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Chemical shifts for monovalent, divalent and trivalent Cu compounds

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Abstract. We study the chemical shift of the Cu 2p core level for Cu_2O, CuO and $NaCuO_2$, where Cu is formally monovalent, divalent and trivalent, respectively. We find that the binding energy increases with the valence, as expected, although the variation in the number of 3d electrons is small and the trivalent Cu atom is found to have a smaller net positive charge than the monovalent or divalent Cu. The origin of the calculated chemical shifts is analysed and the relation with the chemical valence is discussed.

1. Introduction

Core-level x-ray photoemission spectroscopy (XPS) or ESCA can provide important information about the chemical state of a given 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 a given atom is reduced, the electrostatic potential is lowered and the binding energy of the core electron is increased. For small molecules the resulting shift can be quite large. However, in many cases, in particular for solids, the interpretation of the results is not straightforward [3]. Calculations show that a change in the chemical valence of a given atom does not necessarily lead to a large change in its net charge. In addition the contribution to the potential, the Madelung potential, from the other atoms of the system is substantial. Finally, the system relaxes when a core electron is removed. These final-state effects are often large compared with the chemical shifts between different compounds.

Recently, the study of high-T_c superconductors has raised questions about the chemical shift for Cu atoms, in particular to what extent monovalent, divalent or trivalent Cu is observed. For this reason we have studied the chemical shift of the Cu 2p $j = 3/2$ level in Cu_2O, CuO and $NaCuO_2$, where Cu has the chemical valence +1, +2 and +3, respectively. We find that the number of 3d electrons is similar in these compounds, with Cu_2O having about 0.2 3d electrons more than the other two compounds. Surprisingly, we find that the formally trivalent Cu in $NaCuO_2$ has the smallest net positive charge of the cases studied. Nevertheless, according to the calculations the 2p binding energy is largest for $NaCuO_2$ and smallest for Cu_2O, as one would expect from the chemical valence. We discuss the reason for the small

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positive charge of Cu in $NaCuO_2$. In particular, we discuss how the calculated results can be related to the chemical valence. Our calculations are in good agreement with the experimental difference between Cu_2O and CuO, while the experimental situation for the difference between CuO and $NaCuO_2$ is unclear.

In section 2 we describe the method for the calculations. In section 3 we present and discuss the results, and in section 4 we give a summary.

2. Method of calculation

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

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

where $E(N, n_c)$ is the ground-state energy with N valence electrons and n_c electrons in the 2p core level. The first and second brackets give the binding energies of the core level and the highest occupied state, respectively. The second bracket can be written

$$E(N-1, n_c = 6) - E(N, n_c = 6) = -\varepsilon_v \tag{2}$$

where ε_v is the energy of the highest occupied level. This follows since this level is an extended state and there is no relaxation when the electron is removed. To obtain an expression for the first term, we use the theorem [4]

$$\frac{\mathrm{d}E(N, n_c)}{\mathrm{d}n_c} = \varepsilon_c(n_c) \tag{3}$$

where ε_c is the 2p eigenvalue. We then write

$$E(N, n_c = 5) - E(N, n_c = 6) = -\int_5^6 \varepsilon_c(n_c)\,\mathrm{d}n_c \approx -\tfrac{1}{2}(\varepsilon_c(6) + \varepsilon_c(5)). \tag{4}$$

We have here preferred to approximate the integral by the values of the integrand at the end points, instead of using the transition-state method, where the integral is approximated by the integrand at the middle of the interval. The reason is that this allows us to separate in a natural way the traditional chemical shift and the final-state effects. Thus we obtain

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

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

$$\varepsilon_c(n_c) = \varepsilon_c^0(n_c) + \Delta V(n_c) \tag{6}$$

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

$$\Delta V(n_c) = \int \mathrm{d}^3 r\, [V(r, n_c) - V^0(r, n_c)]\rho_c(r, n_c) \tag{7}$$

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

$$\Delta E_{2p} = [\varepsilon_v - \Delta V(6)] + \tfrac{1}{2}[\Delta V(6) - \Delta V(5)] - \tfrac{1}{2}[\varepsilon_c^0(6) + \varepsilon_c^0(5)] \tag{8}$$

where the first term contains the system-dependent part of the location 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 systems. 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.

Ideally, the calculations would be performed as impurity calculations, where one atom (the 'impurity') has a different number of core electrons. We have instead used a supercell method, where we use a large unit cell containing several elementary unit cells. In one of these elementary unit cells a Cu atom is allowed to have a core hole. The number of valence electrons is increased by one so that the system remains neutral. The size of the supercell is increased until the results are reasonably well converged. For example, introducing *two* core holes in the $NaCuO_2$ supercell (*reducing* the size of the supercell by a factor of two) changes the binding energy by less than 0.2 eV. Further we note that in the supercell calculation the energy of the highest occupied state is almost unchanged when a core hole is introduced (introducing *one* core hole in an infinite system would not change the highest occupied level).

The calculations are based on the density functional method in the local density approximation [5]. This method has been found to give reliable results for many ground-state properties, such as the charge density and the geometry of the system. The method often gives poor band gaps, and for the systems considered here it fails to give a band gap for CuO. In the present study we are, however, mainly interested in the charge density.

In the density functional formalism we have to solve a one-particle problem. This was performed using the linear muffin-tin-orbital (LMTO) method in the atomic sphere approximation (ASA) [6]. In this method space is partitioned in (slightly) overlapping spheres, with the sphere radii chosen so that the sphere volumes add up to the unit cell volume (space filling). One sphere is centred on each atom in the unit cell. If the space filling requirement leads to an unphysically large overlap of the spheres, additional (interstitial) spheres are introduced in the open region between the atoms. This is the case for Cu_2O and CuO.

We are in the following particularly interested in the charge on each atom. This charge is defined as the charge inside the sphere of that atom. This definition is to a certain extent arbitrary, since the charge depends on the radius of the sphere. We therefore use the *same* radii for the Cu and O sphere for all the compounds. In this way calculated *changes* between the different compounds become relevant. The Cu sphere radius is chosen to be $R_{Cu} = 2.5a_0$, where a_0 is the Bohr radius. With this choice of radius, between 96 and 97% of the atomic 3d charge falls inside the atomic sphere in the absence of a core hole. With a core hole this fraction is increased to between 98 and 99%. This means that our calculated 3d charges in the solid are

reasonable, although perhaps slightly too low. The oxygen sphere radius was chosen to be $R_O = 2.0a_0$ and for the interstitial spheres we used $R_E = 1.67a_0$ and $1.62a_0$ for Cu_2O and CuO, respectively. No interstitial spheres were needed to obtain a good space filling for $NaCuO_2$. In the calculation with the elementary unit cell, we used 20, 204, 82 k-points in the irreducible Brillouin zone for cubic Cu_2O, orthorhombic CuO and triclinic $NaCuO_2$, respectively. The supercell calculations used approximately 200 k-points in the whole Brillouin zone. All results are well converged with respect to the size of k-mesh. For all atoms the maximum l value was equal to 2, and for the interstitial spheres it was equal to 1 and 2 for Cu_2O and CuO, respectively. The energy E_ν for which the LMTO are calculated was put at the centre of gravity of the corresponding partial density of states.

3. Results

We have calculated the binding energy of the Cu 2p level for Cu_2O, CuO and $NaCuO_2$. These results are in particular compared with results of Steiner *et al* [7], and for $NaCuO_2$ also with a result of Mizokawa *et al* [8]. Steiner *et al* [7] give binding energies relative to the Fermi energy. For Cu_2O and and CuO there are many experiments which give similar results [9]. Similar results were also obtained by Herzog *et al* [10] who considered $NaCuO_2$ as well. The estimated† separation between the top of the valence band and the Fermi energy has been subtracted from the results of Steiner *et al* [7], to obtain the binding energy with respect to the highest occupied state. The same procedure was used by Mizokawa *et al* [8]. These experimental results are compared with the calculated results in table 1. The absolute values of the binding energies are of the order 2 eV too small in the calculations. This rather small relative error (0.2%) is probably due to the LDA approximation and of less interest here. The most interesting quantities ('shift' in the table) are the relative binding energies of the three compounds. The calculated binding energy of CuO is about 1.0 eV larger than for Cu_2O. This is in good agreement with experiment, and follows the chemical intuition that the binding energy should be larger for the divalent compound than for the monovalent compound. For trivalent $NaCuO_2$ the calculated binding energy is about 0.5 eV larger than for CuO, again following the chemical intuition. This agrees rather well with the results of Steiner *et al* but not with the results of Mizokawa *et al*, who obtain a somewhat smaller binding energy for $NaCuO_2$ than for CuO. We observe that it is experimentally hard to determine the exact position of the top of the valence band, and the 0.5 eV disagreement between the two experimental groups is therefore not very surprising. Finally, we mention that Allan *et al* [11] have studied La_2CuO_4 and $LaCuO_3$, where Cu has the valence +2 and +3, respectively. They report that the binding energy with respect to the Fermi energy is 2.5 eV larger for trivalent Cu. Since $LaCuO_3$ is a metal while La_2CuO_4 is

† These estimates were obtained from S Hüfner (private communication), who further observes that the top of the valence band was determined using XPS data of the same samples for which the core levels were measured. This procedure, however, produces uncertainties of unknown magnitude. It cannot be excluded that they amount to ±0.5 eV. Therefore it is not certain whether it is not more appropriate at this stage of our knowledge to use the internal referencing of the XPS machine assuming that it places the Fermi energy at the top of the valence band. In this latter case the shifts in table 1 are 0.0 eV, 1.0 eV and 2.3 eV for Cu_2O, CuO and $NaCuO_2$, respectively.

Table 1. Comparison of theoretical (LDA) and experimental (expt.) Cu 2p core level binding energies. 'Shift' shows the difference to Cu_2O. All energies are in eV and measured relative to the highest occupied level.

	LDA ΔE_{2p}	Shift	Expt.[a] ΔE_{2p}	Shift	Expt.[b] ΔE_{2p}
Cu_2O	930.8	0.0	932.2	0.0	
CuO	931.7	0.9	933.0	0.8	
$NaCuO_2$	932.3	1.5	933.2	1.0	932.7

[a] References [7, 11].
[b] Reference [8].

an insulator, the use of the highest occupied state as the reference level could only increase the difference between divalent and trivalent Cu for these two compounds.

In table 2 we present some results for the ground state, which we use for analysing the results. Naively, one may expect the Cu atoms to have 10, 9 and 8 3d electrons in the monovalent, divalent and trivalent compounds, respectively. It is well known that the actual differences in charges are much smaller. Thus the difference in the 3d charge between Cu_2O and CuO is only 0.17. Interestingly, we find that CuO and $NaCuO_2$ have practically the same number of 3d electrons. Actually, the total Cu electronic charge, including the 4s and 4p electrons, is *larger* for $NaCuO_2$ than for the other two compounds. This is due to the larger number of 4s and 4p electrons for $NaCuO_2$. This can be understood from the geometrical structure. In Cu_2O, Cu has two O nearest neighbours at a distance 1.84 Å. In $NaCuO_2$, Cu has four nearest-neighbour atoms at almost the same distance (1.85 Å). Since the 4p level is relatively high in energy, we may estimate its occupancy from perturbation theory. The hopping matrix elements in $NaCuO_2$ should only be slightly smaller than for Cu_2O, since the distance is only slightly larger. If we neglect the difference in the energy separation between the O 2p and Cu 4p levels for the two cases, we arrive at the conclusion that Cu in $NaCuO_2$ should have almost twice as many 4p electrons as Cu in Cu_2O. The calculations show that the ratio is indeed 1.8. Similar effects may tend to increase the 4s occupation, although a quantitative estimate is harder in this case, since perturbation theory is not valid. In CuO and $NaCuO_2$ the number of nearest neighbours is the same, but the separation (1.95 Å) in CuO is larger. Thus the hopping matrix elements are smaller in CuO, explaining the smaller number of 4p electrons in CuO. We also mention that there are 1.5 electrons inside the Na sphere, i.e. Na has a net negative charge of 0.5 electrons. This may seem to be against chemical intuition. We note, however, that we have used a large atomic sphere with a radius 3.48 a_0. This is much larger than the Pauling ionic radius 1.80 a_0, and it is probably the main reason why Na is negatively charged in our calculation.

Table 2 also shows the shift $\Delta V(6)$ of the core level compared with its position in the atom. The table further shows the Madelung potential. The difference $\Delta V - V_{\mathrm{Mad}}$ shows the difference in the electrostatic potential between the atom and the solid, taking into account only the charge density inside the Cu sphere for the solid. In a naive picture, this quantity would decrease rapidly in going from the monovalent to the trivalent compound, since the charge inside the Cu sphere should be reduced. The potential is indeed reduced by about 0.2 Ryd between Cu_2O and CuO. This is due to the reduction in the number of 3d electrons, which is only partly compensated by an increase in the number of 4s and 4p electrons. For $NaCuO_2$ the potential is,

Table 2. The 4s (n_{4s}), 4p (n_{4p}), 3d (n_{3d}) and total (n_{Cu}) Cu charge density 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 equation (8) to the binding energy is $\varepsilon_v - \Delta V$, where ε_v is the highest occupied state. All energies are in Ryd.

	n_{4s}	n_{4p}	n_{3d}	n_{Cu}	$\Delta V(6)$	V_{Mad}	$\Delta V - V_{Mad}$	ε_v	$\varepsilon_v - \Delta V$
Cu_2O	0.515	0.424	9.296	10.235	0.065	0.702	−0.637	−0.126	−0.191
CuO	0.454	0.551	9.131	10.136	−0.041	0.795	−0.836	−0.132	−0.091
$NaCuO_2$	0.578	0.742	9.121	10.441	−0.315	0.230	−0.545	−0.376	−0.061

however, higher than for the two other compounds. In view of the previous results this is expected, since the total charge is much larger for $NaCuO_2$ than for the other two compounds, but it may seem to contradict chemical intuition.

The initial-state contribution to the binding energy is given by $\varepsilon_v - \Delta V$ (see equation (8)). This quantity does follow chemical intuition. The reason is that the Madelung potential is much lower for $NaCuO_2$ than for the other two compounds. This more than compensates for the less attractive potential from the charge inside the Cu sphere for $NaCuO_2$. These numbers may seem to suggest that it is pure accident that the binding energy follows our chemical intuition. Below we argue that there is, nevertheless, a connection between the chemical valence and the observed results, in particular in going from Cu_2O to CuO.

We first illustrate that we can discuss the initial-state shift of the Cu 3d level instead of the 2p core level. This is not very surprising, since both are determined by the same potential. In table 3 we show $V_{Mad} - \Delta V$, which gives the electrostatic contribution from the Cu sphere to the shift of the core level. We also show C_{3d}, which gives the centre of the Cu 3d band. We can see that the two quantities change in a qualitatively similar way between the three compounds. Between Cu_2O and CuO, the change in C_{3d} is somewhat smaller than the change in $V_{Mad} - \Delta V$. This is natural, since the change in the charge density is mainly a change in the number of 3d electrons. Since the core orbital lies well inside the 3d orbital, simple electrostatics gives that the change in the core level is larger. Between CuO and $NaCuO_2$ the changes in the two quantities are similar. In this case the main change is a change in the number of 4s and 4p electrons. Since both the 3d and 2p orbitals lie inside the 4s and 4p orbitals, we expect similar changes for both of them. The table illustrates that for a qualitative discussion, we can focus on the Cu 3d level instead of the Cu 2p level.

Table 3. The quantities $V_{Mad} - \Delta V$ and $V_{Mad} - C_{3d}$, where C_{3d} is the centre of the Cu 3d band. The changes ('shift') of these quantities relative to the previous line are also shown. All energies are in Ryd.

	$V_{Mad} - \Delta V$	Shift	$V_{Mad} - C_{3d}$	Shift
Cu_2O	0.637		0.993	
CuO	0.836	0.199	1.166	0.173
$NaCuO_2$	0.545	−0.291	0.874	−0.292

In table 4 we compare the centres of the Cu 3d and O 2p bands. For Cu_2O the centre of the Cu 3d band is about 0.14 Ryd higher than the centre of the O 2p

band. In CuO the two band centres are approximately degenerate, and in $NaCuO_2$ the centre of the O 2p band is higher. We further note that the position of the top of the band (ε_v) tends to be determined by the higher of these two band centres. Thus the table illustrates how the centre of the Cu 3d band moves down relative to the top of the band. This tendency we would like to relate to the chemical valence of Cu. We also show the difference $V_{\mathrm{Mad}}^{\mathrm{Cu}} - V_{\mathrm{Mad}}^{\mathrm{O}}$ in the Madelung potential between the Cu and O atoms. This difference is to a substantial extent determined by the Cu Madelung potential shown in table 2, since the changes in the O Madelung potential are smaller. The table illustrates that the changes in the Madelung potential play a rather small role in going from Cu_2O to CuO, but that they are important for the differences between CuO and $NaCuO_2$.

Table 4. The centres of the O 2p (C_{2p}) and Cu 3d (C_{3d}) bands as well as their difference. We also show the difference in the Madelung potential between the Cu and O atoms as well as the energy (ε_v) of the highest occupied state. All energies are in Ryd.

	C_{2p}	C_{3d}	$C_{3d} - C_{2p}$	$V_{\mathrm{Mad}}^{\mathrm{Cu}} - V_{\mathrm{Mad}}^{\mathrm{O}}$	ε_v
Cu_2O	−0.432	−0.291	0.141	0.916	−0.126
CuO	−0.373	−0.371	0.002	0.876	−0.132
$NaCuO_2$	−0.497	−0.644	−0.147	0.318	−0.376

First we consider Cu_2O, where the Cu 3d level is about 0.14 Ryd above the O 2p level. This agrees with the stronger electronegativity of O and it is also in qualitative agreement with the calculated results for free atoms, where the Cu 3d level is about 0.26 Ryd above the O 2p level. We further notice that the number of Cu 3d electrons is only 9.3, i.e. less than 10, as one would naively expect from valence arguments. It is, however, well known that the basically occupied Cu 3d level hybridizes with higher-lying unoccupied levels. The result is a slight depopulation of the 3d level. We also observe that in this case, where the system is formally Cu^+ (i.e. $3d^{10}$) and O^{2-} (i.e. $2p^6$), the bands of mainly Cu 3d and O 2p character are filled and separated from the other bands by a band gap.

We next consider CuO. First we have performed a calculation for CuO, using the potential parameters obtained from a self-consistent Cu_2O calculation. If the system were formally Cu^+ and O^{2-}, the system would have 16 electrons per CuO unit. We first consider this case. We then fill all the bands of Cu 3d character and O 2p character up to a band gap. This is a good starting point for the discussion, as we expect the system to have roughly 10 3d electrons apart from the depopulation due to hybridization with higher-lying states. The results are shown in table 5. The system now has 9.4 Cu 3d electrons. The depopulation of the 3d level due to hybridization with higher bands is here slightly smaller than for Cu_2O. We also show results using the CuO potential but having 16 electrons per CuO unit. The number of 3d electrons is now increased somewhat to about 9.6.

We now have to take into account that the Cu in CuO is divalent and that the system has 15 electrons per CuO unit instead of 16 as assumed in the calculation above. We therefore remove one electron from the system. The result is shown in table 5. The number of 3d electrons now drops by almost 0.6. The reason for this rather large drop is that in Cu_2O, the potential of which was used, the Cu 3d level is about 0.14 Ryd above the O 2p level. The highest states in the Cu 3d and O 2p

Table 5. Charge densities on the Cu atom for a self-consistent Cu_2O calculation, a CuO calculation using the Cu_2O potential and assuming 16 or 15 electrons, N_e, per CuO unit and for a self-consistent CuO calculation.

Syst.	Potential	N_e	n_{4s}	n_{4p}	n_{3d}	n_{Cu}
Cu_2O	Cu_2O	26	0.515	0.424	9.296	10.235
CuO	Cu_2O	16	0.434	0.579	9.431	10.444
CuO	CuO	16	0.462	0.575	9.553	10.590
CuO	Cu_2O	15	0.425	0.560	8.855	9.840
CuO	CuO	15	0.454	0.551	9.131	10.136

band therefore have mainly Cu 3d in character. Thus the drop in the O 2p charge is only about 0.35.

The result of removing 0.6 Cu 3d electrons is, however, a large drop in the Cu potential, since the 3d electrons are quite localized. The calculation we have just discussed must therefore be far from self-consistent. To obtain a self-consistent result we must remove fewer 3d electrons in going from a system with 16 electrons per CuO unit to 15 electrons. This is, however, only possible if the Cu 3d level moves down relative to the O 2p level. Thus we have established a connection between the change in valence of Cu in going from Cu_2O to CuO and the downward movement of the Cu 3d level relative to the O 2p level. The self-consistency is discussed below in a very simple model.

In table 6 we show results for $NaCuO_2$. We here use the CuO potential as a starting point. The potential of Na, which cannot be obtained from the CuO calculation, was taken from the self-consistent $NaCuO_2$ calculation and lined up with the Cu potential as in $NaCuO_2$. If all bands of Cu 3d and O 2p character are filled, there are 22 electrons per $NaCuO_2$ unit and about 9.7 3d electrons per Cu atom. We now take into account that Cu is trivalent and remove two electrons from the system. The result is that the number of Cu 3d electrons is reduced by about 0.8. The fraction of removed 3d electrons is lower than in the CuO case above, since we use a potential where the Cu 3d and the O 2p levels are approximately degenerate. A comparable amount of charge is removed from the O atoms. However, since there are two atoms per cell, the removed charge per atom is only about half as large as for Cu.

Table 6. The same as table 5 but for CuO and $NaCuO_2$.

Syst.	Potential	N_e	n_{4s}	n_{4p}	n_{3d}	n_{Cu}
CuO	CuO	15	0.454	0.551	9.131	10.136
$NaCuO_2$	CuO	22	0.526	0.689	9.729	10.944
$NaCuO_2$	CuO	20	0.525	0.685	8.917	10.127
$NaCuO_2$	$NaCuO_2$	20	0.578	0.742	9.121	10.441
$NaCuO_2$	$NaCuO_2$	22	0.579	0.748	9.701	11.028

As for CuO, we observe that this could not be a self-consistent solution, since such a charge density would lead to too low a Cu potential. The self-consistent solution must have a potential where the Cu 3d level has moved further down relative to the O 2p level than was the case in CuO. In this way the uppermost states in the 3d–2p band have less Cu 3d character and less than 0.8 3d electrons are removed when the

two highest states are emptied. Again we have related the downward movement of the 3d level relative to the 2p level to the valence of Cu and to the number of empty states in the 3d–2p bands. Below we discuss this in a simple model. We shall see there that the arguments given above can only partly explain the results for $NaCuO_2$ and that the Madelung potential indeed is important, as suggested by table 2.

We now want to give a simplified model of the self-consistency. We write the energy of the Cu 3d level as

$$C_{3d} = C_{3d}^0 + U_d(n_{Cu} - n_{Cu}^0) + V_{dd}(n_{Cu} - n_{Cu}^0) + V_{dp}(n_O - n_O^0) + V_{dE}(n_E - n_E^0) + \Delta C_d \tag{9}$$

where C_{3d}^0 is the value of C_{3d} for Cu_2O, and n_{Cu}, n_O and n_E are the charges in the Cu, O and interstitial spheres. The second term takes into account that the 3d level moves up if the Cu charge is increased, due to the interaction with the charge on the same site. We neglect the difference between an increase in the number of 3d, 4s or 4p electrons, and simply use one single value for U_d. This quantity is calculated by applying an external field on the Cu atom and then using the relation

$$U_d = \frac{\partial C_{3d}}{\partial n_{Cu}}. \tag{10}$$

Here we only consider the shift of C_{3d} due to the change of the charge inside the Cu sphere, since changes in the Madelung potential are included explicitly in equation (9). Thus U_d does not include screening from the electrons outside the Cu sphere. We further note that the C_{3d} level is calculated for a fixed *total* Cu charge, while for the U_d to be used in an Anderson model we consider a change in the 3d *charge* so that the 4s and 4p electrons can adjust and give a screened U_d. The U_d obtained here is therefore larger than the U_d used in the Anderson model. The next three terms take into account the Madelung contributions from other Cu atoms, from O atoms and from the interstitial spheres, respectively. Here V_{ij} are the coefficients giving the Madelung potential. It is convenient to use the charges for Cu_2O as reference charges, which are indicated by a superscript 0. Finally, we introduce the value ΔC_d, which is chosen so that the self-consistent value of C_{3d} is reproduced if self-consistent charges are inserted. We can write down a similar formula for the O 2p level. We are particularly interested in the separation of the 2p and 3d levels

$$\begin{aligned}(C_{3d} - C_{3d}^0) - (C_{2p} - C_{2p}^0) = {} & (U_d + V_{dd} - V_{pd})(n_{Cu} - n_{Cu}^0) + (V_{dp} - U_p - V_{pp})(n_O - n_O^0) \\ & + (V_{dE} - V_{pE})(n_E - n_E^0) + (\Delta C_d - \Delta C_p).\end{aligned} \tag{11}$$

For the self-consistency we also need to know how the charges change when the levels are moved. We write

$$n_i - n_i^0 = \Delta n_i + \alpha_i[(C_{3d} - C_{3d}^0) - (C_{2p} - C_{2p}^0)] + \gamma_i(C_E - C_E^0) \tag{12}$$

where i = Cu, O or E. Δn_i is the change in the charge if all potential parameters are the same as for Cu_2O. This change is due to the change in the structure and the coordination of the atoms. It turns out that all γ_i are small and can be neglected for qualitative arguments. The parameters in equations (11) and (12) for CuO are $U_d = 1.6$ Ryd, $V_{dd} = -1.13$ Ryd, $V_{dp} = V_{pd} = -0.23$ Ryd ,$V_{dE} = -0.40$ Ryd,

$\Delta C_d = -0.01$ Ryd, $U_p = 1.6$ Ryd, $V_{pp} = -1.12$ Ryd, $V_{pE} = -0.41$ Ryd, $\Delta C_p = 0.12$ Ryd, $\alpha_{Cu} = -1.50\,\text{Ryd}^{-1}$, $\alpha_O = 1.44\,\text{Ryd}^{-1}$, $\alpha_E = 0.00\,\text{Ryd}^{-1}$, $\Delta n_{Cu} = -0.40$, $\Delta n_O = 0.15$ and $\Delta n_E = 0.15$. The rather large value of U_p may seem surprising, but it is related to the definition of U_p as the Coulomb interaction of charges inside a sphere with a rather small radius ($R_O = 2.0\ a_0$), and should not be compared with the much smaller effective Coulomb interaction between two O 2p electrons.

If we solve the equations (11) and (12), $C_{3d} - C_{2p} = -0.02$ Ryd. Comparison with table 4 shows that this result agrees well with the result of the full calculation (0.00 Ryd), and illustrates that the simple model is well suited for semiquantitative considerations. By inserting the numerical values for the coefficients and by neglecting some of the smaller terms we obtain the simple equations

$$(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p}) = 1.42(n_{Cu} - n^0_{Cu}) - 0.03 \tag{13}$$

and

$$(n_{Cu} - n^0_{Cu}) = -1.50[(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p})] - 0.40. \tag{14}$$

To obtain this we have also assumed that the change in O charge is compensated by a corresponding change in Cu and E charges. Solving these equations we find that the difference $C_{3d} - C_{2p}$ is reduced by 0.19 Ryd in going from Cu_2O to CuO, which still compares fairly well with the value (0.14 Ryd) in table 4.

Equations (13) and (14) are represented graphically in figure 1, and the crossing of the two lines represents the self-consistent solution. In equation (14) the term -0.40 can be considered to represent the effect of the larger valence of Cu in CuO compared with Cu_2O, since this is the change in the Cu charge in going from Cu_2O to CuO, if the potential is unchanged. Alternatively we could use the difference (-0.60) between line 2 and line 4 in table 5 as a measure, since this is the change when we take into account that there are 15 instead of 16 electrons per CuO unit. Thus the effect of the chemical valence is to shift the line representing equation (14) to the left so that it crosses the axis $(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p}) = 0$ at $n_{Cu} - n^0_{Cu} = -0.4$ and not at 0 or 0.2. If the crossing had been at 0.0 or 0.2, the self-consistent solution would have been shifted to $(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p}) \sim 0$, and there would have been a small chemical shift. Equation (14) also illustrates that the removal of the order one electron, suggested by the formal valence, would dramatically lower the 3d level, which would be very far from the self-consistent solution.

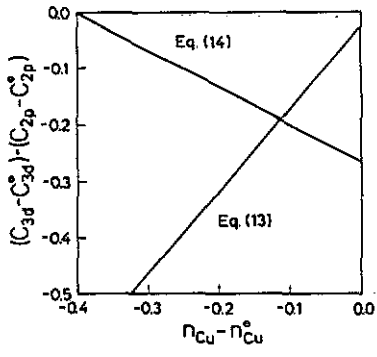

Figure 1. $(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p})$ as a function of $n_{Cu} - n^0_{Cu}$ in equation (13) and $n_{Cu} - n^0_{Cu}$ as a function of $(C_{3d} - C^0_{3d}) - (C_{2p} - C^0_{2p})$ in equation (14).

For $NaCuO_2$ we can write down equations equivalent to equations (11)–(14). We use CuO as the reference compound in this case, i.e. the superscript 0 refers to CuO. For $NaCuO_2$ there are no interstitial spheres but, of course, a Na sphere. We get the formulae

$$(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p}) = (U_d+V_{dd}-V_{pd})(n_{Cu}-n^0_{Cu})+(V_{dp}-U_p-V_{pp})(n_O-n^0_O) + (V_{dNa}-V_{pNa})(n_{Na}-1)+(\Delta C_d-\Delta C_p). \quad (15)$$

$$n_i - n^0_i = \Delta n_i + \alpha_i[(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p})] \quad (16)$$

where i = Cu, O and we have defined $n^0_{Na} \equiv 1$. The parameters are $U_d = 1.3$ Ryd, $V_{dd} = -0.73$ Ryd, $V_{dp} = V_{pd} = -0.08$ Ryd, $V_{dNa} = -0.34$ Ryd, $\Delta C_d = -0.28$ Ryd, $U_p = 1.6$ Ryd, $V_{pp} = -1.05$ Ryd, $V_{pNa} = -0.17$ Ryd, $\Delta C_p = 0.03$ Ryd, $\alpha_{Cu} = -2.18$ Ryd^{-1}, $\alpha_O = 1.40$ Ryd^{-1} and $\alpha_{Na} = -0.62$ Ryd^{-1}, $\Delta n_{Cu} = -0.03$, $\Delta n_O = 0.14$ and $\Delta n_{Na} = 0.38$. Solving equations (15) and (16) gives $(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p}) = -0.15$ Ryd in good agreement with the result (−0.15 Ryd) in table 4. Inserting the values of the parameters, equation (15) takes the form

$$(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p}) = 0.61(n_{Cu}-n^0_{Cu})-0.67(n_O-n^0_O)-0.17(n_{Na}-1)-0.31. \quad (17)$$

From equation (17) we can see that the 3d level tends to be lower than in CuO due to the term −0.31 Ryd. For instance, if we require the Cu and O charges to be the same as in CuO, charge neutrality requires $n_{Na} = 1.66$. The two first terms on the right-hand side in equation (17) are then zero and the third term, due to Na, is −0.11 Ryd. Compared with CuO the 3d level would be lowered by −0.42 Ryd relative to the O 2p level. This is due to the Madelung potential and the different geometrical arrangements of the charges in CuO and $NaCuO_2$. As the charge density is allowed to readjust to its self-consistent form, charge flows to the Cu atom. This leads to a lowering of the Madelung potential on the Cu site and an increase on the O site. As a result the difference −0.42 is lowered further to $V^{Cu}_{Mad} - V^{O}_{Mad} = -0.56$ as seen in table 4. Including the Coulomb terms we obtain the difference $(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p}) = -0.15$ Ryd in table 4.

It may seem that the chemical shift in $NaCuO_2$ is completely unrelated to the valence of Cu. The net Cu charge is 0.86 and 0.56 in CuO and in $NaCuO_2$, respectively. This trend is opposite to what would be expected from the chemical valence for these two systems, and the shift $\Delta V - V_{Mad}$ of the core level from the charge inside the atomic sphere tends to reduce the binding energy in $NaCuO_2$ compared with CuO. Instead we find that the Madelung term strongly increases the binding energy, so that the net result nevertheless agrees with chemical intuition.

To test these arguments further, it is interesting to put the Madelung term −0.31 in equation (17) equal to zero. We then solve again equations (16) and (17) self-consistently. The result is $(C_{3d}-C^0_{3d})-(C_{2p}-C^0_{2p}) = -0.06$ Ryd. Thus even without the Madelung term, there is a tendency to lower the 3d level relative to the O 2p level in going from CuO to $NaCuO_2$. This is due to similar arguments as for the difference between Cu_2O and CuO. The removal of two electrons from the Cu 3d and O 2p band, holding 22 electrons per $NaCuO_2$ unit, would lead to too few 3d electrons to allow a self-consistent solution, unless the 3d level is lowered.

In $NaCuO_2$ this lowering is provided by the Madelung potential. However, if the Madelung potential term −0.31 Ryd in equation (17) had not existed, the calculation above shows that the charge density would nevertheless have rearranged in such a way that the 3d level would have been lowered relative to the O 2p level. To check this further we have applied an external field of 0.31 Ryd to the Cu atom to cancel the effect of this Madelung term. The result is a reduction of the 3d charge to 9.01. This is less than the result 9.13 for CuO, and this difference agrees with the difference in valence. The total charge on the Cu atom is also reduced from 10.44 to 10.20. This is, however, still larger than the charge (10.14) of Cu in CuO. This is due to the contribution from the 4s and 4p electrons, which is related to the small separation to the nearest neighbours in $NaCuO_2$, as discussed above. For the contribution to the chemical shift, we find $\varepsilon_v - \Delta V = -0.095$ Ryd, i.e. about the same as for CuO. To summarize, we find that in the absence of the Madelung term −0.31 Ryd, the valence argument tends to drive $NaCuO_2$ in the expected direction relative to CuO, e.g. the 3d charge is reduced and the 3d level moves down relative to the O 2p level. However, the total charge remains larger and the core level is not more strongly bound than for CuO unless the Madelung term −0.31 Ryd is included.

We observe that the arguments that the Cu 3d level moves down relative to the O 2p level when the valence of Cu is increased, depend on the fact that the Cu 3d level is well above the O 2p level for monovalent Cu. If the 3d level had already been well below the ligand level for monovalent Cu, as may happen for less electronegative ligands than O, the increase in the valence of Cu would not necessarily require a further lowering of the Cu 3d level. This follows since the states at the top of the band would then already have a small Cu 3d character for monovalent Cu.

In view of the importance of the Madelung potential, it is interesting to look more into the detailed origin of the term −0.31 Ryd in equation (17). The main reason for this term is the change in V_{dd} between CuO and $NaCuO_2$. Since the net charge on the Cu atom in CuO is 0.9, the difference $V_{dd}^{CuO} - V_{dd}^{NaCuO_2} = -0.4$ Ryd, leads to a lowering of the 3d level by 0.36 Ryd if we assume the same net Cu charge for CuO and $NaCuO_2$. To understand this difference, we first observe that the Madelung coefficients V_{dd} are calculated as the interaction between one Cu atom and positive point charges placed on all the other Cu atoms. To obtain a convergent result the interaction with a negative neutralizing background is added. This background cancels out of the calculation when the contributions from all the different atoms in the unit cell are added. We now write the Madelung coefficient as

$$V_{dd}^{i} = \frac{v_{dd}^{i}}{R_i} \tag{18}$$

where i labels the compound, v_{dd}^{i} is a quantity which only depends on the structure and R_i is the radius of a sphere which has the same volume as the volume of the unit cell divided by the number of Cu atoms per unit cell. We have $R_{CuO}/R_{NaCuO_2} = 0.76$. This factor can explain about 0.27 Ryd in the difference between CuO and $NaCuO_2$. It simply represents the fact that if the lattice is expanded the Madelung potential is reduced, because of the increased separation between the charges. The remaining difference of 0.13 Ryd is due to the structure-dependent part v_{dd}^{i}. In this context we notice that the two closest Cu atoms are at a distance of 2.75 Å and 2.90 Å in $NaCuO_2$ and CuO, respectively. Thus the closest Cu neighbours are closer in $NaCuO_2$, although the overall dimension R_{NaCuO_2} is larger. This also tends to make the structure-dependent part smaller for $NaCuO_2$.

So far we have exclusively studied the initial-state effects. We now consider the final states. In table 7 we have collected information about the charges and potentials corresponding to the initial-state results given in table 2. In table 8 we show the relaxation energies, due to the adjustment of the valence electrons. In addition there is a large contribution due to the relaxation of the core levels. In the approximation used here this contribution is independent of the solid, and is not interesting here. We also observe that the valence contribution is large and that there is a substantial variation between the different compounds. We now discuss the origin of the differences.

Table 7. Same as for table 2 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_2O	0.621	0.512	9.776	10.909	0.867	0.902	−0.035	−0.993
CuO	0.528	0.625	9.736	10.889	0.818	0.928	−0.110	−0.950
$NaCuO_2$	0.642	0.845	9.676	11.163	0.524	0.385	0.139	−0.900

Table 8. 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 $(\Delta V - V_{Mad})$. $E_{rel} \equiv \frac{1}{2}(\Delta V(5) - \Delta V(6))$ is the valence electron contribution to the relaxation energy.

	Δn_{4s}	Δn_{4p}	Δn_{3d}	Δn_{Cu}	ΔV_{Mad}	$\Delta(\Delta V - V_{Mad})$	E_{rel}
Cu_2O	0.106	0.088	0.480	0.674	0.200	0.602	0.401
CuO	0.074	0.074	0.605	0.753	0.133	0.726	0.430
$NaCuO_2$	0.064	0.103	0.555	0.722	0.155	0.684	0.420

Table 8 shows the changes in the 4s, 4p, 3d and total charge on the Cu atom when a core hole is created. The core hole is only partly screened, i.e. $\Delta n_{Cu} < 1$. This is due to the almost filled 3d shell for the Cu compounds, which means that the 3d electrons cannot screen the hole completely. For 3d compounds to the left in the periodic table of Cu the 3d screening should be much more complete [12]. Table 8 shows that the more efficient 3d screening in CuO is partly compensated by a less efficient screening by the 4s and 4p electrons. This may be due to the somewhat less attractive potential seen by the 4s and 4p electrons, due to the more effective 3d screening. Nevertheless the effective 3d screening in CuO is the dominating factor. This can be seen from Δn_{Cu} or even more clearly from $\Delta(\Delta V - V_{Mad})$, which is the change in the potential due to the change in the Cu charge when a core hole is created. The table also shows the change in the Madelung potential when a core hole is created. This change counteracts the on-site term $\Delta(\Delta V - V_{Mad})$. This is not surprising, since a small on-site term implies a small on-site screening charge. Since the system is neutral and the core hole perfectly screened, the remaining charge must then sit outside the Cu sphere and contribute to the screening via the Madelung term. We have calculated ΔV_{Mad} assuming that the screening charge outside the Cu sphere sits entirely on the nearest-neighbour O sites. We then obtain the results 0.186, 0.134 and 0.159 Ryd for Cu_2O, CuO and $NaCuO_2$, respectively, in good agreement with table 8. It is, however, clear that this screening charge sitting outside the Cu sphere cannot screen as efficiently as the charge sitting inside the Cu sphere. The observed

trends in the 3d screening charge must therefore dominate the physics, and the other two effects, the 4sp screening and the Madelung screening, should only reduce the effects of the 3d screening but not reverse it. The relaxation energy E_{rel} in table 8 has to be subtracted from the initial-state shift $\varepsilon_v - \Delta V(6)$ in table 2 according to equation (8). The result is to reduce the initial-state difference between Cu_2O and CuO and to increase the difference between CuO and $NaCuO_2$ somewhat. In neither case, however, is the trend from the initial-state shift reversed.

4. Conclusions

We have calculated the chemical shift of the Cu 2p core level as well as the charge distribution for Cu_2O, CuO and $NaCuO_2$, where Cu is monovalent, divalent and trivalent. We find that the calculated number of 3d electrons and the total number of Cu electrons decrease as we go from Cu_2O to CuO, as expected from the change in valence. CuO and $NaCuO_2$, however, have about the same number of 3d electrons, and the total number of Cu electrons is about 0.3 larger in $NaCuO_2$ than in CuO, contrary to the expectation based on the difference in the valence. Nevertheless, the calculated Cu 2p binding energy increases monotonically in the series Cu_2O, CuO and $NaCuO_2$ in agreement with the changes in the valence.

We have discussed the relation between the valence and the separation between the O 2p level and the Cu 3d level, and showed that the Cu 3d level tends to move down relative to the O 2p level as the valence of Cu is increased. This also tends to lower the core level in the initial state relative to the highest occupied state and to increase the binding energy. This mechanism dominates the changes between Cu_2O and CuO. For the changes between CuO and $NaCuO_2$ the Madelung potential is found also to play an important role. In particular it lowers the 3d level and the core levels in $NaCuO_2$ and it is one driving force for the initial-state core level being deeper in $NaCuO_2$ than in CuO. The more attractive Cu Madelung potential for $NaCuO_2$ is primarily related to the different spatial location of the atoms in $NaCuO_2$ and CuO. We have tested the effect of removing this geometry-related Madelung contribution for $NaCuO_2$. The difference in the Cu valence between $NaCuO_2$ and CuO then becomes partly operative again in a similar way as for the differences between Cu_2O and CuO. Without this Madelung term the number of Cu 3d electrons becomes smaller for $NaCuO_2$ than for CuO, and the 3d level remains lower relative to the O 2p level, although less so than when the Madelung term is present. However, the initial-state 2p core level is not deeper than in CuO if the Madelung term is missing, and the Madelung term is therefore important for the core level binding energy.

We also find that there are moderate variations in the relaxation energies in the series studied. Thus the relaxation energy is largest for CuO and smallest for Cu_2O. These final-state effects therefore also contribute to making the 2p binding energy smaller in CuO than in $NaCuO_2$, while they reduce the difference between Cu_2O and CuO.

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