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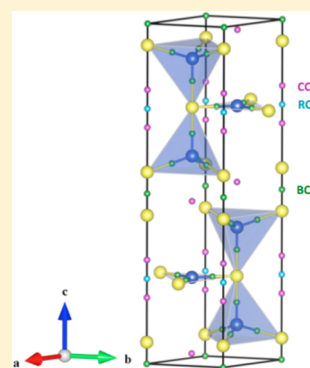
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S Supporting Information

ABSTRACT: Covellite (CuS) is an important mineral sulfide that can be used in many technological applications. It has a simple formula but a complex structure consisting of alternating layers of planar CuS₃ triangles and CuS₄ tetrahedrons with S–S bonds. Accurate first-principles calculations are performed for covellite structure (CuS), aiming to provide insights about its structural, mechanical and electronic properties and to unveil the nature of its chemical bonding. DFT and DFT+*U* methods have been used and showed to be sensitive to the correlation treatment (*U* value). Although it is not possible to extract a universal value of the *U*, this study indicates that *U* = 5 eV is an adequate value. The electronic structure analysis shows a significant metallic character due to p(S)–d(Cu) orbital interactions up to Fermi level. The projected density of states indicates that most of the contribution comes from the atomic orbitals in the [001] plane of the covellite, explaining the conductivity anisotropy observed experimentally. Topological analysis of the electron density was performed by means of quantum theory of atoms in molecules (QTAIM). Two different topological charges in Cu and S were calculated, confirming an ionic model with mix-charges. This mineral presents ionic degree of ~32%. On the basis of the QTAIM analysis, the covalent character of S–S bond is confirmed, and the favored cleavage of CuS at the [001] surface might be at the Cu–S bond. The S atoms occupy most of the cell volume, and their contributions dominate the crystal compressibility: $\kappa(\text{S}) \approx \kappa(\text{CuS})$.



1. INTRODUCTION

Copper sulfide compounds have been applied in various technologies, including solar cell devices, nonlinear optical materials, lithium ion batteries, nanometer-scale switches, and gas sensors.^{1–3} In nature, usually these solids are non-stoichiometric and are associated with other metals, forming a great variety of compounds and phases, such as chalcocite (FeCuS₂), bornite (Cu₅FeS₄), covellite (CuS), and chalcocite (Cu₂S).

Despite the simplicity of its chemical formula, CuS (covellite) has a complex structure consisting of alternating layers of planar CuS₃ triangles and CuS₄ tetrahedrons with S–S bonds (Figure 1). Several experimental and theoretical studies have been carried out in an attempt to understand its electronic structure and the nature of the chemical bonding. Evans and Konnerth⁴ refined the crystal structure of CuS (Figure 1); they confirmed the structure solved by Oftedal⁵ in 1932 with S–S bond length of 2.07(4) Å. At room temperature, the crystal structure has hexagonal symmetry, and at 55 K it undergoes a structural phase transition to orthorhombic symmetry.⁶ A second-order phase transition takes place, leading to orthorhombic distortion with changes in the Cu–S and S–S bonding distances. Peiris et al.⁷ performed compression studies in CuSe. Although CuSe and CuS are similar in composition and

structure, under an increase in pressure, each solid behaves in a different manner. The bulk modulus for CuSe is 97 GPa, while for CuS it is 89 GPa. Taking into account these results, the authors concluded that CuSe presents a more rigid structure than CuS, probably due to the covalence of Cu–Se bonds in comparison with Cu–S bonds.

Recently, covellite structure (CuS) has attracted the attention due to a recent report about possible superconductivity at 40 K. Raveau et al.⁸ showed that CuS exhibits a superconducting-like behavior below 40 K, although the zero resistance cannot be reached at this temperature. The CuS layers, which exhibit the BN structure and a metallic character,⁹ would play a key role in the appearance of superconductivity, whereas the S–S bonds between the layers should be very critical to reach the zero resistance. Previously, Liang and Whangbo¹⁰ studied the conductivity anisotropy; this study shows that CuS is a 3-D metal, but its conductivity should be

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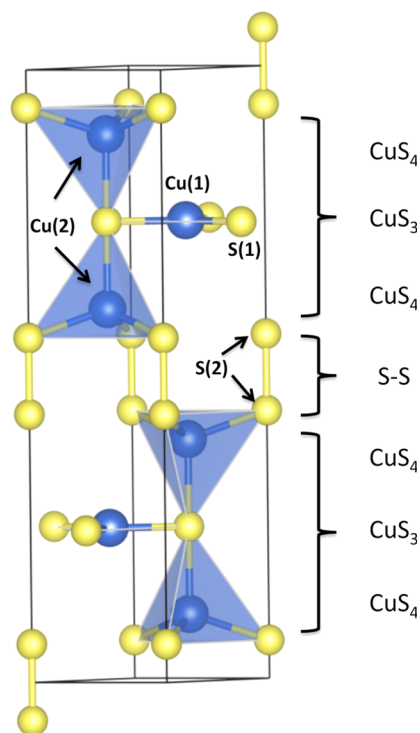


Figure 1. Covellite hexagonal unit cell (CuS). Wyckoff positions are: Cu(1) in 2d (1/3, 2/3, 3/4); Cu(2) in 4f (1/3, 2/3, $z_{\text{Cu}(2)}$); S(1) in 2c (1/3, 2/3, 1/4); and S(2) in 4e (0.00, 0.00, $z_{\text{S}(2)}$). Blue and yellow spheres are copper and sulfur atoms, respectively.

much greater along the directions perpendicular than parallel to the c axis.

Attending to the valences of Cu and S, the appropriate ionic model of the covellite has been the subject of discussion in the literature.^{6,10} Recently, Kumar et al.¹¹ performed a detailed X-ray absorption spectroscopy (XAS) aiming to determinate the electronic structure of CuS. They considered two possible cases: (i) both trigonal and tetrahedral sites have Cu^{2+} centers or (ii) only the tetrahedral site has Cu^{2+} centers, while the trigonal site has only Cu^{1+} centers. Their measurements reveal that the second case is the most consistent. Taking into account the charge neutralization, the ionic model can be described as $(\text{Cu}_{\text{Td}})^+(\text{Cu}_{\text{T}})^+(\text{Cu}_{\text{Td}})^{2+}(\text{S}_2)^{2-}(\text{S})^{2-}$ (Cu_{Td} and Cu_{T} are tetrahedral and trigonal, respectively). The authors suggest a more accurate description considering that the bond distances in all tetrahedral sites are equivalent: $[(\text{Cu}_{\text{Td}})_2]^{3+}(\text{Cu}_{\text{T}})^+(\text{S}_2)^{2-}(\text{S})^{2-}$ with each Cu_{Td} site is $\text{Cu}^{+1.5}$. This result is consistent with the previous study performed by Mazin.¹² His calculations establish that the Cu valency in this compound is 1.33 and the appropriate ionic model is $(\text{Cu}^{4/3+})_3(\text{S}_2^{2-})(\text{S}^{2-})$.

Structural and electronic properties and chemical bonding are investigated employing topological analysis of electron density.^{13–17} Since its origins, quantum theory of atoms in molecules (QTAIM) has evolved to be an invaluable tool for the chemical interpretation of quantum mechanical data. QTAIM starts from a particular division of real space into atomic basins. Given the appropriate operator density, any quantum mechanical observable can be integrated within the atomic basins, giving rise to the partition of properties into additive atomic contributions. This partition permits us to investigate the local properties of CuS and split the compressibility in local contributions associated with the

atoms contained in the crystal and understand the mechanical properties on a local scale.

In this work, we present a detailed study of the structure, electronic properties, and the nature of the chemical bonding in covellite under DFT and DFT+ U formalism. DFT+ U method has been used with remarkable success for investigating the 3d transition-metal sulfides and oxides.¹⁸ Transition-metal compounds such as CuS present strong interatomic exchange and Coulombic repulsion among the d electrons. Because DFT does not properly cancel out the electron self-interaction, the electron–electron repulsion is overestimated. DFT+ U combines the high efficiency of DFT with an explicit treatment of electronic correlation with a Hubbard-like model¹⁹ for a subset of states in the system. Noninteger or double occupations of these states are penalized by the introduction of two additional interaction terms, namely, the one-site Coulomb interaction term U and the exchange interaction term J . In general, the U parameter can be determined self-consistently by a linear response method,²⁰ or by selecting incremental U values to provide the best agreement of the calculated values with the available experimental data.²¹ Different U parameters have been used to calculate the covellite properties to determine the best value.

Three more sections complete this article. Next, we present the computational details used in our electronic and structural calculations, along with the main basic concept of QTAIM analysis. In Section 3, the calculated structural and electronic properties and the nature of the chemical bonding in CuS are discussed. A brief summary and the main conclusions will be presented in the last section.

2. COMPUTATIONAL DETAILS

2.1. Total Energy Calculations. Total energy calculations at selected volumes in CuS unit cell were carried out under the generalized gradient approximation (GGA) of the density functional theory, as implemented in the Vienna ab initio simulation package (VASP).²² The projector-augmented wave (PAW) all-electron description of the electron-ion-core interactions^{23,24} and the exchange and correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE)²⁵ were used. Brillouin zone integrals were approximated using the method of Monkhorst and Pack,²⁶ and the energies were converged with respect to the k -points density ($10 \times 10 \times 2$) and ($14 \times 14 \times 4$) (for density of state calculations), and the plane-wave cutoff (560 eV) was used to ensure convergence of the total energy within 10^{-3} eV. DFT+ U calculations were performed as the form proposed by Dudarev, that is, in the simplified rotationally invariant form.²⁷ In each calculation, the value of the exchange term J was kept constant at 1.00 eV, and four different U values are used ($U = 4, 6, 8$, and 10 eV). We have to consider a $U_{\text{eff}} = U - J$, for the reason from now we refer to $U = 3, 5, 7$, and 9 eV values. The DFT+ U calculated values have been compared with the available experimental data to determine the best U parameter.

For the study of the mechanical properties, numerical and analytical²⁸ equations of state (EOS) were used to describe (E, V) points of the CuS structure and EOS parameters (bulk modulus, B_0 , and its pressure derivative, B_0' , both evaluated at zero pressure). These calculations were performed with the GIBBS2 code.^{29,30}

2.2. Basic Concepts of AIM. Bader's QTAIM^{13,17} represents a fundamental departure from the classical theories of bonding, although, like any bonding model, it has

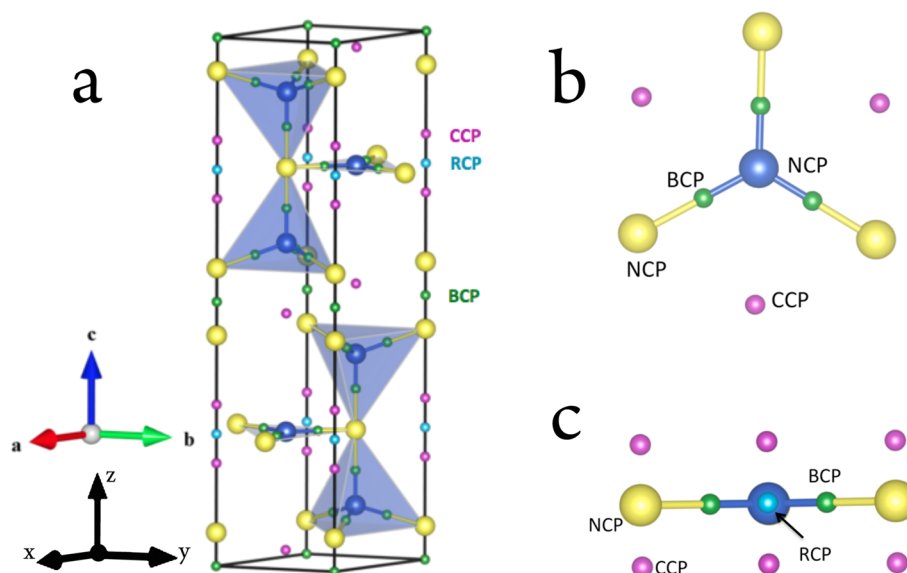


Figure 2. (a) All critical points in the unit cell of covellite. (b,c) CuS₃ unit of the covellite structure with the critical points (CPs): NCPs (nuclear or attractor) are blue and yellow for Cu and S, respectively. BCP (bond) is green. CCP (cage) is dark pink and RCP (ring) is cyan blue.

Table 1. Summary of Zero-Pressure Structural and Cohesive Properties of Covellite^a

	exp.	GGA	GGA+U			
			U = 3 eV	U = 5 eV	U = 7 eV	U = 9 eV
a = b (Å)	3.7938(5)	3.826	3.826	3.791	3.791	3.790
c (Å)	16.341(1)	16.596	16.589	16.400	16.402	16.406
z _{Cu(2)}	0.10733(9)	0.1069	0.1072	0.1076	0.1080	0.1084
z _{S(2)}	0.06337(15)	0.0639	0.0631	0.0633	0.0630	0.0628
Cu(1)–S(1) (Å) × 3	2.190(2)	2.208	2.209	2.188	2.188	2.188
Cu(2)–S(1) (Å)	2.331(2)	2.374	2.368	2.334	2.329	2.322
Cu(2)–S(2) (Å) × 3	2.305(1)	2.322	2.327	2.306	2.309	2.312
S(2)–S(2) (Å)	2.071(4)	2.113	2.092	2.074	2.069	2.063
B ₀ (GPa)	89 ± 10 ^b	77.98	76.12	71.71	68.36	65.72
B ₀ '	–2 ± 2 ^b	4.03	4.62	4.94	3.62	5.00
V ₀ (Å ³)	202.5 ^b	208.13	207.22	206.75	206.64	205.36

^a(× 3) indicates three equal distances. ^bRef 46.

limitations.^{31–37} QTAIM is based on the idea of extracting the bonding information from the best available experimental or theoretical electron density by applying quantum mechanical operators in a way that is locally well-defined. QTAIM analysis starts by determining the critical points (CPs) of the electron density. Those are classified according to the curvature matrix into: maxima, nuclear or attractor CPs (NCP or *n*); first-order saddle or bond (BCP or *b*); second-order saddle or ring (RCP or *r*); and minima or cage (CCP or *c*). An NCP, together with all downward-gradient lines that have their origins in the NCP, constitute an atomic basin and are the most important of the regions fulfilling the zero flux condition. The zero flux surfaces (2D surface on which the charge density is a minimum perpendicular to the surface), which separate two neighbor basins, are made of the downward-gradient lines originated in a BCP. Atomic basins are, in solids, equivalent to polyhedral with curved edged and faces. Each face contains a single RCP, and each vertex is a minimum of the electron density or CCP. The covellite structure and their CPs are shown in Figure 2. CuS₃ unit plane and its CPs are shown in detail in Figure 2b,c.

To perform Bader's analysis, we carried out a single-point calculation of the optimized CuS structure to generate the full electron density. Once the core and valence electron densities

have been calculated, they are taken as input to the CRITIC2 code.^{38,39} For the integration of the basins, Yu and Trinkle⁴⁰ method is applied. This algorithm is based on the assignment of integration weights to each point in the numerical grid by evaluating the flow of the gradient using the neighboring points.

The analysis is based on the partition of the cell volume (*V*) into basin volumes (*V*_Ω), which compress differently upon the application of hydrostatic pressure (*P*). The compressibility (*κ*) and bulk modulus (*B*) of the bulk crystal are defined as:

$$\kappa = \frac{1}{B} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \quad (1)$$

Considering the partition of the cell volume into atomic basin contributions

$$\kappa = \sum_{\Omega} f_{\Omega} \cdot \kappa_{\Omega} \text{ and } \frac{1}{B} = \sum_{\Omega} f_{\Omega} \cdot \frac{1}{B_{\Omega}} \quad (2)$$

where *f*_Ω = *V*_Ω/*V* is the fraction of the cell volume occupied by the Ω basin and

$$\kappa_{\Omega} = \frac{1}{B_{\Omega}} = -\frac{1}{V_{\Omega}} \left(\frac{\partial V_{\Omega}}{\partial P} \right) \quad (3)$$

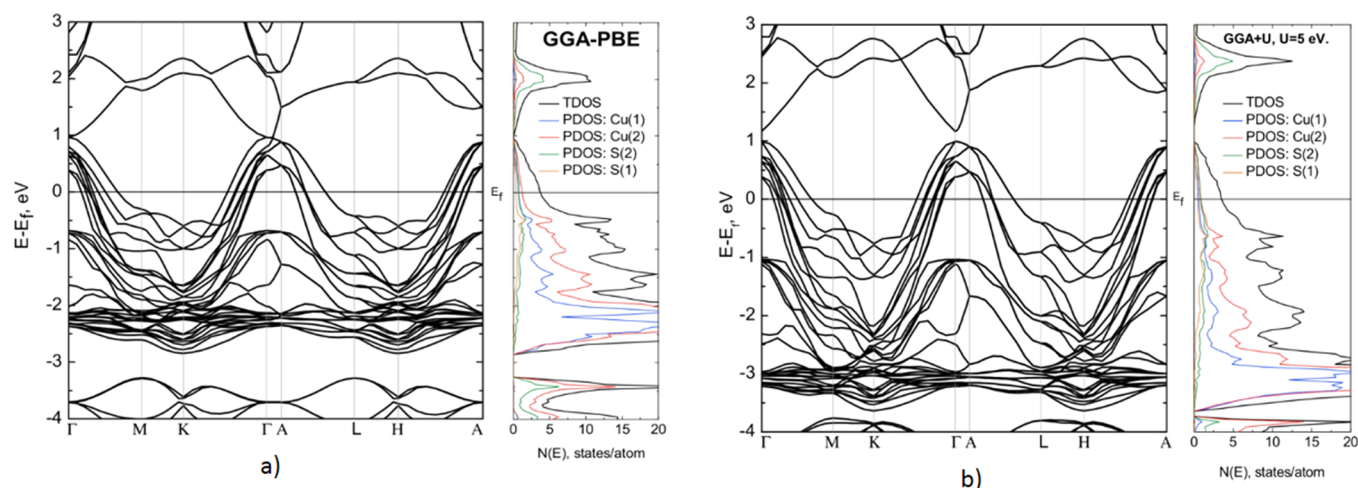


Figure 3. Band structure and density of states of CuS. (a) GGA calculations and (b) GGA+ U , $U = 5$ eV. The points Γ , M, and K are in the central plane ($k_z = 0$) and A, L, and H are in the basal plane ($k_z = \pi/c$).

The local compressibility of a basin, κ_Ω , is thus defined equivalently to the compressibility of the whole crystal. The bulk magnitude, by the previous equations, results from averaging the local compressibility in such a way that the contribution from a basin is proportional to the volume fraction occupied by the basin in the crystal. This study provides knowledge of the mechanical properties of solids (compressibility and bulk modulus) into local contributions (κ_Ω and B_Ω , respectively).⁴¹

3. RESULTS AND DISCUSSION

3.1. Structural Properties. At room temperature, covellite structure belongs to $P6_3/mmc$ (#194) space group (hexagonal symmetry) with $Z = 6$ per unit cell. Cu atoms are in two different environments: CuS_3 units (triangular planes) and CuS_4 units (tetrahedron). The unit cell can be seen as slabs connected by S–S bonds. The tetrahedral units are linked by vortex through triangular layers (Figure 1). The calculated structural and cohesive properties are compared with the available experimental^{4,46} data in Table 1. The Cu–S and S–S bonds are overestimated by less than 0.043 and 0.042 Å, respectively, for the GGA level of theory compared with the experimental values. The lattice parameters are also overestimated by 0.033 and 0.25 Å for $a = b$ and c parameters, respectively. The implementation of U (GGA+ U) improves the structural estimates. The increment of the U parameter leads to the reduction of the lattice parameters for this system, and this is probably a consequence of the observed separation between bands upper Fermi level. (See the next section.)

Experimentally, it is noted that the Cu(1)–S(1) bonds (~ 2.19 Å) are strikingly shorter than the Cu–S bonds in triangular units for the majority of other copper sulfides (~ 2.33 Å).⁴ This fact strongly suggests that the Cu(1)–S(1) bond strength should be large. It has also been reported that Cu(1) ions in the $[\text{Cu(1)}-\text{S(1)}_3]$ triangles have large thermal motion along the c axis.⁴ S–S bond has been assigned to stretching mode A_{1g} (Raman spectra) at 475 cm^{-1} , probably due to covalently bonded S pairs.⁴² This assignment is in agreement with the results observed for pyrite and marcasite-type compounds with similar S–S bonds, reported by Lutz et al.⁴³ The observed S–S bond distance of 2.07 Å, which is shorter than the S_2^{2-} anion group in pyrite (2.14 Å), can be likewise strongly covalent. In the investigation of covellite [001]

surfaces, Rosso et al.⁴⁴ concluded that the S–S bonds are much stronger than the Cu–S bonds and therefore are unlikely to cleave. They suggest that the preferential cleavage occurs at the Cu–S bonds along [001] because the S–S bond is predicted to be significantly stronger. This is also consistent with the fact that phase transformation from hexagonal to orthorhombic involves a slight slipping of the trigonally coordinated Cu layers with respect to the tetrahedrally coordinated Cu layers.⁶

Our optimal U value is 5 eV, similar to the previously reported value by first-principles calculations of systems containing Cu.⁴⁵ In Table 1, we see significant improvement in the lattice parameters and bond distances at $U = 5$ eV. The Cu–S and S–S bond distances are only 0.003 Å different from the experimental results. For $a = b$ and c lattice parameters, the difference with respect to the experimental data is not larger than 0.002 and 0.06 Å, respectively. The influence of the U value in the GGA+ U calculations for estimating other properties, such as electronic and chemical bonding for several values of U , is shown in the Supporting Information.

3.2. Electronic Properties. The calculated band structure and total-partial density of states (GGA and GGA+ U) of CuS indicate the metallic behavior for this system (Figure 3). Our results are in agreement with other theoretical calculations like those of Mazin¹² under DFT formalism within LDA approximation. Experimental studies⁴⁷ indicated the excellent metallic conduction of CuS among 3d orbitals of transition metal (Cu) and the 3p orbitals of S. Two significant effects occur with the increment of U : (i) a separation is observed between bands above the Fermi level (this tendency increases with U value) and (ii) the gap between bands in the energy range -3 and -4 eV in GGA results (Figure 3a) tends to decrease with U value and for $U = 7$ eV disappears. (See Figure S1 in the Supporting Information.)

Considering these results, DFT+ U seems to be an appropriate methodology for studying electronic properties due to high electronic correlation of CuS. The separation between bands above the Fermi level for $U = 5$ eV is ~ 0.2 eV; analogous results are obtained with other DFT packages. Liang and Whangbo¹⁰ argued that the highest occupied states in S(2) orbitals should lie higher in energy and be only partially filled as compared with the more completely filled S(1) orbitals. This argument implies that the Fermi level should be flanked by S 3p

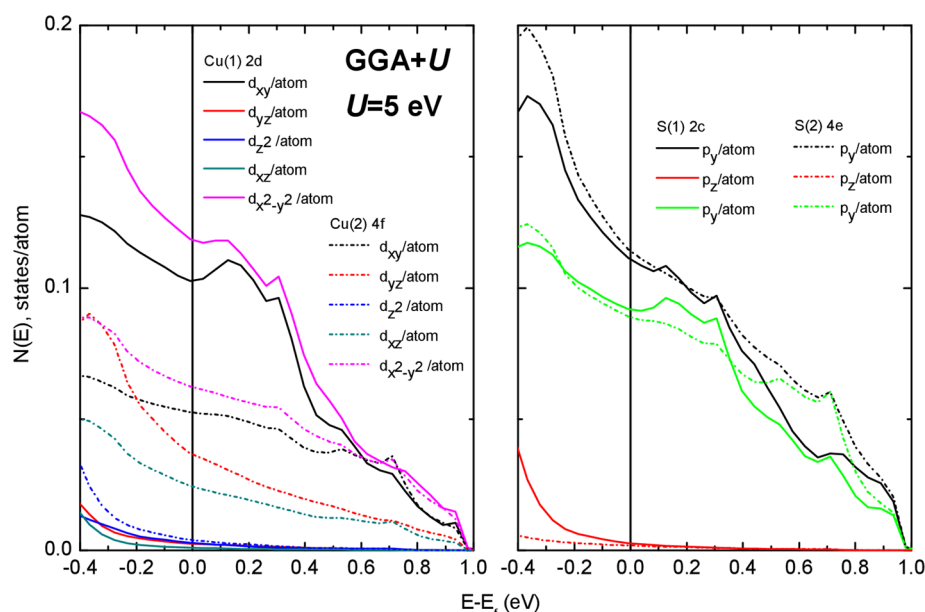


Figure 4. Projected density of states (PDOS)/atom for GGA+ U ($U = 5$ eV) is shown in the vicinity of the Fermi level. The contributions of each atomic orbitals to the DOS are shown.

states, which are theoretically confirmed from our results (Figures 4 and Figure S2 in the Supporting Information). Calculated total and projected valence band densities of states (DOS) by Rosso et al.⁴⁴ showed that the highest occupied states indeed predominantly comprise S 3p and lesser Cu 3d states. Their calculations are in a good agreement with UPS spectra. Our analysis is consistent with these previous results.^{10,44} Attending to the structural properties, our results confirm that the Cu(2)–S(1) bonds are weaker than S(2)–S(2). (See the discussion below.)

The electric conductivity anisotropy observed experimentally¹⁰ is coherent to the fact that at the Fermi level the DOS has more contribution from the atomic orbitals in the xy plane, as shown at Figure 4. The projected density of states (PDOS) has larger contributions from the copper d_{xy} and $d_{x^2-y^2}$ atomic orbitals and sulfur p_x and p_y atomic orbitals. This explains why the electric conductivity is larger in the xy plane of the covellite. In this plane, the electronic states are mostly responsible for the valence and conduction bands close to the Fermi level and hence for the electric conductivity in this plane. We can see from Figure S2 in the Supporting Information that the profiles of Cu(2) and S(2) are similar; analogous situation occurs for Cu(1) and S(1). These analogies seem to indicate that the interactions between d orbitals (Cu) with p orbitals (S) occur between Cu(1)–S(1) and Cu(2)–S(2). Therefore, we conclude that this conductivity is observed along the tetrahedral coordinated Cu layers: Cu(2)–S(2) and triangular plane (CuS₃): Cu(1)–S(1). The U parameter does not change the analysis and the conclusions as one can compare with the GGA pure calculations shown in Figure S3 in the Supporting Information.

3.3. Bonding Properties. For the analysis of the chemical bonding in CuS, we applied the topological analysis approach of electron density (QTAIM). In Table 2, the topological volumes and charges resulting from integration of the basins evaluated using the DFT and DFT+ U ($U = 5$ eV) total electron densities are shown. S presents the largest volume basin with the same number of atoms as Cu at the unit cell, which means that most of the cell volume, 59.6%, is occupied by S atoms,

Table 2. Atomic Properties of CuS Calculated from DFT and DFT+ U ($U = 5$ eV)^a

atom	Wyck	χ	GGA		GGA+ U ($U = 5$ eV)	
			V	Q	V	Q
Cu(1)	2d	1.90	99.50	+0.48	96.56	+0.40
Cu(2)	4f		93.69	+0.52	91.05	+0.44
S(1)	2c	2.58	139.68	−0.76	134.84	−0.66
S(2)	4e		141.58	−0.38	137.68	−0.31
total			1419.44		1377.72	

^a V is the volume (Bohr³), Q is the charge (e), and χ is Pauling's electronegativity value. Wyck is the Wyckoff position of each atom.

and Cu atoms occupy 40.4% (GGA case). Unit-cell volume decreases by U effect, taking into account that the volume of the unit cell is the sum of the volume of each basin: $V = \sum_{\Omega} V_{\Omega}$ (Ω corresponds to basin); the volumes of each basin decrease with U . (See Table S1 in the Supporting Information.) The occupation of each basin with respect to unit cell volume is important for understanding the local properties and the contribution of each basin to the mechanical properties of the crystal. (See the next section.)

Attending to charges associated with each basin, we can determine a single parameter describing the global charge transfer by averaging the ratios between topological charges $Q(\Omega)$ and nominal oxidation states $OS(\Omega)$:

$$c = \frac{1}{N} \sum_{\Omega=1}^N \frac{Q(\Omega)}{OS(\Omega)} \quad (4)$$

c index has been used to measure the degree of ionicity of the crystal,⁴⁸ where $1 - c$ is a degree of covalency. This index defines a charge-transfer by using the topological charges (the integrated net charge within each atomic basin from Bader's analysis). The ratio between $Q(\Omega)$ and $OS(\Omega)$ provides a measurement of the deviation from the ideal ionic model for a given basin Ω . Several crystals have been characterized under this index, indicating that the polar compounds with c ranging from 0.3 to 0.6 include most III-V crystals and nitrides.⁴⁸

Table 3. Crystallographic Position and Properties of the CuS Electron Density Critical Points^a

type	Wyckoff	position	GGA		GGA+U (U = 5 eV)		CHM
			$\rho(r_c)$	$\nabla^2\rho(r_c)$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	
Cu(1)	2d	(0.3333,0.6666,0.75)					
Cu(2)	4f	(0.3333,0.6666,0.1069)					
S(1)	2c	(0.3333,0.6666,0.25)					
S(2)	4e	(0.00,0.00,0.0636)					
b_1	4f	(0.3333,0.6666,0.3272)	0.06231	0.10985	0.06824	0.10350	Cu(2)–S(1)
b_2	12k	(0.1822,0.3645,0.0867)	0.07182	0.09830	0.07376	0.10210	Cu(2)–S(2)
b_3	12j	(0.0281,0.5139,0.75)	0.08881	0.12912	0.09299	0.09800	Cu(1)–S(1)
b_4	2a	(1.00,1.00,0.00)	0.13478	−0.07863	0.14379	−0.09323	S(2)–S(2)
r_1	2b	(0.00,1.00,0.75)	0.00438	0.01225	0.00454	0.01275	
r_2	6g	(0.50,0.50,0.00)	0.00502	0.01418	0.00509	0.01500	
r_3	12k	(0.6215,0.8107,0.8433)	0.00727	0.01598	0.00712	0.01681	
c_1	4f	(0.3333,0.6666,0.5262)	0.00292	0.00882	0.00297	0.00926	
c_2	4e	(0.00,0.00,0.6945)	0.00321	0.00970	0.00328	0.01011	

^aGGA and GGA+U (U = 5 eV) results. $\rho(r_c)$ and $\nabla^2\rho(r_c)$ are the electron density and its Laplacian. CHM is the chemical meaning. (See Figure 1.)

There is an open discussion about what is the appropriate ionic model for describing CuS. (See the Introduction.) The empirical formula suggests the description $\text{Cu}^{2+}\text{S}^{2-}$; however, previous studies have assumed the monovalent copper: $(\text{Cu}^{1+})_3(\text{S}_2^{2-})(\text{S}^{1-})^6$ and $(\text{Cu}^{1+})_3(\text{S}_2^{1-})(\text{S}^{2-})^{10}$. Recently, quantitative X-ray absorption and emission spectroscopy¹¹ suggested the formula $[(\text{Cu}_{\text{Td}})_2]^{3+}(\text{Cu}_{\text{T}})^+(\text{S}_2)^{2-}(\text{S})^{2-}$, and each Cu_{Td} site has +1.5 net charge. This model is in agreement with the studies that indicate that Cu valence is larger than 1.¹² We consider this last ionic model and $\text{Cu}^{1+}\text{S}^{1-}$ to study the ionicity degree and the effect of U value in this parameter. (See Figure S4 in the Supporting Information.) In both models, U parameter promotes a decreasing of the degree of ionicity of the crystal. The topological charges (Q) are not close to nominal charges (OS); however, we observe different topological charges for the same atoms depending on the atomic environment. Kumar et al.¹¹ observed similar discrepancies between charges. According to our QTAIM analysis of basin volumes and charges of each basin, the mix-valence model proposed by Kumar et al.¹¹ is the most appropriate for the covellite. For the $[(\text{Cu}_{\text{Td}})_2]^{3+}(\text{Cu}_{\text{T}})^+(\text{S}_2)^{2-}(\text{S})^{2-}$ model, the covellite presents 32% of ionicity degree (for U = 5 eV).

Concerning the QTAIM CPs, the solids Morse relationship ensures that: $n - b + r - c = 0$ with $n, c \geq 1$, and $b, r \geq 3$ on the repetitive unit cell. The location and properties of the CPs of CuS are presented in Table 3 and Figure 2; these results correspond to a pure GGA calculation. Four nonequivalent types of bonds, three rings, and two cages appear for a total of 70 CPs in the hexagonal unit cell. Looking at Table 3, the first column labels the symmetry unique CPs in the unit cell: nuclei (Cu, S); bonds (b_1 and b_2 connects Cu–S in tetrahedral, b_3 connects Cu–S in triangular planar, and b_4 connects S–S); rings (r_1 , r_2 , and r_3); and cages (c_1 and c_2). The rest of the columns enlist: Wyckoff positions, coordinates of the CP, and values of the electron density and of its Laplacian (atomic units are used on the four columns). Similar results are obtained with DFT+U formalism in all cases. One important data is the value of the Laplacian of the electron density of b_4 . The Laplacian is constructed from second partial derivatives, so it is essentially a measure of the curvature of the function in three dimensions. The Laplacian of any scalar field shows where the field is *locally concentrated or depleted*, and it has a negative value wherever the scalar field is locally concentrated and a positive value where it

is locally depleted. The negative value of b_4 (see Table 3) should be considered the telltale of a significant covalent character. The electron density at the b_4 is higher than that for the Cu–S bond parallel to the c axis. Considering that these bonds occur the same number of times per unit cell, the logical conclusion is that the latter bond will be preferentially broken during cleavage along [001]. This is another indication that the preferential cleavage of the covellite is at the Cu–S bond along the [001] plane.

To have a better understanding of the implications of the QTAIM analysis of covellite, we compared the estimated values with diamond crystal structure like C and Pb; both systems present the same topology.⁴⁹ The values of the electron density, $\rho(r_c)$, and its Laplacian (between parenthesis), $\nabla^2\rho(r_c)$, for C and Pb bond (b) CP are 0.240 (−0.551) and 0.038 (+0.030), respectively. Our results show the covalent character associated with b_4 (S–S) of covellite due to high electron density compared with the other bonds and its Laplacian negative value as a result of high localization of the density. For U = 5 eV, the electron density is 0.144 (−0.093) for b_4 , indicating an increment in the electron density in the S–S bonding direction. These results are in good agreement with previous theoretical studies,⁵⁰ where electron density distributions at Cu–sulfide bonds were calculated. Their comparisons between sulfide crystals (marcasite, smythite, pyrite, and vaesite) with native sulfur (S8 rings) suggest that stronger S–S interactions are present (covalent character). Aray et al.⁵¹ studied the topological properties of transition-metal bisulfides. They observed CP associated with S–S bonds, and their results reveal that sulfur atoms form covalently bonded S–S groups. Electron density values, $\rho(r_c)$, in b(S–S) bonding direction are 0.125, 0.117, 0.119, 0.132, and 0.147 for RuS_2 , OsS_2 , IrS_2 , FeS_2 , and NiS_2 , respectively. These values are in the same magnitude order compared with our results, concluding that with our topological analysis, the S–S bond (b_4 in Table 3) in the covellite structure (CuS) is covalently bonded.

The inclusion of U parameter in the DFT/GGA calculations of covellite is important. It causes the appearance of an energy gap promoting the electron density localization. This localization affects the structural properties with the decrease in the cell volume. The use of U parameter is important for the accuracy of the estimated properties of the copper sulfides and has to be taken into account for studying the reconstruction and chemical reactivity of the surfaces.

Table 4. DFT and DFT+*U* Results of QTAIM Partition of the Compressibility and Bulk Modulus into Atomic Basin Contribution (Ω)

Ω	GGA			GGA + <i>U</i> (<i>U</i> = 5 eV)		
	f_{Ω}	κ_{Ω} (TPa ⁻¹)	B_{Ω} (GPa)	f_{Ω}	κ_{Ω} (TPa ⁻¹)	B_{Ω} (GPa)
Cu(1)	0.2097	12.14	82.37	0.2098	12.65	79.05
Cu(2)	0.1974	12.15	82.30	0.1979	12.60	79.36
S(1)	0.2944	13.74	72.78	0.2930	14.86	67.29
S(2)	0.2984	12.04	83.06	0.2992	12.96	77.16
total		12.58	79.47		13.38	74.73

3.4. Local Properties. The contribution of each of the Cu and S atomic basins to the crystal bulk modulus is analyzed based on the partition of the cell volume into basin volumes and the compressibility and bulk modulus of the bulk crystal, defined as eqs 1–3. An important aspect of this topological partition of the bulk modulus is the transferability of the atomic local contributions. A fundamental point of view is that the local compressibility depends only on the atomic basins.

The QTAIM partition of the CuS compressibility and bulk modulus is shown in Table 4. We notice, first, a small error in *B* (bulk modulus) compared with the results already discussed in Table 1, which is mostly due to the errors in the integrated volume of the basins. This error is small enough to be neglected in the analysis of the partition. The S atoms occupy most of the cell volume (~59%), and their contribution dominates the crystal compressibility, being important for estimating the mechanical properties. An important aspect is the compressibility of S(2); these atoms present larger bulk modulus than S(1) due to the covalent character, as it has been observed in the bond CP b_4 (Table 3). The high compressibility of S(1) basin with respect to the rest of the basins indicates that this basin can be weak spot of the unit cell if this structure is subjected to pressure. This is the zone where the transition phase occurs.⁶ Similar results are observed in the crystal bulk modulus (Table 1). The increment of *U* promotes a decreasing in the bulk modulus, which is associated with the reduction of the bulk modulus basins.

4. CONCLUDING REMARKS

By means of first-principles calculations, the structural and electronic properties of covellite are investigated through DFT and DFT+*U* formalism. The suitability of DFT+*U* methodology to investigate CuS is discussed and compared with conventional DFT. As expected, it is not possible to extract a universal value of *U* parameter to reproduce all CuS properties; we found that the GGA+*U* (*U* = 5 eV) method is adequate to investigate the properties of CuS. For this *U* value, an energy gap is observed in covellite upper Fermi level in the band structure, leading to high electron density localization around the bonds and to decrease the volume of the unit cell with respect to the GGA pure calculations.

The AIM topological analysis of the covellite was performed aiming to reveal the Cu–S and S–S bond character. The topological analysis confirms the covalent character for S–S bond, taking into account the values of electron density compared with other transition-metal sulfides. The global ionic character is 32%. The *U* effect shows an increment in the localization electron density around the Cu–S and S–S bonds. The differences in calculated topological charges are in agreement with the mix-charge ionic model. The calculated volumes of each basin show that S basins occupy ~59%, and

the bulk compressibility of covellite is close to S local compressibility: $\kappa(S) \approx \kappa(\text{CuS})$.

An accurate concordance between experimental and DFT+*U* is obtained for covellite structure. The results indicate that the favored cleavage of CuS at the [001] surface occur at the Cu–S bond. The GGA+*U* (*U* = 5 eV) is an adequate methodology for investigating the surface reconstruction and chemical reactivity of the copper sulfide. The surface reconstruction of the covellite is presently being investigated in our laboratory.

■ ASSOCIATED CONTENT

● Supporting Information

Electronic properties calculated with four different values of *U*. The ionicity degree variation with the employed methodology. QTAIM analyses with the integration of the basins and the partition of the compressibility and bulk modulus for different values of *U*. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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