Stability of the Oxidation States of Copper

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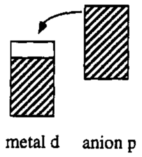
Abstract: An electronic model is developed to understand the empirical observation that high oxidation states of transition metals may be stabilized as their oxide by the addition of an electropositive element. Thus, although copper is known as Cu(I) and Cu(II) in compounds with oxygen, no binary Cu(III) oxide (Cu_2O_3) is presently known. Cu(III), however, may be stabilized as a ternary oxide as in $KCuO_2$. Interpretation of the results of LMTO calculations on a series of copper oxides leads to a model which focuses on the interaction between copper and oxygen orbitals by considering the energy gap between them. The orbitals on silver and gold interact more strongly with the oxygen levels than the contracted d orbitals of the first-row element copper. The interactions between gold and oxygen are enhanced by relativistic effects. Thus the strength of the interaction increases in the order Cu < Ag < Au. Of the series, Cu_2O_3 has not yet been synthesized, Ag_2O_3 has only recently been made with great difficulty, but Au_2O_3 is well-known as a stable system. In $KCu^{III}O_2$ the calculations show that there is effective charge transfer from potassium to oxygen, which leads to a raising of the oxygen levels, a decrease in the metal spd−oxygen 2p separation, and the generation of a stronger interaction between copper and oxygen, i.e., an increase in Cu−O covalency. Calculations on copper(II) halides show that there is nothing inherently peculiar concerning electronic structure of the unknown solid CuI_2, but it is probably just unstable with respect to Cu^II and elemental iodine.

Introduction

The question of the stability of solids is one of longstanding interest to chemists. Why one particular compound is stable, or rather has been successfully characterized, when other closely related compounds have yet defied synthesis, is a question which is invariably difficult to answer since it usually requires a detailed energetic understanding of the phase diagram of the collection of elements concerned. Such energetic information is difficult to acquire, although arguments using an electrostatic model have often proved to be quite enlightening.[1] One question of this type is associated with the empirical observation[2] that high oxidation states of transition metals may be stabilized as their oxide by the addition of an electropositive element. This is of relevance to several areas of solid state chemistry and is particularly important in compounds of interest in the area of high-temperature superconductivity. Two examples will illustrate the point. Although copper is known as Cu(I) and Cu(II) in compounds with oxygen, Cu_2O (cuprite) and CuO (tenorite), respectively, no binary Cu(III), oxide (Cu_2O_3) is presently known. Cu(III) however, may be stabilized in a *ternary* oxide with potassium as in $KCuO_2$, and compounds with oxidation states between II and III are known such as $La_{2-x}Sr_xCuO_4$. Similarly, although Bi(V) does not exist as a binary oxide, $KBiO_3$ is known. Sleight has suggested[2] that the fully occupied oxygen 2p band is stabilized by the presence of the electropositive ion in both cases and that this leads to stability of the high oxidation state. He has also suggested that this stabilization arises via an increase in the "covalency" of the Cu−O or Bi−O linkage when electropositive ions are involved. These observations concerning copper chemistry are all the more tantalizing when we recall that both Ag_2O_3 and Au_2O_3 are known as characterized solids, the former being synthesized[3] relatively recently after many unsuccessful attempts. Similar statements may be made outside of oxide chemistry. Binary nitrides do not exist with Ce(IV) but $BaCeN_2$ is known.

These considerations are reminiscent of ones[4] concerning the solids Cu^IX and $Cu^{II}X_2$ where X = halide. All the monohalides are known with the exception of CuF. The entire dihalide series is known with the exception of CuI_2; synthetic attempts lead to the production of CuI and I_2. The traditional argument is that the iodide levels lie above those of the metal in CuI_2 (since iodine is the least electronegative of the halogens) leading to a spontaneous reduction of Cu(II) to Cu(I) as shown in **1**. The arrow shows the movement of the electrons. Thus one possibility for the "nonexistence" of Cu_2O_3 may lie in the position of the Cu 3d-band with respect to the position of the O 2p-band. For the lower metal oxidation states Cu 3d should lie above O 2p, as in most of the common oxides. However, as the oxidation state increases the 3d band will drop in energy and the opposite may be a possibility.



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This paper examines theoretically the electronic reasons behind the stability of Cu(III) in $KCuO_2$ versus its apparent instability in Cu_2O_3, and the known instability of $Cu^{II}I_2$. We develop a simple electronic model based on high-quality first principles LMTO calculations on both sets of these materials.

Theoretical Approach

The calculations in this paper used the scalar-relativistic linear muffin-tin-orbital (LMTO) method in the atomic sphere approximation (ASA).[5-8] Since it is a density functional method in the local density

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[1] E.g.: Johnson, D. A.: *Some Thermodynamic Aspects of Inorganic Chemistry*; Cambridge University Press: Cambridge, UK, 1968.

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Table 1. Calculated Electron Populations and Band Barycenters (Ry) for Some Copper Oxides

compd	N_s[a]	N_p	N_d	N_{tot}	C−M_s[b]	C−M_p	C−M_d	C−O_p
Cu_2O	0.546	0.464	9.340	10.350	−0.308	0.856	−0.286	−0.502
CuO	0.480	0.564	9.271	10.316	−0.327	0.833	−0.327	−0.410
Cu_2O_3[c] 1.83 Å	0.549	0.785	9.008	10.343	−0.436	0.721	−0.553	−0.507[d] −0.453
Cu_2O_3 1.95 Å	0.466	0.557	9.060	10.083	−0.471	0.683	−0.571	−0.530[d] −0.498
$KCuO_2$	0.681	0.918	9.138	10.737	−0.504	0.644	−0.542	−0.446
$NaCuO_2$[e]	0.578	0.742	9.121	10.441				
Ag_2O	0.567	0.423	9.34	10.330	−0.341	0.685	−0.455	−0.493
Ag_2O_3	0.577	0.760	9.013	10.350	−0.444	0.577	−0.626	−0.508 −0.449
Au_2O_3	0.728	0.767	8.634	10.130	−0.613	0.571	−0.564	−0.514 −0.442
$RbAuO_2$	0.956	1.013	8.821	10.790	−0.620	0.550	−0.497	−0.391

[a] N = number of electrons per copper. [b] C = energy barycenter of bands located on metal (M) and oxygen (O). [c] Since Cu_2O_3 is unknown two sets of calculations were performed using different Cu−O distances (1.83, 1.95 Å). [d] These two figures refer to the two different types of oxygen atom (see Figure 3). [e] From Ref 10.

approximation, it usually gives reliable results for ground-state properties, such as the charge density. The method very often underestimates band gaps (mainly due to poor estimation of the excited states). For CuO it gives no band gap, underestimating the importance of electron correlation. However, in our study we are interested mainly in the charge density distribution, and in the positions of the bands. No geometry optimization was performed; the experimentally observed geometries[4,9] were used except for Cu_2O_3 as described later.

In the LMTO method the space of the unit cell is set equal to the sum of the volumes of slightly overlapping spheres, one sphere per each atom. Frequently, when the overlap between the spheres is unreasonably large, interstitial (empty) spheres are added in the regions between the atoms. In order to compare charges on a particular atom in different compounds, we kept constant the sphere radii for the metal and oxygen in all the calculations. These were 2.50, 2.84, 2.85, and 2.00 au for Cu, Ag, Au, and O, respectively. The radii for the Cu and O atoms were chosen to be the same as the ones used in the calculations of Karlsson et al.[10] in order to compare results. For Cl, Br, I, K, and Rb we used 3.00, 3.20, 3.50, 4.31, and 4.57 au, respectively. The charge on each atom, defined as the charge inside the sphere of this atom, is not necessarily the real charge that the atom may have in the compound. The charge is quite arbitrary and depends on the radius of the corresponding sphere, as well as on the ratio of that radius to the radii of the spheres of the other atoms. However, by keeping the radii constant, the differences between the charges on a particular atom in the different compounds become quite reliable. In order to have the same radii for the metals in the different compounds we introduced empty spheres with radii 1.67 (5), 1.63 (2), 2.31 (3), 1.78 (5), 2.10 (3), 2.20 (3), 1.70 (7), 1.79 (7), and 1.80 (7) au in Cu_2O, CuO, Cu_2O_3, Ag_2O, Ag_2O_3, Au_2O_3, $CuCl_2$, $CuBr_2$, and CuI_2, respectively. (The numbers in parentheses indicate the number of empty spheres per formula unit.)

In all calculations we used between 160 and 180 k-points in the irreducible Brillouin zone, and the results are converged with respect to the size of the k-mesh. The latter are also converged with respect to total energy to better than 10^{-8} Ry/cell. The wave functions of the valence electrons within Cu, Ag, and Au were expanded through $l = 2$, and for the rest of the atoms as well as the empty spheres through $l = 1$. The core electrons were treated by the frozen core approximation.

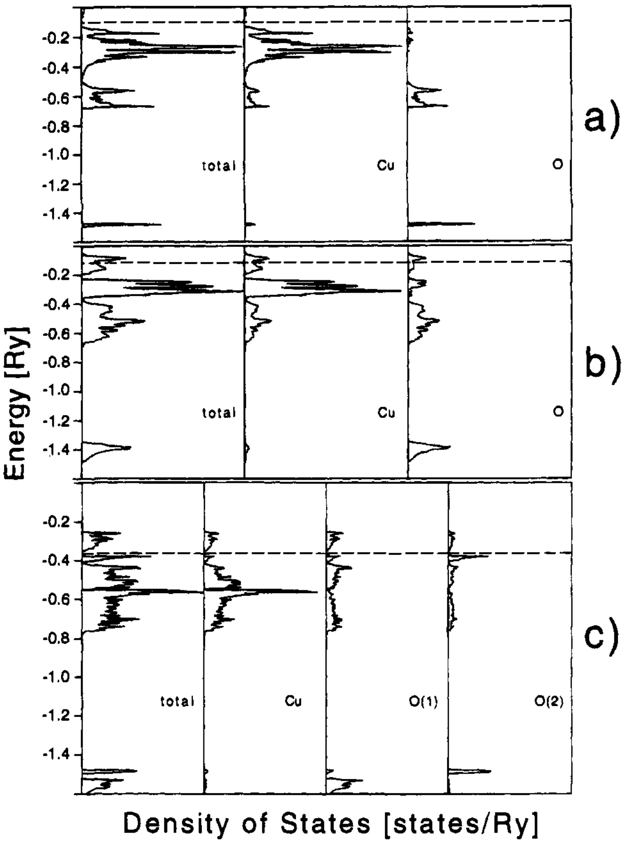

Figure 1. Calculated total and projected electronic densities of states for (a) Cu_2O (cuprite), (b) CuO (tenorite), and (c) Cu_2O_3. There are two types of oxygen atoms in M_2O_3 (see Figure 3): three-bonded O(1) and two-bonded O(2).

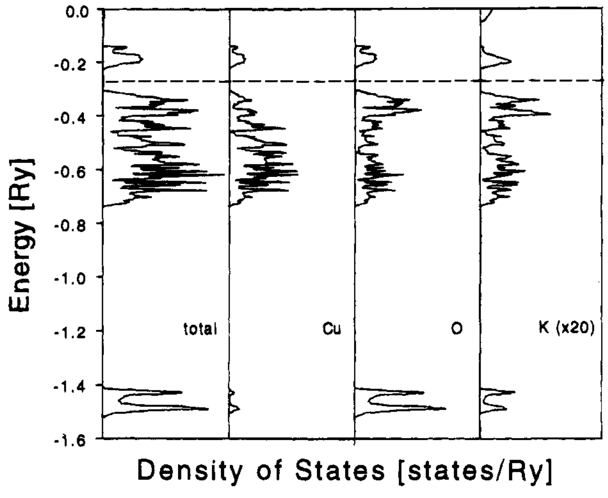

Figure 2. Calculated total and projected electronic densities of states for $KCuO_2$.

Results for Copper Oxides

Table 1 and Figures 1 and 2 show some results of our first principles LMTO calculations described above on a series of copper oxides with varying oxidation states, designed to explore the role of the electropositive element. The geometries used for the known systems came from the relevant crystal structures. Since Cu_2O_3 is unknown, the structure of Ag_2O_3 was used with a Cu−O distance (1.83 Å) expected for this oxidation state and local coordination geometry. In fact two sets of calculations were performed to test the dependence of the results on Cu−O distance (1.83, 1.95 Å). Related calculations by Karlsson *et al.* on these oxides are to be found in ref 10. The calculations

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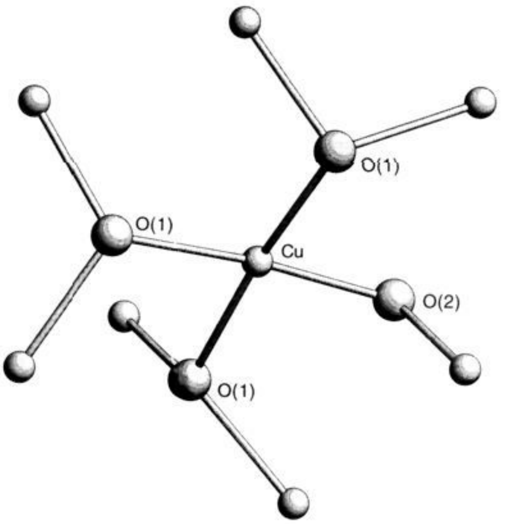

Figure 3. Part of the structure of M_2O_3 (M = Au, Ag, Cu) showing the different coordination of O(1) and O(2).

indicate semiconductors for Cu_2O and Cu_2O_3 and a metal for CuO with a half-filled x^2-y^2 band. It is clear from the density of states of Cu_2O_3 that there are two different regions of electron density with large oxygen contributions. One is sharper and lies at higher energy than the other. These two regions represent the two different oxygen coordination environments found in the structure (Figure 3).

Shown in Table 1 are the total number of $(n + 1)$s, $(n + 1)$p, and *n*d electrons and the energy barycenters of these bands along with that of oxygen 2p. First, we point out that our results for Cu_2O, CuO, and $KCuO_2$ agree well with the results[10] of Karlsson *et al.* on Cu_2O, CuO, and $NaCuO_2$. The tendency of the decreasing number of d-electrons in the series and the quite large 4s and 4p involvement in $ACuO_2$ (A = Na, K) have been noted by these authors and observed in our results as well. Contrary to the expectations of chemical intuition, of 10, 9, and 8 valence electrons for Cu(I), Cu(II), and Cu(III), respectively, we find 10.35, 10.32, and 10.74 electrons, a result which does not follow this trend. The d-electron populations do follow the expected decrease but with much smaller change than expected: 9.34, 9.27, and 9.14.

What do these numbers actually mean? The integral numbers of electrons used in our statement above assume the occupancy of "metal orbitals" which are 100% metal in character. Thus these figures for the total number of "metal" electrons are a measure of the copper 4s, 4p, and 3d character which is mixed into the filled oxygen 2p band as a result of covalent interactions. The values for 4s, 4p in Table 1 indicate a significant rehybridization at the metal atom, especially that involving the p orbital, from system to system. This is easy to understand. The metal 4s, 4p, and 3d levels change in energy with oxidation state and their interaction with the oxygen orbitals increases as their energy separation with oxygen 2p decreases. This movement of the band barycenters is seen to be an irregular one in Table 1, influenced as it is by local geometry too. It is important to realize that this behavior will not be revealed by one-electron calculations (although we do note that the interpretation of our results has a one-electron flavor). The copper 4s and 4p electron populations do depend on Cu−O distance and hence on the strength of the interactions. The shorter distance (larger interaction) leads to larger metal orbital involvement as shown by the results from the calculations on Cu_2O_3.

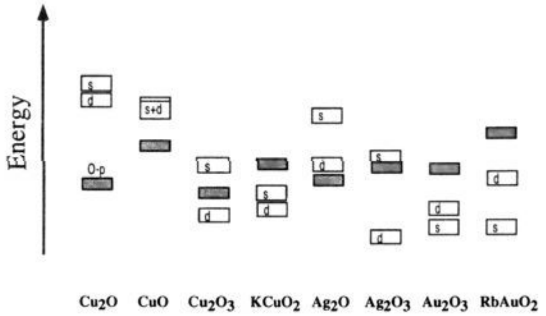

Figure 4. The computed energy band barycenters for group 11 oxides. The M $(n + 1)$p levels lie much higher in energy and are not shown. The shaded boxes represent the centers of the O 2p-bands, and the open boxes show the positions of the M $(n + 1)$s- and M *n*d-band centers (the s- and d-bands are indicated with letters in the boxes).

Perhaps the most interesting observation is that the total number of metal electrons, roughly equal in Cu^{I}_2O, $Cu^{II}O$, and $Cu^{III}_2O_3$, is much larger in $KCu^{III}O_2$. In other words the bonds are computed to be much more covalent (in accord with Sleight's ideas[2]) and thus presumably stronger in $KCuO_2$. This comes about as we have just noted through an increase in metal 4s, 4p, and 3d involvement with the oxygen levels. An explanation of the results for the ternary compound from the data is the following. In $KCu^{III}O_2$ there is effective charge transfer from potassium to oxygen, which leads to a raising of the oxygen levels (Table 1), a decrease in the metal spd−oxygen 2p separation, and thus, on energy gap arguments, the generation of a stronger interaction between copper and oxygen, i.e., an increase in what is often loosely called covalency, between Cu and O. This increased interaction is particularly important in stabilizing the structure containing Cu(III), where the copper levels lie closest to those on oxygen. This is a result which has a strong similarity to the electronic underpinnings[11,12] of the non-stoichiometry of ScS (to give $Sc_{1-x}S$). Here the driving force for loss of scandium is the stronger interaction between metal and sulfur orbitals as the average oxidation state of the metal increases. This arises as the metal levels drop in energy on oxidation, driving the two sets of levels closer to each other energetically. Such effects are certainly widespread in chemistry but have received little attention from chemists.

How valid then is the model of **1**? Figure 1 shows the total and partial electronic densities of states for the binary oxides. It is clear that by going from M(I) to M(III) the positions of the metal and oxygen bands change from metal-above-oxygen to oxygen-above-metal. We can be more precise numerically by using (Table 1 or Figure 4) the computed barycenters of the bands for the group 11 metal and oxygen 2p in the various compounds. These results at first sight could lend credence to the idea described in **1** for the "nonexistence" of Cu_2O_3. However, that this cannot be a satisfactory model is shown by examination of the results for $KCuO_2$ and the silver and gold oxides. In $KCuO_2$, Ag_2O_3, and Au_2O_3 the barycenters of the metal *n*d-bands lie below the O 2p band just as in Cu_2O_3, but these compounds do exist. Moreover, the Ag 4d, band lies much further below the O 2p-band than the Cu 3d-band in Cu_2O_3. The same is true to a lesser degree for $KCuO_2$. Thus consideration of the energies of the barycenters of the bands alone with the model of **1** cannot explain why Cu_2O_3 does not exist. The explanation, however, is straightforward. As may be seen in Figure 1, the bands are of finite width and do not just overlap with each other in the way shown in **1**, but strongly mix together. The model of **1** is just too simple.

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(12) Burdett, J. K.; Sevov, S.; Mryasov, O. *J. Phys. Chem.* **1995**, *99*, 2696.

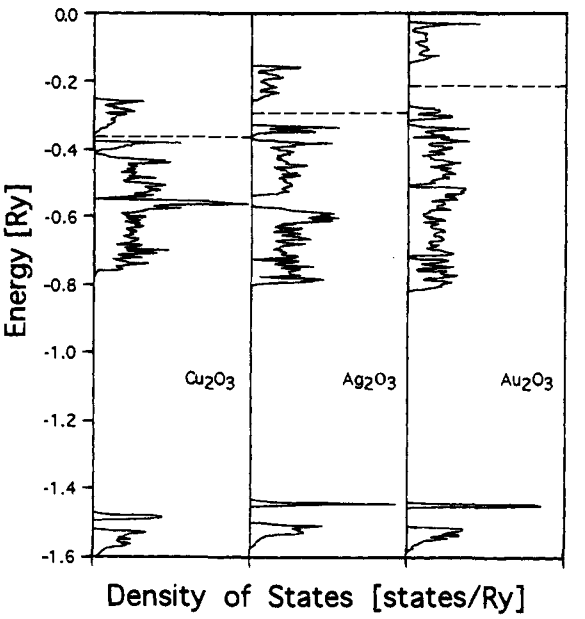

Figure 5. Calculated electronic densities of states for Cu_2O_3, Ag_2O_3, and Au_2O_3.

While the differences in the s and p populations will be influenced, as we have noted, by the different M—O distances in MO and M_2O_3, and the different M-coordination numbers in M_2O and M_2O_3, in AMO_2 and M_2O_3 there are very similar M—O distances and the same coordination numbers for the transition metal. The different effective charge on the "MO_2" unit in these compounds is a vital parameter. We can, in a very simplistic way, consider M_2O_3 as (MO)•(MO_2) and consider the electronegativity of MO vs that of the alkali metal. It is obvious that the electron transfer will be much more complete from the alkali metal to the "MO_2" units than from the "MO" unit. In other words (A)•(MO_2) will be much more ionic than (MO)•(MO_2) since the alkali metals are much more electropositive than MO. As a result of this, "MO_2" has a higher effective negative charge in the ternary compounds AMO_2 than in the binary oxides M_2O_3. This charge affects mostly the oxygen atoms by lifting the O p-band and placing it closer to the transition metal 4s- and 4p-bands as shown by the band barycenters of Table 1. As a result, better mixing occurs between metal and ligand orbitals, with, as a result, higher *n*s- and *n*p-electron populations in AMO_2. Also, there is in general a larger degree of s—p—d hybridization for the transition metal since all three bands are closer to oxygen in these AMO_2 compounds than in the binary oxides.

Understanding the trends in the electronic picture is not quite so simple for the group 11 congeners. Trying to link the differences between the location of the metal and oxygen electronic densities of states with metal electronegativity is not very fruitful. The electronegativities of copper and silver are very similar on all scales (including the more common ones and those derived from pseudopotential radii[13]) and that of gold much larger. However, the non-zero difference in the band barycenters (Figure 4) between Cu_2O_3 and Ag_2O_3 shows that these traditional electronegativity arguments are not very useful. Figure 5 compares the electronic densities of states of the three M_2O_3 solids. Noticeable is the larger band gap and broader bands in the order Cu < Ag < Au, indicating much stronger interactions between metal and oxygen on moving down the group. A part of the reason for the deep-lying 6s-band for gold for Au_2O_3 in Figure 5 surely comes from relativistic effects. This is shown too by the larger change in N_s between silver and gold compared to that between copper and silver in Table 1. Thus for both silver and gold there are stronger interactions with the oxygen orbitals than for copper. There may be an energy gap argument involved (but not one in accord with traditional electronegativity ordering) but there is certainly one involving the more contracted nature of the first-row *n*d orbitals compared to their heavier analogs. For gold, as noted, relativistic effects enhance the interaction with oxygen 2p and gold 6s. Thus the interaction of the metal and oxygen is in the order Cu < Ag < Au. Recall that, of the series, only Cu_2O_3 has not yet been synthesized, and that Ag_2O_3 has only recently been made with great difficulty and by using special methods. Au_2O_3 is well-known. Thus the results of Figure 5 are in qualitative agreement with these observations if band width is taken as a measure of the strength of the metal—oxygen interaction. This apparently can occur for Ag and Au in their binary III oxides alone, but for Cu there is a need of an "assistant", in this case, the alkali metal. In other words, MO in (MO)•MO_2 is electropositive enough for M = Ag, Au but not for M = Cu. Just as in the $KCuO_2/Cu_2O_3$ comparison, the Au 6s- and 6p-electron populations are higher in $RbAuO_2$ than in Au_2O_3.

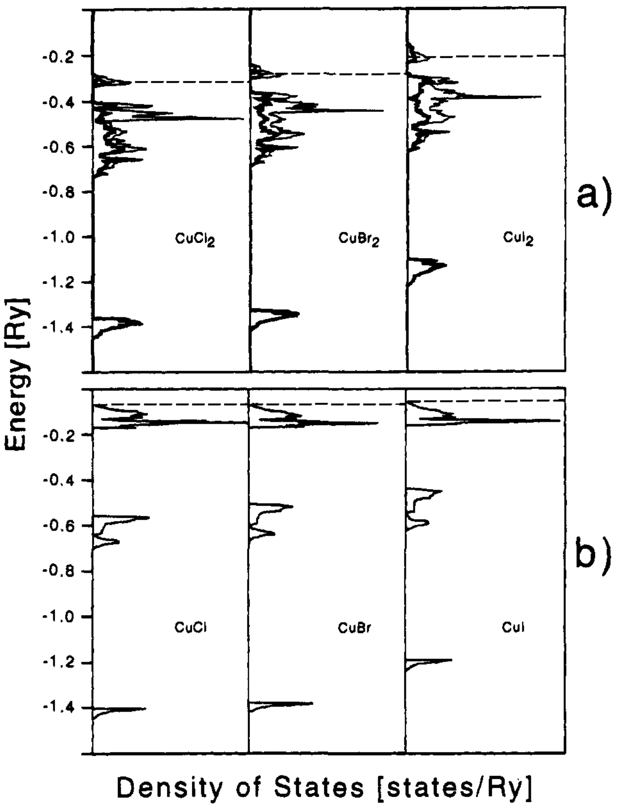

Figure 6. Calculated electronic densities of states for (a) CuX_2 (the thick line represents the projected halogen partial densities of states) and (b) CuX, where X = Cl, Br, and I.

Results on Copper Halides

Figure 6 shows the calculated electronic densities of states for $CuCl_2$, $CuBr_2$, and CuI_2, assuming for the latter a geometry simply scaled from that of the chloride and bromide using the relevant ionic radii. Notice that the broad features of these systems are very similar. The half-filled $x^2{-}y^2$ orbital of the copper is found in all three systems. There was no hint during the convergence of the calculation of any problem which could

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Table 2. Calculated Electron Populations for Some Copper Halides

compd	N_s	N_p	N_d	N_{tot}
CuCl	0.298	0.369	9.772	10.440
$CuCl_2$	0.375	0.400	9.299	10.075
CuBr	0.312	0.368	9.800	10.480
$CuBr_2$	0.386	0.378	9.368	10.133
CuI	0.349	0.360	9.825	10.535
CuI_2	0.424	0.406	9.439	10.270

be identified with an electronic instability of the type shown in **1**. In fact there is no hint at all from the calculations of the instability of CuI_2, just as for Cu_2O_3 above. It is clear that, just as expected on simple electronegativity grounds, the halogen s- and p-bands go up in energy from Cl to I, the halogen p-band being heavily intermixed with the Cu d-band in all three compounds. Figure 6 also shows the results of similar calculations on the corresponding monohalides. Here the halogen bands are well-separated from the copper bands (the X s- and p-bands lie between −1.5 and −1.2 Ry and between −0.7 and −0.5 Ry, respectively). Table 2 shows the copper 3d, 4s, and 4p contributions to the electronic picture. Notice that both 4s and 3d contributions increase in the order Cl < Br < I for both CuX and CuX_2, as expected on simple energy gap (electronegativity) grounds. The contributions from 4p remain either constant (CuX) or move irregular along the series. The total contribution from metal electrons increases in both series Cl < Br < I and would suggest that the compounds with iodine should be the strongest bound if such electron distributions were all that important. One has to look therefore elsewhere for the reasons for the instability of CuI_2.

We have calculated the energetics of the reaction in (1) using our computed total energies for CuX_2 and CuX, along with computed total energies of the halogens as solids. This is a real test of any calculational method and the one we have used does not lead to results in accord with observation. The calculated enthalpy of reaction 1 is positive for all three halogens.

$$Cu^{II}X_2 \rightarrow Cu^{I}X + {}^{1}/_{2}X_2 \qquad (1)$$

However, the *differences* between the computed heats of reaction 1 for the halides may be more reliable. Using the known[14] value for ΔH for this reaction where X = Cl, ΔH is computed to be only +6 kcal/mol for X = I. This result suggests that $Cu^{II}I_2$ is not particularly stable.

There are reactions of Cu(II) coordinated by a variety of ligands which support[15] the same picture. Thus attempts to synthesize Cu(II) with SCN−, CN−, SR, and I invariably lead to the coupling reaction of (2), the products being dicyanogen NCCN, disulfides RSSR, etc. Sometimes the decomposition may be thwarted by the presence of other ligands. Thus $(bpy_2)CuI_2$ and $(bpy)_2(SCN)_2$ are both known. Mercapto Cu(II) centers are known in plastocyanin where perhaps it is the steric bulk of the local environment at Cu(II) which prohibits formation of Cu(I) and the disulfide.

$$-Cu^{II} + X \rightarrow [-Cu^{II}X_2] \rightarrow 2\text{-}Cu^{I} + X_2 \qquad (2)$$

Conclusions

A comparison of the electronic structure of the oxides of copper, especially of $KCuO_2$ and Cu_2O_3, leads to the ready generation of a model which allows insight into the stabilization of Cu(III) by electropositive elements in a ternary oxide. The response of the oxygen and metal energy levels as a function of charge is readily appreciated and the origin of the stabilization in $KCuO_2$, absent in Cu_2O_3, is clear. Interestingly, the result is similar to that identified[11,12] earlier as the factor behind the stabilization of defect structures in $Sc_{1-x}S$.

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