501	−0.087	−0.277

in particular since the analysis of the experimental data has often been done under the assumption that the splitting is 1.4 eV.

In Table II we present some results for the ground state. Cu"1+" and Cu"2+" have almost the same 3d charge and Cu"3+" only 0.2 fewer 3d electrons. Contrary to chemical intuition, we find that Cu"2+" and Cu"3+" have the smallest net positive charge. This is due to the larger amount of 4p electrons in these compounds, which can be understood from the local geometrical structure. Cu"1+" has only two nearest O neighbors but Cu"2+" and Cu"3+" have four nearest O neighbors. Cu"3+" has slightly more 4p electrons than Cu"2+", due to a smaller Cu-O distance locally around Cu"3+". The increased coupling means that the 4p level, which is located well above the Fermi energy, is more strongly mixed into the occupied bands.

In our previous work[4] we used a counting argument to show that the difference between the centers of gravity for the Cu 3d band and the O 2p band, ($C_d - C_p$), decreases as the formal valence of Cu increases. This counting argument simply tells us how many holes (dictated by the formal valence) there will be in the Cu 3d–O 2p bands. For example, when going from the formally monovalent compound Cu_2O to the formally divalent compound CuO we have to create a hole at the top of the otherwise filled Cu 3d–O 2p bands. If $C_d > C_p$, as in the case of Cu_2O, the missing electron has mainly Cu 3d character and due to the large 3d-3d Coulomb interaction this is not a self-consistent solution. The self-consistent solution is obtained if the Cu 3d level is lowered relative to the O 2p level to achieve less Cu 3d character at the top of the band when the hole is created. As seen in Table III the same trend is also observed for Cu"1+", Cu"2+", and Cu"3+" in $YBa_2Cu_3O_{6.5}$ if we compare with C_p for the nearest O neighbors of the Cu atoms. This shift in the positions of the bands translates into the initial-state contribution to the chemical shift, $\varepsilon_v - \Delta V$, which is shown in Table II. Going from Cu_2O to CuO, the reduction in $C_d - C_p$ results from a reduction in the Cu 3d charge.[4] Comparing CuO with $NaCuO_2$ there is a large reduction of the Cu Madelung potential. In this case no reduction of the Cu 3d charge is needed to obtain the reduction of $C_d - C_p$ required by the counting argument.[4] We now turn to $YBa_2Cu_3O_{6.5}$. Going from Cu"1+" to Cu"2+" there is a large reduction of the Cu Madelung potential and no reduction of the Cu 3d charge is needed to lower $C_d - C_p$. However, between Cu"2+" and Cu"3+" there is an increase in the Cu Madelung potential and therefore a substantial reduction of the Cu 3d charge is needed to obtain a further lowering of the Cu 3d level. Thus while $C_d - C_p$ is reduced in going from Cu"1+" to Cu"2+" to Cu"3+" in both the model compounds and in $YBa_2Cu_3O_{6.5}$, the mechanisms for this reduction are combined in different ways in the two cases. To obtain the charge transfer energy $[E(d^9) \rightarrow E(d^{10}L^{-1})]$ for the different Cu atoms, the transition-state argument[12] can be used and $C_{3d} - C_{2p}$ rescaled to $n_{3d} = 9.5$. The charge transfer energies are then 2.6 eV, 1.7 eV, and 1.7 eV for Cu"1+", Cu"2+", and Cu"3+", respectively.

We now consider the final states. Table IV gives information about the changes of the charges and potentials relative to the initial-state results in Table II. The relaxation energies due to adjustment of the valence electrons are shown in Table V. The large relaxation of the core charge is in the present approximation independent of the solid-state environment and not interesting here. We note that the valence contribution is large and that there is an appreciable difference between Cu"2+" and Cu"3+" in $YBa_2Cu_3O_{6.5}$. In Table V we can see that the core hole is only partly screened, i.e., $\Delta n_{Cu} < 1$. That is owing to lack of states locally on the Cu atom due to the almost filled 3d shell for the Cu compounds. Since the core hole is perfectly screened the remaining of the screening charge is sitting outside the atomic sphere and contributing via the Madelung terms. The charge sitting outside can of course not screen as efficiently as the charge inside the Cu sphere. For the Cu"2+", Cu"3+" atoms the screening charge sits almost entirely on the nearest O neighbors.

In conclusion, we have calculated the initial-state chemical shift of the Cu 2p core level for the inequivalent Cu atoms in $YBa_2Cu_3O_{6.5}$ and also the binding energy for in-plane Cu and intact chain Cu. The relative chemical shifts (initial-state shifts) are similar to those obtained for the formally mono-, di-, and trivalent compounds Cu_2O, CuO, and $NaCuO_2$, respectively. Interestingly, the net charge of Cu"1+" is more positive than for

TABLE IV. Same as for Table II but for the final state.

	n_{4s}	n_{4p}	n_{3d}	n_{Cu}	$\Delta V(5)$	V_{Mad}	$\Delta V - V_{Mad}$	$\varepsilon_v - \Delta V$
Cu"2+"	0.61	0.74	9.91	11.27	0.724	0.435	0.289	−1.001
Cu"3+"	0.64	0.83	9.80	11.26	0.713	0.512	0.201	−0.990
Cu_2O	0.62	0.51	9.78	10.91	0.87	0.902	−0.035	−0.993
CuO	0.53	0.63	9.74	10.89	0.818	0.928	−0.110	−0.950
$NaCuO_2$	0.64	0.85	9.67	11.16	0.524	0.385	0.139	−0.900

TABLE V. Changes in the $4s$, $4p$, $3d$ and total charge on the Cu atom when a core hole is created. We also show the change in the Madelung potential and in $(\Delta V - V_{\text{Mad}})$. $E_{\text{rel}} \equiv \frac{1}{2}[\Delta V(5) - \Delta V(6)]$ is the valence electron contribution to the relaxation energy.

	Δn_{4s}	Δn_{4p}	Δn_{3d}	Δn_{Cu}	ΔV_{Mad}	$\Delta(\Delta V - V_{\text{Mad}})$	E_{rel}
Cu$^{\text{"}2+\text{"}}$	0.08	0.10	0.62	0.80	0.110	0.742	0.426
Cu$^{\text{"}3+\text{"}}$	0.06	0.11	0.66	0.82	0.083	0.821	0.452
Cu_2O	0.11	0.09	0.48	0.67	0.200	0.602	0.401
CuO	0.07	0.07	0.61	0.75	0.133	0.726	0.430
$NaCuO_2$	0.06	0.10	0.56	0.72	0.155	0.684	0.420

Cu$^{\text{"}2+\text{"}}$ and Cu^{3+}, but the $2p$ level is nevertheless lower for Cu$^{\text{"}2+\text{"}}$ and Cu$^{\text{"}3+\text{"}}$, as it should be. These shifts can be understood in terms of a lowering of the Cu $3d$ level relative to the nearest-neighbor O $2p$ level when the Cu valence is increased, and it follows from a counting argument. The Cu atoms in the intact chains (Cu$^{\text{"}3+\text{"}}$) have 0.5 eV higher binding energy than the Cu atoms in the plane (Cu$^{\text{"}2+\text{"}}$). This small difference may be the reason for the problems in seeing the approximately trivalent Cu experimentally.

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