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The bond valence model as a prospective approach: examination of the crystal structures of copper chalcogenides with Cu bond valence excess

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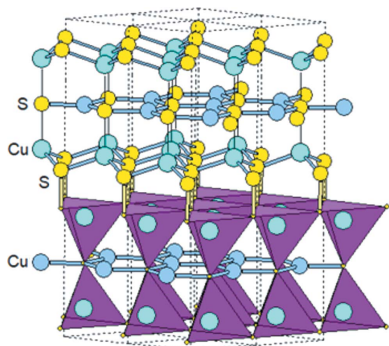
Keywords: bond valence model; copper chalcogenide; bond valence excess; multicentre bonding; metallic behaviour.

Supporting information: this article has supporting information at journals.iucr.org/b

Bond valence analysis has been applied to various copper chalcogenides with copper valence excess, *i.e.* where the formal valence of copper exceeds 1. This approach always reveals a copper bond valence excess relative to the unit value, correlated to an equivalent ligand bond valence deficit. In stoichiometric chalcogenides, this corresponds to one ligand electron in excess per formula unit relative to the valence equilibrium considering only Cu^I. This ligand electron in excess is 50/50 shared between all or part of the Cu-atom positions, and all or part of the ligand-atom positions. In Cu₃Se₂, only one of the two Cu positions is involved in this sharing. It would indicate a special type of multicentre bonding ('one-electron co-operative bonding'). Calculated and ideal structural formulae according to this bond valence distribution are presented. At the crystal structure scale, Cu–ligand bonds implying the single electron in excess form one-, two- or three-dimensional subnetworks. Bond valence distribution according to two two-dimensional subnets is detailed in covellite, CuS. This bond valence description is a formal crystal–chemical representation of the metallic conductivity of holes (mixing between Cu 3*d* bands and ligand *p* bands), according to published electronic band structures. Bond valence analysis is a useful and very simple prospective approach in the search for new compounds with targeted specific physical properties.

1. Introduction

Generally, in transition metal chalcogenides, the oxidation states of the metals are integers; mixed oxidation states are also known, for instance, in iron chalcogenides, as indicated by Mössbauer spectroscopy (*e.g.* Ba–Fe sulfides; Steinfink, 1980). More problematic examples are known in the field of copper chalcogenides. One knows that the pure Cu^{II} oxidation state cannot be stabilized by chalcogens (*ch*), due to the lower position of the Cu 3*d* level relative to the *ch p* level, and is only rarely observed in a minor amount relative to Cu^I (Pearce *et al.*, 2006). On this basis, a copper oxidation state of +1 would be favoured in chalcogenides (remark: due to the non-integer value of some oxidation states, Arabic numerals will be used in this article instead of Roman numerals). On this basis, what is the oxidation state of copper in chalcogenides with a *ch* excess, *i.e.* where there is a significant deficit of (formal) Cu⁺ to balance formally *ch*^{2−}? Classic examples of such compounds are, for instance, covellite CuS and umangite Cu₃Se₂. Different methods have been applied to solve this question. It is pertinent from now on to cite the fundamental study of Folmer & Jellinek (1980), which concludes exclusively, on the basis of X-Ray Photoelectron Spectroscopy (XPS) measurements on several copper chalcogenides, that the oxidation state is +1 for Cu, while the mean oxidation state of *ch* appears in deficit (down to $-\frac{1}{2}$ in CuS₂ and CuSe₂, instead of −2).



Various physical measurements, as well as calculations, have provided solutions to this question through the band–structure model and the formation of holes in the ligand band. In this study, we will show that the bond valence model, despite its semiquantitative character, constitutes an interesting prospective approach, which allows a crystal–chemical representation of the ligand–hole description.

In this way, an examination of the crystal structures of various copper chalcogenides through bond valence analysis permitted the fraction of the bond electrons provided specifically by the ligand to be revealed, corresponding generally to an additional one-electron bonding per formula unit. This approach permits a (sub-)network of ligand–metal bonds to be selected in complex structures which would favour electron conduction and the metallic state.

2. The bond valence model: reminders and particular aspects

2.1. Conventional bond valence model

The bond valence model is a semi-empirical approach (Brown, 1976, 2016) relating bond valences and bond lengths which permits the prediction of the bond lengths of an atom given its valence state and its coordination with neighbouring atoms, or, inversely, the estimation of its valence state within a molecule, ion or solid.

Given a bond between two atoms A and B , with distance d_{AB} (Å), bond valence fraction v_{AB} of A and B is calculated according to the formula:

$$v_{AB} = \exp[(R_{A,B} - d_{AB})/b] \quad (1)$$

where $R_{A,B}$ (in Å) is the bond valence parameter of the (A , B) element pair and b is the bond softness parameter, generally adjusted to 0.37 Å. Tables where B has a negative oxidation state (O, F, Cl, Br, I, S, Se, Te, N, P and As) have been computed (Brese & O'Keeffe, 1991).

In a crystal structure, knowledge of the bond lengths between atoms allows the calculation of the value of the bond valence (generally, a bond valence fraction) shared by any atom pair. For an A atom surrounded by atoms of different elements, *viz.* B , C , *etc.* (possibly A too – see below for the example of realgar As_4S_4), its total bond valence (or, more simply, 'bond valence V_A ') is the sum of all bond valence fractions. This sum is generally close to an integer, one of the possible valence states of the A element. Due to the fact that bond valence parameters are established empirically through the compilation of various crystal structures, the relative error margin on the bond valence total is about $\pm 5\%$, as far as crystal structures are precisely known, but more generally a deviation from an integer up to $\pm 15\%$ is acceptable, taking also into account second-order factors which may affect the choice of the b parameter (Brown, 2016; Gagné & Hawthorne, 2015).

In a recent monograph on the bond valence model by Brown (2016), some aspects have not been considered, or were only briefly discussed, although they can be approached

fruitfully in this way: homonuclear bonding, dative/coordination bonding and odd-electron bonding. It is useful to present them briefly, as they can be taken into account for the examination of copper chalcogenides.

Brown (2016) focused his approach on the ionic model, as each bond is heteronuclear, between a cation and an anion. When some homonuclear (or homopolar) bonds are considered (*i.e.* Hg_2^{2+} , O_2^{2-}), Brown introduced a virtual ion (an anion between two cations or a cation between two anions) in order to maintain the ionic model.

A simplified approach has been proposed by O'Keeffe & Brese (1992), who have tabulated bond valence parameters for anion–anion bonds, *i.e.* bonds between pairs of atoms among the 17 more electronegative elements. It is a simple extension of the bond valence model. This database thus includes the case where the two atoms belong to the same element (homonuclear bond). For instance, in the O_2 molecule, the O–O distance (1.21 Å), with $R_{\text{O,O}} = 1.48$ Å, gives a bond valence (BV) = 2.07 vu (vu is valence units). Here, the ideal bond valence of 2, as an integer, corresponds to the bond order, *i.e.* half the number of bonding electrons minus the number of antibonding electrons, and also to the valence state of oxygen.

The notion of 'bond valence' is more general than that of 'oxidation state'. The oxidation state corresponds to the charge (positive or negative) that an atom would have if all the electrons from its surrounding bonds are given exclusively to the most electronegative atom. Electrons shared in homonuclear bonds are not considered. On the contrary, the bond valence of an atom, here always a positive number, integrates the bond valences exchanged with all bonded atoms (no matter their electronegativity). For instance, in molecular hydrogen peroxide, H_2O_2 , the oxidation state of O is -1 , but the molecular structure indicates one O–O bond (1.747 Å) and the total bond valence for O is 2. In realgar (molecular crystal As_4S_4), the oxidation state of As is $+2$ (and -2 for S), but the crystal structure indicates As–As pairs (2.566 Å) and thus the structural formula should be written as $[(\text{As}_2)^{4+}]_2(\text{S}^{2-})_4$. An additional electron is engaged in the As–As pair, with the result that the total bond valence of As is 3, corresponding to one of the two possible valence states of arsenic.

This approach is also valid for metallic elements. For instance, Hg frequently forms ion pairs corresponding to the $(\text{Hg}_2)^{2+}$ cation, in synthetics, as well as in minerals. According to the FIZ/NIST Inorganic Crystal Structure Database (ICSD) (2021), the mean Hg–Hg distance is close to 2.52 Å, which can be taken for the value of $R_{\text{Hg,Hg}}$. If one considers now crystalline mercury (trigonal; Mehl & Barret, 1930), each Hg atom has six closest neighbours at 3.005 Å, with a BV total of 1.62 vu, and six others at 3.470 Å, with a BV total of 0.46 vu. The bond valence of Hg metal is thus $1.62 + 0.46 = 2.08$ vu, in agreement of the valence state of 2 for Hg. This example shows that the bond valence model also applies to metallic bonding.

For any (A , B) atom bond, O'Keeffe & Brese (1991) have tabulated two parameters, *i.e.* the atom size parameter r and the 'electronegativity' parameter c , in such a way that $R_{A,B}$ is

the sum of r_A and r_B , minus an adjustment factor ' f ' function of r_A , r_B , c_A and c_B . 75 elements have been considered and this approach can be applied to derive bond lengths of various bond types, *i.e.* covalent, ionic, as well as metallic. Inversely, it can also be applied to calculate bond valences for any (A , B) combination among these 75 elements, including homonuclear metal–metal bonding. For homonuclear bonds, ' f ' = 0, and thus $R_{A,A} = 2r_A$.

2.2. Dative/coordination bonding

2.2.1. Bond valence and dative bond. Generally, the bond valence of an A atom in an ion, a molecule or a crystal represents also the number of 'effective' electron pairs (bonding minus antibonding pairs) implied in the bonding of this atom with surrounding B atoms. But, in fact, formula (1) is 'half right', as it implicitly signifies that $v_{AB} = v_{BA}$, *i.e.* that the A and B atoms have the same electronic contribution to the chemical bonds (electron pairs) between them. But in the peculiar case of dative bonding, such as in coordination compounds, the electron pair is provided by one of the two bound atoms, and not equally by both of them. As a consequence, the calculated bond valences of the atoms are different from the absolute values of their oxidation states (even if there is no homonuclear bond – see before), as revealed by bond valence calculations, according to the following examples.

2.2.2. Dative bonding in nitrogen compounds. NH_4^+ ion: In this cation, there are four identical N–H bonds (1.03 Å), close to the length of the three N–H bonds of the NH_3 molecule (1.07 Å). As $R_{N,H}$ is 1.03 Å, the BV is 1 vu for each H atom and 4 vu for N. But the oxidation number of N is -3 and the difference between the bond valence and oxidation number reveals one dative bond ($4 - 3 = 1$). In fact, formally, one of the four N–H bonds corresponds to a dative bond, where one $2p$ electron pair is provided by the N atom. The total electron contribution of N in the bonds is 5, while the total electron contribution of the H atoms is 3 (*i.e.* the mean contribution of each H atom is 0.75). Thus, in the NH_4^+ ion, one can say that the oxidation number of N is -3 , its bond valence is 4 and its valence state is 5.

NH_3AlCl_3 : In the classic example of NH_3AlCl_3 (Semenenko *et al.*, 1978), the N–Al bond, with $d = 1.921$ Å, corresponds to a bond valence fraction $v_{N,Al} = 0.83$ vu, quite close to the ideal integer 1. As a consequence, the N atom, bound also to three H atoms, and the Al atom, bound also to three Cl atoms, have the same bond valence of 4 vu. Here, the dative bond between N and Al is assumed by one electron pair furnished by the N atom. Thus, the valence state of N is 5, that of Al is 3, with oxidation numbers of -3 and 3, respectively. Considering the oxidation states, the formula is written as $N^{-3}H^{+1}_3Al^{+3}Cl^{-1}_3$. If one considers the bonding electrons e furnished by each atom, the formula ought to be written as $N^{5e}H^{1e}_3Al^{3e}Cl^{1e}_3$. If one considers the 50/50 partitioning of the electron pair between N and Al, the bond valence formula (BVF) will be $N^{5e-d}H^{1e}_3Al^{3e+d}Cl^{1e}_3$, or $N^{4v}H^{1v}_3Al^{4v}Cl^{1v}_3$ (v is the bond valence).

Formally, one electron (d) is subtracted from the donor atom N and added to the acceptor atom Al.

HNO_3 : In the molecule, the bond lengths are H–O = 0.964 Å (0.963 vu), N–(OH) = 1.406 Å (0.885 vu), and N–O = 1.211 (1.500 vu) and 1.199 Å (1.549 vu). Ideally, the N atom exchanges 1 vu with the O atom of the OH group and 1.5 vu with each of the two other O atoms, *i.e.* a total of 4 vu. As the oxidation number of N is +5, the difference between 5 and 4 reveals one dative bond. This dative electron pair of the N atom is shared between two O atoms. In the crystal structure of solid HNO_3 (Allan *et al.*, 2010; see Fig. S1 in the supporting information), one obtains similar results, with short N–O distances between 1.195 and 1.223 Å (1.57–1.45 vu), and longer N–O distances (with the OH group) between 1.350 and 1.360 Å (1.03–1.00 vu).

In HNO_3 , the oxidation number of N is +5, its bond valence 4 and its valence state 5. For two O atoms, the oxidation number is -2 , the bond valence 1.5 and the valence state 1, while for the third O atom, these values are -2 , 2 and 2, respectively. Here, the formula based on the bond valence electrons ought to be written as $H^{1v}N^{4v}O^{2v}O^{1.5v}_2$.

2.2.3. General aspects of dative bonding. An examination of these examples of dative bonding shows that:

- the bond valence approach is valuable for confirming dative bonding;
- it applies to classic examples of ions and molecules, but also to crystalline solids;
- atoms of elements implied in dative bonding have bond valences distinct from the absolute values of their oxidation states, as well as from their valence states;
- the electron pair given by an atom of an element (ligand) for a dative bond corresponds to a higher valence state relative to the ordinary valence state of this element (5 *versus* 3 for N or As);
- chemical formulae can be written according to three symbolisms, based on the example of HNO_3 :
 - (1) oxidation state: $H^+N^{+5}(O^{-2})_3$;
 - (2) valence state (number of bonding electrons e): $H^{1e}N^{5e}O^{2e}O^{1e}_2$;
 - (3) bond valence: $H^{1v}N^{4v}O^{2v}O^{1.5v}_2$.

2.3. Odd-electron bonding

The case of bonds in molecules with an uneven number of electrons (bond order $n + \frac{1}{2}$) was proposed by Pauling (1939). Various examples are known today for $n = 0$ or 1. One-electron bonds ($n = 0$) are known for homonuclear diatomic ions, for instance, the dihydrogen cation (H_2)⁺ and molecular ions (M_2)⁺ (M is an alkali metal). The calculated BV of H in (H_2)⁺, taking the bond length in the neutral molecule (0.741 Å) as the $R_{H,H}$ parameter, is 0.42 vu, close to the ideal value of 0.5, *i.e.* one electron shared by the two H atoms.

A classic example of a three-electron bond ($n = 1$) is NO_2 , where two N–O bonds (1.20 Å), based on $R_{N,O} = 1.35$ Å, each give BV = 1.50 vu. In benzene, the six C–C bonds (1.09 Å) each give 1.50 vu. The case of N_2O is more complex: based on N–N = 1.126 Å and N–O = 1.186 Å, one obtains BVs of 2.67

and 1.60 vu, respectively. Together with the three-electron N—O bond, N—N is a five-electron bond ($n = 2$).

Like the bond order in a molecule, the calculated bond valence of an atom with odd-electron bonding will be close to a half-integer value.

The following study is an application of the bond valence approach to copper chalcogenides with ‘*ch* excess’ (*ch* is a chalcogen, S or Se). The term ‘copper perchalcogenides’ (or ‘polychalcogenides’) refers to compounds where there are also *ch—ch* bonds (Zhang *et al.*, 1996). As indicated in the *Introduction*, in such compounds, only monovalent copper is considered, together with a possible valence deficit of the chalcogen (Folmer & Jellinek, 1980). Bond valence calculations give results that are apparently contradictory with respect to this former study, but such a discrepancy can be resolved taking into account the contribution of the valence electron in excess of the ligand to one-electron bonding.

3. Ligand excess electron bonding in copper chalcogenides

Based on crystal structures archived in the Inorganic Crystal Structure Database (ICSD), bond valence calculations have been performed on various mixed-valent synthetic copper chalcogenides, sometimes also known as minerals (*i.e.* covellite, CuS). First, the bond valences of each atom position (Cu and chalcogen *ch*) of a given structure were determined. Then the total of the bond valences in the formula unit was compared to the theoretical one, taking into account only monovalent copper and divalent *ch*.

3.1. Binary Cu chalcogenides

3.1.1. CuSe₂. There are two polymorphs for this composition, with Se₂ pairs around the Cu atom in an octahedral coordination:

- pyrite type, cubic (mineral: krut’aite; see Fig. S2 in the supporting information); BVs (vu): Cu—Se 1.37, Se—Se 0.95 and a formula total of 4.64;

- marcasite type, orthorhombic (mineral: petříčekite; Bindi *et al.*, 2016); BSs (vu): Cu—Se 1.40, Se—Se 1.00 and formula total 4.80.

Relative to the oxidation states Cu +1 and Se $-\frac{1}{2}$ proposed by Folmer & Jellinek (1980), Cu and Se appear overbonded, with bond valence excesses of 0.37 or 0.40 for Cu and 0.185 or 0.20 for Se in pyrite or marcasite types, respectively. As confirmed by the following examples, these bond valence excesses cannot be imputed to an overestimation of the bond valence parameters. Although a little low, the formula totals are compatible, with a theoretical total of 5 vu, taking into account valences of 1 and 2 for Cu and Se, respectively. In other words, the 4*p* ligand electron ‘in excess’ in the Se₂²⁻ dianion participates in the Cu—Se bonding, and is formally half-shared between these two atomic species, analogous as the N-atom electron pair in dative bonding.

Instead of considering these previous oxidation states, it appears more judicious to consider here, and in the following

examples, the distribution of bond valence electrons based on normal valences of 1 (Cu) and 2 (Se). As in classic dative bonding, the bond valence excess of copper (electron acceptor) in the formula is balanced by the bond valence deficit of Se (electron donor). The absolute sum of bond valence excess and deficit corresponds to the valence (electron) excess furnished by the valence-deficit element.

One can remark that in this compound the Cu—(Se₂) bonding is similar to a three-electron bond with a bond order of $\frac{3}{2}$ in molecular chemistry. But here the ‘third’ electron represents a quite distinct bond. And, contrary to the case of dative bonding, only a single electron, and not an electron pair, is furnished by the ligand Se atom, which presents here its lowest valence state. It can be defined formally as a ligand unpaired electron, giving delocalized one-electron bonding.

Considering oxidation states, the formula of CuSe₂ is ‘Cu⁺(Se₂)⁻’. Considering all valence electrons engaged in bonding (Cu—Se, as well Se—Se bonds), the formula becomes Cu^{1e}(Se^{2e})₂. The ideal BVF deduced from bond valence calculation is Cu^{1.5v}(Se^{1.75v})₂. This represents the 50/50 partitioning of the *d* ‘ligand excess electron’ (LEE) between Cu atoms (addition) and ligand atoms (subtraction).

3.1.2. Umangite, Cu₃Se₂. In the crystal structure of this selenide (Heyding & Murray, 1976), there are two Cu positions (in tetrahedral coordination), *i.e.* Cu1 and Cu2 (Fig. 1), with multiplicities of 1 and 2, respectively, while there is only one Se position (multiplicity 2). The Cu1 site (four equivalent Cu1—Se distances of 2.538 Å) is larger than the Cu2 site [Cu2—Se distances of 2.356, 2.464 (× 2) and 2.485 Å]. Bond valence calculation (BVC) gives 0.99 vu for Cu1, 1.29 vu for Cu2 and 1.78 vu for Se. For the unit formula, the bond valence formula total is 7.14 vu, against a theoretical value of 7 vu, with three Cu⁺ and two Se²⁻ atoms.

Thus, in umangite, Cu1 appears as a normal monovalent Cu atom, while Cu2 shows a bond valence excess, which is compensated by a valence deficit of Se. As in Cu(Se₂), there is one Se valence in excess per formula unit (*pfu*), which would correspond formally to the partitioning of an Se 4*p* unpaired electron between two Se and two Cu2 atoms (*i.e.* 0.25 electron for each atom). This result contradicts Okamoto *et al.* (1969), who stated that Cu1 and Cu2 were mono- and divalent,

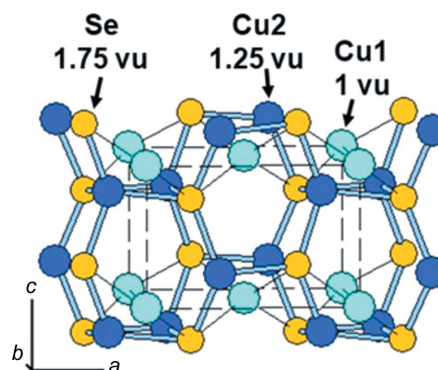


Figure 1
The crystal structure of umangite, Cu₃Se₂. Thick blue–grey lines are Cu₂–Se bonds.

respectively. According to the formalism proposed above, the ideal BVF would be: $\text{Cu}1^{1v}(\text{Cu}2^{1.25v})_2(\text{Se}^{1.75v})_2$.

From a crystal–chemical viewpoint, one can consider that the metallic state corresponds to electron delocalization in the space between atoms sharing the unpaired electron. While the whole structure ought to be implied for $\text{Cu}(\text{Se}_2)$, in umangite, the Cu1 atom ought to be excluded, as only Cu2 and Se are involved. This has been represented in Fig. 1 by emphasizing the Cu2–Se bonds, which also form a three-dimensional (3D) network, but as a subpart of the global network of the structure of umangite.

3.1.3. Covellite, Cu_3S_3 . Covellite, with the simplified formula CuS , together with the CuSe isotype (klockmannite), presents an original layered structure (Evans & Konner, 1976; Fjellvåg *et al.*, 1988). Every layer is built from three sheets of S atoms with hexagonal planar coordination (Fig. 2). In lateral sheets, every S2 atom is bound to an equivalent atom of the neighbouring layer to form an $(\text{S}_2)^{2-}$ pair. The S1 atoms of the central sheet form tetrahedra with those of the lateral sheets. These tetrahedra are filled by Cu2 atoms (multiplicity 2), while one of every two S triangles of the central sheet is occupied by Cu1 (multiplicity one). The structural formula of covellite is thus: $\text{Cu}_3\text{S}(\text{S}_2) = \text{Cu}1 (\text{Cu}2)_2 \text{S}1 [(\text{S}2)_2]$.

BVC gives $\text{Cu}1 = 1.23$, $\text{Cu}2 = 1.15$, $\text{S}1 = 1.79$ and $\text{S}2 = 2.06$ vu. Cu1 and Cu2 show a bond valence excess and S1 a deficit, while the bond valence of S2 would agree with a divalent state. But for the S2–S2 single bond, the bond valence is overestimated (1.19 vu). Adjusting it to a single-bond valence, the full bond valence of S2 becomes 1.87 vu. Thus, in covellite, the Cu1 bond valence excess (0.23 vu) is offset by the S1 valence deficit (0.21 vu), while the Cu2 excess (0.15 vu) is offset by the S2 deficit (0.12 vu). The ligand electron shared with Cu is the sum of Cu excess and S deficit, *i.e.* for one formula unit: $0.23 + 0.21 + [2 \times (0.15 + 0.12)] = 0.98$. Ideally, it corresponds to an S 3*p* LEE, taking into account Cu^{+1} and S^{-2} .

The proposed ideal BVF is $\text{Cu}1^{1.22v}(\text{Cu}2^{1.14v})_2(\text{S}2^{1.86v})_2\text{S}1^{1.78v}$.

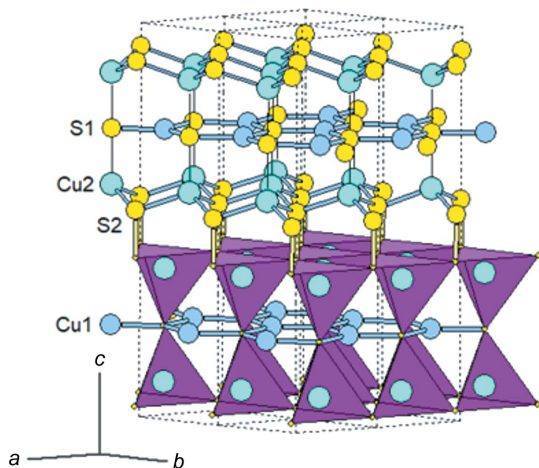


Figure 2
The crystal structure of covellite, $\text{Cu}_3\text{S}(\text{S}_2)$.

Although all the Cu and S atoms are implied in the distribution (*i.e.* delocalization here) of the unpaired electron, the S–S bonds form a wall separating adjacent Cu_3S_3 layers. The LEE distribution has a two-dimensional (2D) character.

3.2. Ternary copper chalcogenides

3.2.1. NaCu_4S_4 . This structure with trigonal symmetry (see Fig. S3 in the supporting information; Zhang *et al.*, 1996) is derived from that of covellite through two geometric transformations: (i) removal of the central CuS layer and (ii) intercalation of one of every two layers of octahedrally coordinated Na atoms between two S-atom layers after breaking S_2 pairs. Along *c*, one obtains the sequence ... Na–(S1–Cu1)–[Cu2–(S2–S2)–Cu2]–(Cu1–S1)–Na ..., where the two Cu positions present a tetrahedral coordination.

BVC (vu) gives $\text{Cu}1 = 1.07$, $\text{Cu}2 = 1.11$, $\text{Na} = 1.05$, $\text{S}1 = 1.87$ and $\text{S}2 = 1.78$, with a total of 12.69 (ideal: 13, with an S 3*p* LEE).

The sulfur valence deficit (total of 0.70 vu for four S atoms), which is most pronounced for S2, is partly counterbalanced by a copper bond valence excess (0.36 vu), the most significant being for Cu2. One must point out here that only a slight increase of the $R_{\text{Cu,S}}$ bond valence parameter from 1.86 to 1.87 is sufficient to fit the equilibrium between S deficit and Cu excess. This would lead to the proposed ideal BVF $\text{Na}^{1v}(\text{Cu}1^{1.10v})_2(\text{Cu}2^{1.15v})_2(\text{S}1^{1.90v})_2(\text{S}2^{1.85v})_2$, also with a single LEE *pfu*.

3.2.2. TlCu_2Se_2 . This crystal structure (see Fig. S4 in the supporting information; Brun *et al.*, 1979) is composed of Cu_2Se_2 layers, equivalent to the (100) F_2Ca_2 layers of the fluorite type, with the intercalation of Tl atoms. This structure with quadratic symmetry is the origin of the higher homologues MeCu_4ch_3 . BVC (vu) gives $\text{Cu} = 1.17$, $\text{Tl} = 1.38$ and $\text{Se} = 1.86$, with a total of 7.44 (ideal: 7, with an Se 4*p* LEE *pfu*).

The too-high valence value of Tl seems to be due to an overestimation of the bond valence parameter of the (Tl, Se) couple, as pointed in out Tl sulfide minerals (Biagioni *et al.*, 2014). According to this study, a decrease of the (Tl, Se) parameter of about 0.1 Å (2.60 against 2.70 Å) would give $\text{Cu} = 1.17$, $\text{Tl} = 1.05$ and $\text{Se} = 1.70$ vu, with a total of 6.77 vu, in better agreement with the ideal total.

The proposed ideal BVF is $\text{Tl}^{1v}(\text{Cu}^{1.25v})_2(\text{Se}^{1.75v})_2$ (similar to that of umangite).

3.2.3. NaCu_4Se_3 and KCu_4Se_3 . These parent compounds have distinct layered structures. NaCu_4Se_3 is trigonal (see Fig. S5 in the supporting information; Sturza *et al.*, 2016), while KCu_4Se_3 is tetragonal (see Fig. S6; Klepp *et al.*, 1980). There is a double layer of tetrahedral Cu atoms connected by a central Se plane (formula Cu_4Se_3), with intercalation of Na or K; Na has an octahedral coordination, like the central Se atom, while the bigger K atom has a cubic coordination (also like the central Se atom), which induces the symmetry change. Some vacancies for the Cu1 and Cu2 positions for the Na compound give the final formula $\text{NaCu}_{3.82}\text{Se}_3$. BVC (vu) gives:

– for $\text{NaCu}_{3.82}\text{Se}_3$: Na = 1.22, Cu1 = 1.18 ($\times 2$; s.o.f. = 0.99), Cu2 = 1.16 ($\times 2$; s.o.f. = 0.92), Se1 = 1.96 ($\times 2$) and Se2 = 1.75, with a total of 11.36 (ideal: 11, with a single Se 4p LEE);
 – for KCu_4Se_3 : K = 1.15, Cu1 = 1.15 ($\times 4$), Se1 = 1.91, Se2 = 1.92 ($\times 2$), with a total of 11.49.

The bond valence of the alkali is significantly overestimated (as for Tl; see above).

The model of one-electron bonding would give the BVFs $\text{Na}^{1v}\text{Cu}^{1.154v}_{3.82}\text{Se}^{1.80v}_3$ and $\text{K}^{1v}\text{Cu}^{1.125v}_4\text{Se}^{1.83v}_3$. For stoichiometric compositions, with a single Se 4p LEE *pfu*, the ideal BVF would be $(\text{Na,K})^{1v}\text{Cu}^{1.125v}_4\text{Se}^{1.833v}_3$.

3.3. Complex oxychalcogenides

3.3.1. $\text{YBi}_2\text{O}_4\text{Cu}_2\text{Se}_2$. This quinary compound presents a layered structure (see Fig. S7 in the supporting information; Evans *et al.*, 2002), with a Cu_2Se_2 sublayer [*anti*- CaF_2 (100) slab] alternating with a YO_4 sublayer, with Bi as a junction atom bound to O and Se atoms. BVC (vu) gives Bi = 3.31, Y = 2.99, O = 2.11, Cu = 1.21 and Se = 1.79. Bi and Y agree with a +3 oxidation state and O with -2 , but there is a significant bond valence excess for copper, identical here with the valence deficit of selenium.

Previously, this compound was presented formally as $[\text{YBi}_2\text{O}_4]^{+2}[\text{Cu}_2\text{Se}_2]^{-2}$ (Xiao *et al.*, 2016), but the oxide part must correspond to $[\text{YBi}_2\text{O}_4]^+$ and thus the selenide part to $[\text{Cu}_2\text{Se}_2]^-$. Ideally, with a single Se 4p LEE *pfu*, the ideal BVF would be $\text{Y}^{3v}\text{Bi}^{3v}\text{O}^{2v}_4\text{Cu}^{1.25v}_2\text{Se}^{1.75v}_2$.

3.3.2. $(\text{Bi}_{1-x}\text{M}_{2+x})\text{CuOSe}$ ($M = \text{Pb, Sr}$). These compounds are Pb- or Sr-doped derivatives of stoichiometric BiCuOSe, which presents a tetragonal composite layered structure (see Fig. S8 in the supporting information), where one (100) fluorite BiO layer and one (100) antiferroite CuSe layer (Kusainova *et al.*, 1994) alternate along *c*. The solid solution $(\text{Bi}_{1-x}\text{Pb}_x)\text{CuOSe}$ has been synthesized up to $x = 0.2$ (Luu & Vaqueiro, 2013). BVC gives:

– for BiCuOSe: Bi = 3.19, Cu = 0.99, O = 2.09 and Se = 2.10 vu, in agreement with the formula $\text{Bi}^{+3}\text{Cu}^+\text{O}^{-2}\text{Se}^{2-}$;
 – for $(\text{Bi}_{0.8}\text{Pb}_{0.2})\text{CuOSe}$: (Bi+Pb) = 2.93, Cu = 1.12, O = 2.12 and Se = 1.93 vu.

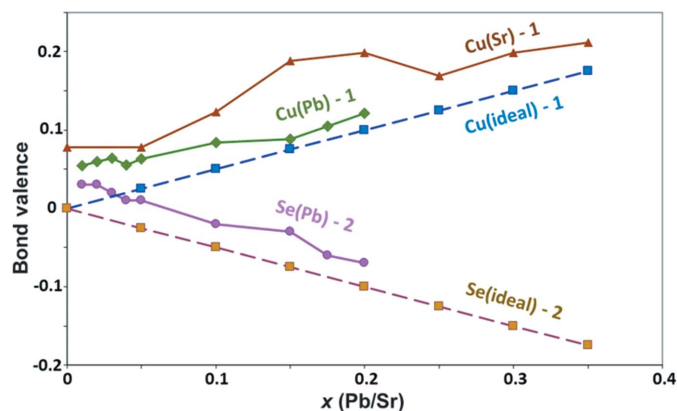


Figure 3 Variation with x of the bond valences of Cu and Se in $(\text{Bi}_{1-x}\text{Pb}_x)\text{CuOSe}$.

Relative to the Pb-free compound, the increase of the bond valence of copper and the decrease of that of selenium agree with the model of LEE bonding, with an ideal BVF of $[(\text{Bi}^{3v})_{0.8}(\text{Pb}^{2v})_{0.2}]^{2.8v}\text{Cu}^{1.10v}\text{O}^{2v}\text{Se}^{1.90v}$. With 0.2 Pb^{2+} substituting 0.2 Bi^{3+} there is 0.2 Se valence electron in excess, which is equally shared on the Cu and Se bond valences, according to LEE partitioning.

In the Sr-doped derivative (up to $x = 0.35$; Barreteau *et al.*, 2012), crystal structures are not detailed, but the variation of the Cu–Se distance is given, allowing the calculation of Cu bond valence. Fig. 3 plots the variation with x of this bond valence, as well as the Cu and Se bond valences of the Pb-doped derivative. The regular increase of the Cu bond valence with x agrees with the slope of the theoretical bond valence, as well as consequently the decrease of Se bond valence with the symmetric straight line.

From the isotypic sulfide BiCuOS (Kusainova *et al.*, 1994; Hiramatsu *et al.*, 2008), a Cu-poor derivative, $\text{BiCu}_{1-y}\text{OS}$ ($y \sim 0.1$), has been obtained, here with an anionic electron excess due to copper deficit. The compound HgCuOSe (Kim *et al.*, 2011), structurally similar to BiCuOSe, would represent the ideal case with one Se LEE *pfu*, but its exact crystal structure is not known.

3.4. Interpretation

Taking into account the semi-empirical character of the bond valence approach, calculations on these mixed-valent copper chalcogenides indicate that the ‘bond valence excess’ (over 1) of copper is significantly correlated to a symmetrical ‘bond valence deficit’ (below 2) of the chalcogen, according to the model of LEE bonding. In all stoichiometric compounds, this would agree with a single valence electron of the ligand in excess *pfu*, shared with copper through one-electron bonding. The total Cu bond valence excess (0.5 vu) is shared by up to

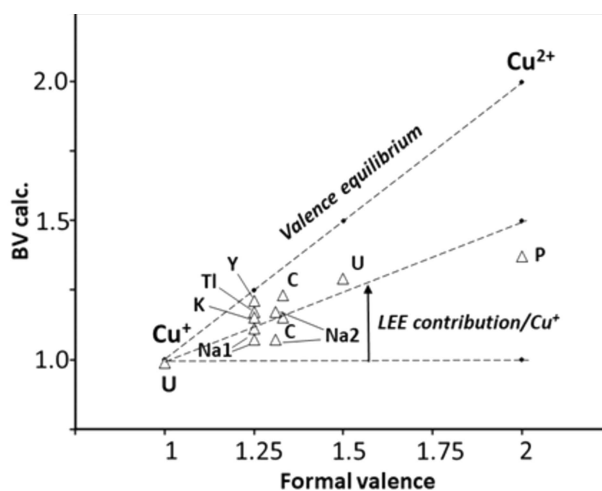


Figure 4 Copper bond valence as a function of its formal valence according to valence equilibrium. C = covellite, K = KCu_4Se_3 , Na1 = NaCu_4S_4 , Na2 = $\text{NaCu}_{3.82}\text{Se}_3$, P = petřicekite, Tl = TlCu_2Se_2 , U = umangite and Y = $\text{YBi}_2\text{O}_4\text{Cu}_2\text{Se}_2$.

four atoms in the formula unit (Fig. 4). According to this model, copper is always monovalent.

Covellite is the best example to illustrate the evolution of ideas concerning the valences of copper and sulfur. Numerous interpretations were successively proposed (for each formula, based on three CuS, the total number Σe of the bond valence electrons is given, taking into account the electron pair implied in the S–S bond of the S_2^{2-} group):

(a) primary, before the resolution of the crystal structure: $Cu^{+2}S^{-2}$ ($\Sigma e = 12$);

(b) $(Cu^+)_3(S_2^{-2})(S^-)$ ($\Sigma e = 8$) (Fjellvåg *et al.*, 1988);

(c) $(Cu^+)_3(S_2^{-2})(S^{-2})$ ($\Sigma e = 8$) (Liang & Whangbo, 1993);

(d) based on copper nuclear quadrupole resonance (NQR), the dominance of monovalent Cu, with the mean value $Cu^{+1.3}$ (Gainov *et al.*, 2009);

(e) $(Cu^{+4/3})_3(S_2^{-2})(S^{-2})$ ($\Sigma e = 10$) (Mazin, 2012);

(f) $[(Cu_{Td})_2]^{+3}(Cu_{Tr}^+)(S_2^{-2})(S^{-2})$, where $Cu_{Td} = Cu2$ (in tetrahedral coordination) and $Cu_{Tr} = Cu1$ (in trigonal coordination) ($\Sigma e = 10$) (Kumar *et al.*, 2013);

(g) Morales-García *et al.* (2014), based on DFT and DFT+U (DFT is density functional theory and U is the Coulomb interaction potential) calculations, agree with this last formulation;

(h) based on DFT calculations (Conejeros *et al.*, 2014), two distinct but equivalent formulations have been given: $[(Cu^+)_2(S_2^{-2})(Cu^+)(S^{-2})] \cdot 1e$ ($e = \text{hole}$), (2), and $[(Cu^{+(1+\delta)})_2(S_2^{-2(1-\delta)})(Cu^{+(1+\delta)})(S^{-(2-\delta)})]$, (3), with $\delta = \frac{1}{6}$. Based on (2), $\Sigma e = 9$.

The proposed model of LEE bonding gives the same Σe as study (h). Bond valence calculations exclude the formulae of (b) (S1 with oxidation state -1) and (c) (S2 of the S_2 pair also with valence state -1). Other formulae, with $\Sigma e = 10$, imply a true mixed-valence state of copper (>1). Relative to (h), the model of LEE specifies the electron-donor effect of S atoms relative to Cu atoms, as Cu1 seems to be a higher acceptor of S $3p$ excess electron (0.22 vu in excess) than Cu2 (0.14 vu in excess) [while in (f), only Cu2 (Cu_{Td}) is considered as an acceptor, with an oxidation state of 1.5].

Formula (2) of Conejeros *et al.* (2014) corresponds to the ligand–hole description, while the antisymmetric formula (3) is equivalent to the bond valence description. The mixed-valence, or more exactly, the bond valence excess of copper is a formal artefact due to delocalized ligand one-electron bonding, correlated to a formal valence deficit of the ligand. Such a model of bonding is thus in accordance with the fundamental study of Folmer & Jellinek (1980), who found by XPS measurements exclusively monovalent copper in various copper sulfides, among which were CuS, CuSe and Cu_3Se_2 , while an electron deficit related to the chalcogen was explained by holes in the valence band of the chalcogen. Cu^+ was also proved in CuS_2 (Schmid-Beurmann & Lottermoser, 1993).

According to band–structure calculations (Morales-García *et al.*, 2014; Conejeros *et al.*, 2014), the mixing of S $3p$ electrons with Cu $3d$ levels corresponds to the formation of holes at the top of the valence band of the chalcogen in the band structure. More generally, band–structure calculations indicate a strong

mixing of the Cu $3d$ and ch p electronic states at the Fermi level, as indicated for $NaCu_4Se_3$ (Sturza *et al.*, 2016), and also for (Tl, Cu) chalcogenides (Karlsson *et al.*, 1990).

Vajenine & Hoffmann (1996) have deepened the nature of electronic structure in compounds of the general formula MCu_2nX_{n+1} containing copper–sulfur layers. Density-of-state (DOS) calculations on the model $(Cu_2S_2)^-$ indicate that holes are hosted by two bands, made quite exclusively by Cu d_{xz} and d_{yz} , and S p_x and p_y , and equally distributed among Cu and S atoms. This study specifies that ‘the presence of holes by itself creates a substantial driving force toward compression in the xy plane’, which is a logical consequence of the shortening of the Cu– ch bonds due to one-electron-excess bonding. On the other hand, these authors, discussing the location of holes {‘entirely on copper [e.g. $(Cu^{+1.5})_2(S^{-2})_2$], entirely on sulfur [e.g. $(Cu^+)_2(S^{-1.5})_2$] or partially on both’}, citing previous XPS experiments indicating a +1 oxidation state of copper, accept their conclusion that holes must be exclusively in S $3p$ levels! These authors consider that this contradiction is due to their choice of atomic parameters in their calculations.

Contrary to the classic example of dative bonding presented in §2, where such a bond corresponds to the donation of an electron pair by the ligand in addition to its ordinary (lowest) valence state, in stoichiometric chalcogenides with a copper bond valence excess there is donation of a single ligand electron through one-electron bonding. This ligand unpaired electron is part of electrons corresponding to the ordinary valence state 2 of the ligand. While the band–theory studies rarely specify which bonds are affected by hole formation, the valence–bond approach indicates that this delocalization is generally driven by a subpart of the Cu– ch bonding (*i.e.* a Cu– ch subnetwork).

At the crystal structure scale, Cu– ch bonds sharing the unpaired LEE are organized in various ways:

– 3D network (rare), implying the whole structure (pyrite-type derivatives) or a subpart (umangite: one Cu atom position excluded);

– 2D network (the most frequent), implying essentially hexagonal or tetragonal sublayers of tetrahedral Cu;

– 1D network (rare): $Na_3Cu_4S_4$ (Burschka, 1979; bond valence calculations not significant due to a too-low bond valence total).

Thus, the bond valence analysis permits a visualization of the distribution of the LEE among the Cu– L bonds of the studied crystal structures.

4. Electric conduction, superconductivity and electronic structure

In agreement with the prediction of Robin & Day (1968), all copper chalcogenides with formal copper valence excess (over one) present poor metallic p -type conductivity due to hole mobility (*i.e.* here delocalization of excess chalcogen p -electrons *via* LEE bonding).

Resistivity measurements indicated the metallic character of Cu_3Se_2 , CuS, CuSe, $CuSe_2$ and $Cu_{1.8}Se$. Cu_3Se_2 and CuS have similar conductivities, lower than those of $Cu_{1.8}Se$, CuSe

and CuSe₂ (while Cu₂Se is a bad metal) (Zhang *et al.*, 1996). Superconductivity has been revealed in CuS (Meissner, 1929; Di Benedetto *et al.*, 2006), CuS₂ (Munson *et al.*, 1967; Hull & Hulliger, 1968) and CuSe₂ (Hull & Hulliger, 1968).

Metallic character has also been proved in ternary chalcogenides: MeCu₄ch₃ (2D type; Ghosh *et al.*, 1983), NaCu₄S₄ (Zhang *et al.*, 1996), Na₃Cu₄S₄ (1D type; Ghosh *et al.*, 1983; Peplinski *et al.*, 1982), TiCu₂Se₂ and KCu₄S₃ (Folmer & Jellinek, 1980).

This is also the case for various oxyselenides: Bi₂YO₄Cu₂Se₂ (Xiao *et al.*, 2016), (Bi_{0.8}Pb_{0.2})CuOSe (Luu & Vaqueiro, 2013) and (Bi_{1-x}Sr_x)CuOSe (Barreateau *et al.*, 2012), BiCu_{1-y}OSe (*y* ~ 0.1) (Ubalini *et al.*, 2010; *T*_c = 5.8 K), HgCuOSe (Kim *et al.*, 2011) and its Fe-doped derivative HgCu_{0.95}Fe_{0.05}OSe (Kim *et al.*, 2012).

The 1D, 2D or 3D character of the (sub-)network of Cu—*ch* bonds implying excess ligand electron would generally determine the same dimensionality, or dissymmetry, for the electric conductivity. Covellite presents an original feature, with two types of 2D subnetworks, one corresponding to the central (Cu1, S1) one-atom-thick plane, sandwiched between two (Cu2, S2) two-atom-thick planes. This duality agrees with the thorough calculation of the electronic structure of covellite (Conejeros *et al.*, 2014). Such a peculiarity is also encountered in NaCu₄S₄, with one central [Cu2—(S2—S2)—Cu2] four-atom-thick plane sandwiched between two (S1—Cu1) two-atom-thick planes.

Based on the simplest example of the band structure of pyrite-type CuS₂ (Bullett, 1982; Temmerman *et al.*, 1993; Jobic *et al.*, 1992), the delocalized S 3*p* unpaired electron would correspond to the half-filled band at the Fermi level, as indicated by the strong mixing of S 3*p* and Cu 3*d* contributions.

Remark: several authors (Okamoto *et al.*, 1969; Ghosh *et al.*, 1983), based on the study of Robin & Day (1968), consider that short Cu—Cu distances in these structures rank them in the 3B class of mixed-valence compounds, and thus ought to present a metallic conductivity. Based on our bond valence calculations, such Cu—Cu distances appear outside the limit specific to justify a direct chemical bond. However, in band structures, these short Cu—Cu distances will involve a band closely above the half-filled band at the Fermi level.

5. Discussion

The re-examination through the bond valence model of the crystal structures of various copper chalcogenides and oxychalcogenides reveals a bond valence excess on copper, correlated to a bond valence deficit on the chalcogen (LEE model). In stoichiometric compounds, there is a single electron in excess *pfu* on the ligand relative to the valence equilibrium, which is formally equally shared between copper and the ligand. This LEE bonding would correspond to a Cu–ligand bonding of the one-electron type, as there is only electron contribution from the ligand (here the donor of the electron in excess). Table 1 presents the results of the bond valence analysis, comparing the structural formulae with the bond valence formulae.

Table 1

Structural and bond valence formulae of studied compounds.

Notes: *M* is measured, *I* is ideal and *D* is the dimensionality of LEE bonding.

Structural formula	Bond valence formula	<i>M/I</i>	<i>D</i>
Cu(Se ₂)	Cu ^{1.5v} (Se ^{1.75v}) ₂	<i>I</i>	3
Cu ₃ Se ₂ /umangite	Cu ^{1.1v} (Cu ^{2.25v}) ₂ (Se ^{1.75v}) ₂	<i>I</i>	3
Cu ₃ (S ₂)S/covellite	Cu ^{1.22v} (Cu ^{2.14v}) ₂ (S ^{2.86v}) ₂ S ^{1.78v}	<i>M</i>	2
NaCu ₄ (S ₂)S ₂	Na ^{1v} (Cu ^{1.10v}) ₂ (Cu ^{2.15v}) ₂ (S ^{2.85v}) ₂ (S ^{1.90v}) ₂	<i>I</i>	2
TiCu ₂ Se ₂	Ti ^{1v} (Cu ^{1.25v}) ₂ (Se ^{1.75v}) ₂	<i>I</i>	2
NaCu ₄ Se ₃	Na ^{1v} (Cu ^{1.154v}) _{3.82} (Se ^{1.80v}) ₃	<i>M</i>	2
KCu ₄ Se ₃	K ^{1v} (Cu ^{1.125v}) ₄ (Se ^{1.83v}) ₃	<i>M</i>	2
(Na,K)Cu ₄ Se ₃	(Na,K) ^{1v} (Cu ^{1.125v}) ₄ (Se ^{1.833v}) ₃	<i>I</i>	2
YBi ₂ O ₄ Cu ₂ Se ₂	Y ^{3v} Bi ^{3v} ₂ O ^{2v} ₄ (Cu ^{1.25v}) ₂ (Se ^{1.75v}) ₂	<i>I</i>	2
(Bi _{0.8} Pb _{0.2})CuOSe	[(Bi ^{3v}) _{0.8} (Pb ^{2v}) _{0.2}] ^{2.8v} Cu ^{1.10v} O ^{2v} Se ^{1.90v}	<i>I</i>	2

In copper chalcogenides with heteronuclear metallic bonding, one electron *pfu* is furnished by one or several ligand positions, and shared by one or several Cu positions. It can be considered a special case of multicentre bonding ('co-operative electron delocalization' or CED).

We should now stress that the bond valence approach, simple as it is, could nevertheless be a guide in the exploration of materials, especially in the search for new superconductors. We already mentioned the clue of a possible unconventional superconductivity in covellite (Gainov *et al.*, 2009). It is appealing to submit this material on state-of-the-art techniques, both experimentally and theoretically. Good single crystals can be found in nature or growth synthetically (Gonçalves *et al.*, 2008). Covellite is a 2D material with a very good cleavage parallel to the basal plane and atomic resolution have been achieved by Scanning Tunnelling Microscopy/Spectroscopy (STM/STS) at room temperature (Rosso & Hochella, 1999). Due to the low *T*_c, STS experiments could be conducted using the same methodology as Renner *et al.* (1998) on cuprates: a sweep in temperature well above and well below *T*_c in order to check for a pseudo-gap above *T*_c, as suggested by NMR experiments (Gainov *et al.*, 2009). These experiments will also check for the *f-wave* symmetry claimed by Mazin (2012).

On the theoretical side of the problem, the limitations of DFT with strong electronic correlations are well known and this is the reason why Morales-García *et al.* (2014) have conducted DFT+U calculations. Nevertheless, these calculations omit the dynamical aspects of electron correlations. An important breakthrough in the problem of strong correlations has been made by Dynamical Mean Field Theory (DMFT) (Georges *et al.*, 1996; Georges, 2004). DMFT is a quantum extension of the classical concept of Mean Field. The Hubbard model is mapped in the Anderson model, corresponding to an impurity into a metallic bath, and a hybridization parameter between the impurity and the metallic bath. In order to capture the Mott metal–insulator transition, the hybridization parameters have to be self-consistency determined in an energy-dependent manner, hence the word 'dynamical'. In this theory, both the high-energy features (the Hubbard bands corresponding to broadened atomic transitions) and the low-energy features (a renormalized Fermi liquid) are treated on

an equal basis. This could be combined with DFT calculations (Georges, 2004) or carried out on a cluster of several sites (Kotliar *et al.*, 2001). In order to take a further step in the assessment of electron correlations, it would also be relevant to conduct similar DFT+DMFT calculations on copper chalcogenide superconductors. In a nutshell, both the suggested experimental and the theoretical work would clarify if these materials are ‘low T_c among high T_c superconductors’.

6. Conclusion

This comparative bond valence analysis of the crystal structures of copper chalcogenides indicates that a copper bond valence excess generally corresponds to monovalent copper, with one ligand electron in excess *pfu* shared with copper. This electron, classically described as a ligand hole, may be provided by a subpart of the ligand atoms, and shared by a subpart of the Cu atoms, in contrast with classic types of chemical bonding (ionic, covalent or metallic), where each atom contributes to the bonding through an integer number of electrons. It thus corresponds to a special type of multicentre bonding (‘one-electron co-operative bonding’), superimposed on ordinary bonding. The metallic state, always present, is constrained by this type of collective ligand–Cu combination, which generally constitutes a subnetwork within the structure. The most original example is that of covellite, where the excess electron is shared between two adjacent Cu/S sublayers.

Bond valence analysis is a useful and very simple prospective approach, prior to in-depth physical studies. In a complementary study (Moëlo *et al.*, in progress), the same bond valence approach is being applied to copper oxides with a high formal valence of copper (*i.e.* >2), sometimes with metallic conductivity, in order to examine the similarities between these two groups of copper compounds.

References

- Allan, D. R., Marshall, W. G., Francis, D. J., Oswald, I. D. H., Pulham, C. R. & Spanswick, C. (2010). *Dalton Trans.* **39**, 3736–3743.
- Barreteau, C., Bérardan, D., Amzallag, E., Zhao, L. D. & Dragoe, N. (2012). *Chem. Mater.* **24**, 3168–3178.
- Biagioni, C., Bonaccorsi, E., Moëlo, Y., Orlandi, P., Bindi, L., D’Orazio, M. & Vezzoni, S. (2014). *Miner. Mag.* **78**, 101–117.
- Bindi, L., Förster, H.-J., Grundmann, G., Keutsch, F. N. & Stanley, C. J. (2016). *Minerals*, **6**, 33.
- Brese, N. E. & O’Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (1976). *J. Chem. Educ.* **53**, 100–102.
- Brown, I. D. (2016). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. IUCr Monographs on Crystallography 27. Oxford University Press.
- Brun, G., Gardes, B., Tedenac, J. C., Raymond, A. & Maurin, M. (1979). *Mater. Res. Bull.* **14**, 743–749.
- Bullett, D. W. (1982). *J. Phys. C: Solid State Phys.* **15**, 6163–6174.
- Burschka, C. (1979). *Z. Naturforsch. Teil B Anorg. Chem. Org. Chem.* **34**, 396–397.
- Conejeros, S., Moreira, I. P. R., Alemany, P. & Canadell, E. (2014). *Inorg. Chem.* **53**, 12402–12406.
- Di Benedetto, F., Borgheresi, M., Caneschi, A., Chastanet, G., Cipriani, C., Gatteschi, D., Pratesi, G., Romanelli, M. & Sessoli, R. (2006). *Eur. J. Mineral.* **18**, 283–287.
- Evans, H. T. & Konnert, J. A. (1976). *Am. Mineral.* **61**, 996–1000.
- Evans, J. S. O., Brogden, E. R., Thompson, A. L. & Cordiner, R. L. (2002). *Chem. Commun.* pp. 912–913.
- FIZ/NIST Inorganic Crystal Structure Database (ICSD) (2021). FIZ Karlsruhe (Germany) & National Institute of Standards and Technology (U. S. Department of Commerce).
- Fjellvåg, H., Grønvold, F., Stølen, S., Andresen, A. F., Müller-Käfer, R. & Simon, A. (1988). *Z. Kristallogr.* **184**, 111–121.
- Folmer, J. C. W. & Jelinek, J. (1980). *J. Less-Common Met.* **76**, 153–162.
- Gagné, O. C. & Hawthorne, F. C. (2015). *Acta Cryst.* **B71**, 562–578.
- Gainov, R. R., Dooglav, A. V., Pen’kov, I. N., Mukhamedshin, I. R., Mozgova, N. N., Evlampiev, A. V. & Bryzgalov, I. A. (2009). *Phys. Rev. B*, **79**, 075115.
- Georges, A. (2004). *AIP Conf. Proc.* pp. 3–74.
- Georges, A., Kotliar, G., Krauth, W. & Rozenberg, M. J. (1996). *Rev. Mod. Phys.* **68**, 13–125.
- Ghosh, B. P., Chaudhury, M. & Nag, K. (1983). *J. Solid State Chem.* **47**, 307–313.
- Gonçalves, A. P., Lopes, E. B., Casaca, A., Dias, M. & Almeida, M. (2008). *J. Cryst. Growth*, **310**, 2742–2745.
- Heyding, R. D. & Murray, R. M. (1976). *Can. J. Chem.* **54**, 841–848.
- Hiramatsu, H., Yanagi, H., Kamiya, T., Ueda, K., Hirano, M. & Hosono, H. (2008). *Chem. Mater.* **20**, 326–334.
- Hull, G. W. Jr & Hulliger, F. (1968). *Nature*, **220**, 257–258.
- Jobic, S., Brec, R. & Rouxel, J. (1992). *J. Alloys Compd.* **178**, 2536283.
- Karlsson, L., Keane, M. P. & Berger, R. (1990). *J. Less-Common Met.* **166**, 353–365.
- Kim, G. C., Cheon, M., Park, I. S., Ahmad, D. & Kim, Y. C. (2011). ArXiv: 1105.5868v1. <https://arxiv.org/pdf/1105.5868.pdf>.
- Kim, G. C., Cheon, M., Park, I. S. & Kim, Y. C. (2012). *J. Korean Phys. Soc.* **61**, 1425–1429.
- Klepp, K., Boller, H. & Vollenkle, H. (1980). *Monatsh. Chem.* **111**, 727–733.
- Kotliar, G., Savrasov, S. Y., Pálsson, G. & Biroli, G. (2001). *Phys. Rev. Lett.* **87**, 186401.
- Kumar, P., Nagarajan, R. & Sarangi, R. (2013). *J. Mater. Chem. C*, **1**, 2448–2454.
- Kusainova, A. M., Berdonosov, P. S., Akselrud, L. G., Kholodkovskaya, L. N., Dolgikh, V. A. & Popovkin, B. A. (1994). *J. Solid State Chem.* **112**, 189–191.
- Liang, W. & Whangbo, M.-H. (1993). *Solid State Commun.* **85**, 405–408.
- Luu, S. D. N. & Vaqueiro, P. (2013). *J. Mater. Chem. A*, **1**, 12270–12275.
- Mazin, I. I. (2012). *Phys. Rev. B*, **85**, 115133.
- Mehl, R. F. & Barret, C. S. (1930). *Trans. AIME*, **89**, 575–588.
- Meissner, W. Z. (1929). *Z. Phys.* **58**, 570–572.
- Morales-García, A., Soares, A. L., Dos Santos, E. C., de Abreu, H. A. & Duarte, H. A. (2014). *J. Phys. Chem. A*, **118**, 5823–5831.
- Munson, R. A., DeSorbo, W. & Kouvel, J. S. (1967). *J. Chem. Phys.* **47**, 1769–1770.
- Okamoto, K., Kawai, S. & Kiriyama, R. (1969). *Jpn J. Appl. Phys.* **8**, 718–724.
- O’Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.
- O’Keeffe, M. & Brese, N. E. (1992). *Acta Cryst.* **B48**, 152–154.
- Pauling, L. (1939). In *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*. Ithaca: Cornell University Press.
- Pearce, C. I., Patrick, R. A. D., Vaughan, D. J., Henderson, C. M. B. & van der Laan, G. (2006). *Geochim. Cosmochim. Acta*, **70**, 4635–4642.
- Peplinski, Z., Brown, D. B., Watt, T., Hatfield, W. E. & Day, P. (1982). *Inorg. Chem.* **21**, 1752–1755.
- Renner, C., Revaz, B., Genoud, J.-Y., Kadowaki, K. & Fischer, Ø. (1998). *Phys. Rev. Lett.* **80**, 149–152.
- Robin, M. B. & Day, P. (1968). *Adv. Inorg. Chem. Radiochem.* **10**, 248–422.
- Rosso, K. M. & Hochella, M. F. Jr (1999). *Surf. Sci.* **423**, 364–374.

- Schmid-Beurmann, P. & Lottermoser, W. (1993). *Phys. Chem. Miner.* **19**, 571–577.
- Semenenko, K. N., Lobrovskii, E. B., Polyakova, V. B., Korobov, I. I. & Kravchenko, O. V. (1978). *Koord. Khim.* **4**, 1649–1652.
- Steinfink, H. (1980). In *Solid State Chemistry: A Contemporary Overview*, edited by S. L. Holt, J. B. Milstein & M. Robbins, Vol. 186, pp. 409–420.
- Sturza, M., Bugaris, D. E., Malliaks, C. D., Han, F., Chung, D. Y. & Kanatzidis, M. G. (2016). *Inorg. Chem.* **55**, 4484–4490.
- Temmerman, W. M., Durham, P. J. & Vaughan, D. J. (1993). *Phys. Chem. Miner.* **20**, 248–254.
- Ubal dini, A., Giannini, E., Senatore, C. & van der Marel, D. (2010). *Physica C*, **470**, S356–S357.
- Vajenine, G. V. & Hoffmann, R. (1996). *Inorg. Chem.* **35**, 451–457.
- Xiao, Y., Pei, Y., Chang, C., Zhang, X., Tan, X., Ye, X., Gong, S., Lin, Y., He, J. & Zhao, L.-D. (2016). *J. Solid State Chem.* **239**, 178–183.
- Zhang, X., Kanatzidis, M. G., Hogan, T. & Kannewurf, C. R. (1996). *J. Am. Chem. Soc.* **118**, 693–694.