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Bond ionicities in CuBC_2 chalcogenides (B=Al, Ga, In; C=S, Se, Te)

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The bond ionicities, $f_{i,\mathrm{Cu}\text{-}C}$ and $f_{i,BC}$ of several CuBC_2 (B=Al, Ga, In, and C=S, Se, Te) chalcopyrite compounds are estimated by means of the Phillips–Van Vechten dielectric theory for binary tetrahedral compounds and Levine's extension to multibond crystals in the same way as Neumann [Crystal Res. Technol. **18**, 1299 (1983)]. The influence of Cu 3d electrons has been taken into account considering Jaffe-Zunger [Phys. Rev. B **29**, 1882 (1984)] band-structure calculations in chalcopyrite compounds, and performing a simple extrapolation for Te compounds. The Cu-C bond susceptibilities have been estimated from the static dielectric constant values obtained by Márquez and Rincón [Phys. Status Solidi B **191**, 115 (1995)], and a set of Cu-C bond susceptibilities is proposed. The evaluated $f_{i,\mathrm{Cu}\text{-}C}$ bond ionicities were found to increase with the atomic fractional coordinate of the C atom, x[anion], indicating that the anion position is a good estimation of the Cu-C bond ionicity.

I. INTRODUCTION

The concept of crystal ionicity has proved to be a useful unifying concept for understanding chemical trends in diverse problems in solid-state physics and chemistry. In particular, the dielectric description of the ionicity developed by Phillips[1,2] and Van Vechten[3,4] has been successfully employed in a wide variety of areas including multibond crystals and complex crystal structures.[5–7] However, the dielectric model of bond ionicity encounters some difficulties when noble or transition metals are considered, particularly in the case of CuBC_2 compounds, where the Cu-C bond is highly influenced by the Cu 3d electrons. Some attempts[5,8] have been made to evaluate the bond ionicity of these compounds including the effect of the d electrons, but the inaccuracy in the determination of both the dielectric constants and the fraction of d electrons that contribute to the Cu-C bond makes it difficult to generalize the considerations. More recently, Márquez and Rincón[9] calculated the values of the static, ε_0, and high-frequency, ε_∞, dielectric constants of several ABC_2 chalcopyrite compounds, using an empirical model proposed by Nag[10] for cubic semiconductors which relates these constants to the average atomic number of its constituent atoms. In addition, a linear relation between the inverse of the ε_0 and ε_∞ dielectric constants and the average atomic number for several ABC_2 chalcopyrites was found.

On the other hand, CuBC_2 chalcopyrite compounds, other than Cu-(Ga,In)-Se$_2$, although being promising candidates for optical, electrical, and photovoltaic devices are not as well characterized as Cu-(In,Ga)-Se$_2$ compounds. In particular, the tellurides (C=Te) are usually excluded from the general relations and considerations concerning this type of compound.

Neumann[8] proposed that the bond ionicities $f_{i,AC}$ and $f_{i,BC}$ of the chalcopyrite ABC_2 compounds can be evaluated if the bond susceptibilities, χ_{AC} and χ_{BC}, the number of valence electrons Z_A, Z_B, and Z_C, and the bond lengths d_{AC} and d_{BC} are known, obtaining a set of bond ionicities for chalcopyrites. However, in the evaluation of these ionicities, the Cu 3d electrons are considered to fully contribute to the Cu-C bond, and the dielectric constant values are rather old.

In this work, we have estimated the bond ionicities of several chalcopyrite compounds CuBC_2 (B=Al, Ga, In, and C=S, Se, Te), following the previous Neumann[8] calculations, by means of the Phillips–Van Vechten[1–4] dielectric theory for binary tetrahedral compounds, and Levine's[5–7] extension to multibond crystals. To compute the bond ionicities, the influence of the Cu 3d electrons and recent dielectric constant values have been taken into account. In order to evaluate the fraction of d electrons that contribute to the Cu-C bond, we have considered the band-structure calculations of Jaffe and Zunger[11,12] in chalcopyrite compounds, and made a simple extrapolation for Te compounds. The B-C bond susceptibilities have been taken from Neumann,[8] while we have estimated the Cu-C ones from the static dielectric constant values obtained by Márquez and Rincón.[9] A set of Cu-C (C=S, Se, Te) bond susceptibilities is proposed. Finally, the evaluated bond ionicities are compared with calculations and predictions from diverse authors.

II. GENERAL RELATIONS

From the dielectric theory, the bond ionicity of an X-Y bond in an XY binary system can be evaluated through[8]

$$f_{i,XY}=\frac{C_{XY}^2}{E_{g,XY}^2}, \tag{1}$$

where $E_{g,XY}$ is the dielectrically defined average gap energy which can be separated into an heteropolar part, C_{XY}, and an homopolar one, $E_{h,XY}$, as

$$E_{g,XY}^2=E_{h,XY}^2+C_{XY}^2. \tag{2}$$

According to Phillips,[1] Van Vechten,[3] and Levine,[7] $E_{h,XY}$ can be computed from

$$E_{h,XY}=E_{h,Si}\left(\frac{d_{Si}}{d_{XY}}\right)^{2.48}, \tag{3}$$

where $E_{h,\mathrm{Si}}$ is the average gap energy in silicon, and d_{Si}/d_{XY} is the ratio between the silicon and XY binary bond lengths. By other side, the susceptibility χ_{XY} of a binary system XY is related to $E_{g,XY}$ by[1,3,7]

$$\chi_{XY}=\frac{(\hbar\omega_{p,XY})^2}{E_{g,XY}^2}D_{XY}\left[1-\frac{E_{g,XY}}{4E_{F,XY}}+\frac{1}{3}\left(\frac{E_{g,XY}}{4E_{F,XY}}\right)^2\right], \quad (4)$$

where $\omega_{p,XY}$ and $E_{F,XY}$ are the plasma frequency and the Fermi energy of the valence electrons, respectively, and D_{XY} is a correction factor of order unity accounting for the influence of d-state cores. For the plasma frequency and Fermi energy, we have

$$\omega_{p,XY}^2=\frac{N_{e,XY}}{m\varepsilon_\nu},$$

$$E_{F,XY}=\frac{\hbar^2}{2m}(3\pi^2N_{e,XY})^{2/3}, \quad (5)$$

where $N_{e,XY}$ is the number of valence electrons per unit volume, ε_ν is the permittivity of free space, and m is the free-electron mass. $N_{e,XY}$ can be expressed in terms of the individual bond properties,

$$N_{e,XY}=\frac{n_{e,XY}}{\nu_{b,XY}}, \quad (6)$$

with $n_{e,XY}$ the number of valence electrons per bond and $\nu_{b,XY}$ the bond volume. $n_{e,XY}$ can easily be obtained from

$$n_{e,XY}=\frac{Z_X}{N_{cX}}+\frac{Z_Y}{N_{cY}}, \quad (7)$$

where Z_X and Z_Y are the numbers of valence electrons and N_{cX} and N_{cY} are the coordination numbers of atoms X and Y, respectively.

In the case of the ABC_2 compounds, which crystallize in the chalcopyrite structure, the coordination numbers of the three types of atoms are $N_{cA}=N_{cB}=N_{cC}=4$, and the bond volume is[8]

$$\nu_{b,XY}=4\left(\frac{d_{XY}}{\sqrt{3}}\right)^3, \quad (8)$$

where d_{XY} is the bond length, and two different bonds should be considered: A-C and B-C. In such compounds, Z_B and Z_C can be assumed to be $Z_B=3$ and $Z_C=6$, while for the CuBC_2 chalcopyrites Z_{Cu} will include the Cu $4s$ electron plus the effect of the Cu $3d$ electrons. This point will be considered in detail in Sec. III.

Hence, by means of all previous equations (1)–(8), as Neumann[8] proposed, the bond ionicities $f_{i,\mathrm{Cu}\text{-}C}$ and $f_{i,BC}$ can be evaluated if the bond susceptibilities $\chi_{\mathrm{Cu}\text{-}C}$ and χ_{BC}, the number of valence electrons Z_{Cu}, Z_B, and Z_C, and the bond lengths $d_{\mathrm{Cu}\text{-}C}$ and d_{BC} are known.

III. EVALUATION OF BOND IONICITIES

In order to estimate the bond ionicities of the CuBC_2 chalcopyrite compounds, the bond lengths have been taken from previous works[13,14,15] of our group and from diverse authors[16–21] in their latter published works as far as we could find.

B-C bond

In the case of the B-C bond, the number of valence electrons for both elements B and C has been taken as fixed to $Z_B=3$ and $Z_C=6$, as mentioned above, and the bond susceptibilities χ_{BC} and correction factors D_{BC} were taken from Neumann[8] and Levine,[7] respectively.

Table I shows the evaluated bond ionicities $f_{i,BC}$ for all the considered compounds computed from Eq. (1), as explained in Sec. II. The bond susceptibilities, correction factors, and bond distances with the bond ionicities reported by Neumann[8] are also shown.

Cu-*C* bond

For the Cu-C bond, the question arises of how to estimate both the number of valence electrons, Z_{Cu}, and the bond susceptibilities, $\chi_{\mathrm{Cu}\text{-}C}$. As in the case of the B-C bond, the correction factors $D_{\mathrm{Cu}\text{-}C}$ can be taken from Levine,[7] and Z_C has been fixed to $Z_C=6$.

In order to solve the problem of the number of Cu valence electrons, Z_{Cu}, we will consider the Jaffe-Zunger[11] band-structure calculations. They calculated the ''d character'' α_d in several CuBC_2 chalcopyrites at the top of the valence band by decomposing the wave functions into angular momentum components and evaluating the fraction of d charge enclosed in a sphere of Pauling's radius around the Cu atom. Thus α_d could be considered as the percentage of Cu $3d$ electrons that remain around the Cu, atom while the rest of the Cu $3d$ electrons contribute to the Cu-C bond, as well as the Cu $4s$ electron. Then the effective number of valence electrons, Z_{Cu}, could be evaluated through

$$Z_{\mathrm{Cu}}=Z_{\mathrm{Cu}(4s)}+\frac{(100-\alpha_d)}{100}Z_{\mathrm{Cu}(3d)} \quad (9)$$

with $Z_{\mathrm{Cu}(4s)}=1$ and $Z_{\mathrm{Cu}(3d)}=10$.

The calculated α_d values from Jaffe and Zunger[11] in CuAlS$_2$, CuAlSe$_2$, CuGaS$_2$, CuGaSe$_2$, CuInS$_2$ and CuInSe$_2$ compounds are 35.2%, 27.5%, 31.5%, 26.6%, 24%, and 22%, respectively. Unfortunately the tellurides are not considered in their calculations. So, in order to estimate the α_d values for the latter compounds we will consider another work of Jaffe and Zunger,[12] where they proposed that the band-gap anomaly ΔE_g in chalcopyrites—computed from the difference between the optical band gap and the corresponding one of the zinc-blende analog—is influenced by two factors: the chemical contribution $\Delta E_g^{\mathrm{chem}}$, arising out of the Se $4p-$Cu $3d$ hybridization effect, and the structural contribution ΔE_g^S, due to variations in the anion position in the lattice. Accordingly, the total band-gap anomaly can be computed from

$$\Delta E_g=\Delta E_g^{\mathrm{chem}}+\Delta E_g^S. \quad (10)$$

In this way, the structural contribution can be expressed as a linear function of the anion position;[14] $x[\mathrm{anion}]$, while the chemical contribution follows a linear trend with the percentage of d character (see Table III of Ref. 12):

TABLE I. Susceptibilities χ_{BC}, correction factors D_{BC}, interatomic distances d_{BC}, and the references from which are taken, and bond ionicities $f_{i,BC}$ for the B-C bond in the CuBC_2 compounds.

Compound	χ_{BC}[a]	D_{BC}[b]	d_{BC} (Å)	Ref.	$f_{i,BC}$	$f_{i,BC}$ (Neumann)
$CuAlS_2$	4.26	1.0000	2.239	16, 17	0.60	0.62
$CuGaS_2$	5.59	1.0975	2.224	16	0.52	0.55
			2.235	17	0.53	
$CuInS_2$	6.02	1.1650	2.517	16, 17	0.62	0.60
$CuAlSe_2$	4.76	1.0975	2.347	16	0.63	0.65
			2.3578	18	0.63	
$CuGaSe_2$	6.80	1.2093	2.417	16	0.55	0.55
			2.4183	15	0.56	
			2.3756	15	0.54	
$CuInSe_2$	7.30	1.2876	2.598	16	0.61	0.60
			2.5962	14	0.61	
			2.559	14	0.60	
$CuAlTe_2$	7.19	1.1650	2.572	19	0.57	0.56
			2.558	20	0.56	
			2.5842	21	0.57	
$CuGaTe_2$	9.17	1.2876	2.590	19	0.51	0.51
			2.577	13	0.51	
$CuInTe_2$	9.35	1.3739	2.763	19	0.59	0.57
			2.816	13	0.60	

[a] After Neumann (Ref. 8).

[b] After Levine (Ref. 7).

$$\Delta E_g^S = 19.64(7)\left[\frac{1}{4} - x[\text{anion}]\right], \qquad \Delta E_g^{\text{chem}} = -2.8(6) + 0.16(2)\,\alpha_d \tag{11}$$

(deviations in last place digits are in brackets).

The values of the band-gap anomalies were compiled by Jaffe and Zunger,[12] while the anion positions in the lattice can be taken from another authors.[12–20] This fact allows us to estimate, using Eqs. (10) and (11), the structural and chemical contributions and hence the d character for the tellurides and for the rest of the considered compounds. By means of Eq. (9), the effective number of Cu valence electrons, Z_{Cu}, can also be computed. Table II summarizes the band-gap anomaly values, the anion positions, the estimated structural and chemical contributions, and the estimated d character and effective number of Cu valence electrons for these chalcopyrites. As it can be expected, the estimated α_d values are not far from the calculated ones, of Jaffe and Zunger.

Finally, to evaluate the Cu-C bond ionicities, the Cu-C bond susceptibilities have to be estimated. From the dielectric theory, the electronic dielectric constant ε for ABC_2 tetrahedrally coordinated crystals, composed of equal number of A-C and B-C bonds, is given by[7]

$$\varepsilon = 1 + \frac{1}{2}(\chi_{AC} + \chi_{BC}), \tag{12}$$

where χ_{AC} and χ_{BC} are the susceptibilities of A-C and B-C bonds, respectively, and ε can be considered as the static dielectric constant ε_0. From the estimated values of the static dielectric constant reported by Márquez and Rincón[9] for these compounds, and the B-C bond susceptibilities compiled by Neumann,[8] a set of Cu-C bond susceptibilities can be computed by means of Eq. (12), which are gathered in Table II.

The Cu-C bond ionicities $f_{i,\text{Cu-}C}$ have been computed using the previous values of the effective number of valence electrons, Z_{Cu}, and the Cu-C bond susceptibilities, $\chi_{\text{Cu-}C}$, for all the compounds considered in this work, in a similar way as in the case of the B-C bond. These values and corresponding bond lengths are also shown in Table II.

IV. DISCUSSION

From Tables I and II it can be seen that the $f_{i,BC}$ ionicities are, in general, larger than $f_{i,\text{Cu-}C}$ ones, accounting for the fact that Cu 3d electrons partly contribute to the Cu-C bond, making it more covalent, according to predictions by Jaffe and Zunger.[11] Moreover, the In-C bond can be considered, in general, as the most ionic bond in each C series, the Cu-C bond being the most covalent in the compounds with In content. The introduction of In in place of Ga highly increases the B-C bond ionicity and decreases the Cu-C one, in agreement with Jaffe and Zunger's calculations[11] for $CuInSe_2$. The calculated $f_{i,BC}$ ionicities are of the same order as those calculated by Neumann[8] (Table I), while the $f_{i,\text{Cu-}C}$ ones are lower, varying and of a broader range (Table II). This difference can be attributed mainly to the different effective number of valence electrons and dielectric constant values considered in the evaluation of the ionicities.

From Jaffe and Zunger's calculations[12] of the charge densities at the top of the valence band as a function of the anion position in the $CuInSe_2$ lattice, it can be deduced that as x[anion] increases the shared charge in the Cu-Se bond decreases, while it increases the shared charge in the In-Se

TABLE II. Susceptibilities $\chi_{\text{Cu-}C}$, static dielectric constants ε_0, correction factors D_{BC}, anion positions x[anion], interatomic distance $d_{\text{Cu-}C}$, and the references from which are taken, and structural ΔE_g^S and chemical ΔE_g^{chem} contributions and ionicities $f_{i,\text{Cu-}C}$ for the Cu-C bond in CuBC_2 compounds.

Compound	x(anion)	$d_{\text{Cu-}C}$ (Å)	Ref.	ΔE_g[a] (eV)	ΔE_g^S (eV)	ΔE_g^{chem} (eV)	α_d (%)	Z_{Cu}	ε_0[b]	$\chi_{\text{Cu-}C}$	D[c]	$f_{i,\text{Cu-}C}$	$f_{i,\text{Cu-}C}$ (Neumann)
$CuAlS_2$	0.275	2.351	16	2.41	−0.498	2.908	36.1	7.39	7.0	7.74	1.0000	0.58	0.78
	0.268	2.351	17		−0.361	2.771	35.2	7.48				0.58	
$CuGaS_2$	0.275	2.380	16	1.37	−0.498	1.868	29.5	8.05	7.7	7.81		0.60	0.77
	0.272	2.372	17		−0.439	1.809	29.1	8.09				0.60	
$CuInS_2$	0.214	2.288	16, 17	1.64	0.700	0.940	23.6	8.64	8.5	8.98		0.53	0.77
$CuAlSe_2$	0.269	2.470	16	1.47	−0.380	1.850	29.3	8.06	8.5	10.24	1.0575	0.55	0.79
	0.2578	2.4468	18		−0.160	1.630	28.0	8.20				0.54	
$CuGaSe_2$	0.250	2.417	16	1.00	−0.007	1.007	24.0	8.60	9.6	10.4		0.54	0.76
	0.249	2.411	15		0.013	0.987	23.9	8.61				0.54	
	0.263	2.457	15		−0.262	1.262	25.6	8.44				0.55	
$CuInSe_2$	0.224	2.425	16	1.29	0.504	0.786	22.6	8.74	10.9	12.5		0.46	0.77
	0.2242	2.4245	14		0.500	0.790	22.6	8.74				0.46	
	0.2348	2.4578	14		0.292	0.998	23.9	8.61				0.47	
$CuAlTe_2$	0.25	2.572	19	1.44	−0.007	1.447	26.8		10.9	12.61	1.0850	0.51	0.75
	0.2556	2.596	20		−0.117	1.557	27.5	8.25				0.52	
	0.2543	2.6144	21		−0.091	1.531	27.3	8.27				0.52	
$CuGaTe_2$	0.25	2.590	19	1.06	−0.007	1.067	24.4	8.56	12.7	14.23		0.47	0.81
	0.2566	2.623	13		−0.137	1.197	25.2	8.48				0.48	
$CuInTe_2$	0.225	2.585	19	0.93	0.484	0.446	20.4	8.96	15.3	19.25		0.30	0.76
	0.2136	2.557	13		0.708	0.222	19.0	9.10				0.29	

[a] After Jaffe and Zunger (Ref. 12).

[b] After Márquez and Rincón (Ref. 9).

[c] After Levine (Ref. 7).

bond.[13] Thus x[anion] could be considered as a control of the balance between the ionicity and the covalency of the Cu-Se bond: the larger the x[anion] value, the more ionic the bond. This concept can be extended to all the compounds considered in this work. Figure 1 shows a plot of the effectivenumber of the Cu valence electrons, Z_{Cu}, versus the anion position: Z_{Cu} decreases with x[anion], applying this trend for all these Cu chalcopyrites, implying that as x[anion] increases the shared charge in Cu-C, and hence the covalency of this bond, decrease. In Fig. 2, the ionicity of the Cu-C bond is represented versus the anion position, increasing linearly with x[anion] for all the compounds, in accor-

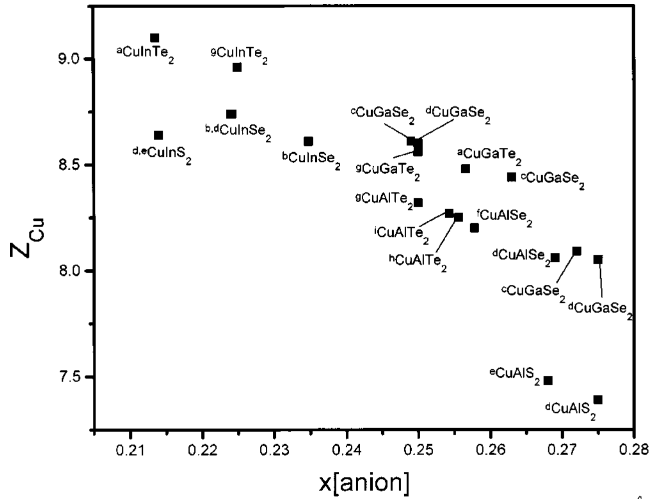

FIG. 1. Effective valence number of Cu electrons, Z_{Cu} vs the anion fractional coordinate values x[anion], taken from (a) Ref. 13, (b) Ref. 14, (c) Ref. 15, (d) Ref. 16, (e) Ref. 17, (f) Ref. 18, (g) Ref. 19, (h) Ref. 20, and (i) Ref. 21.

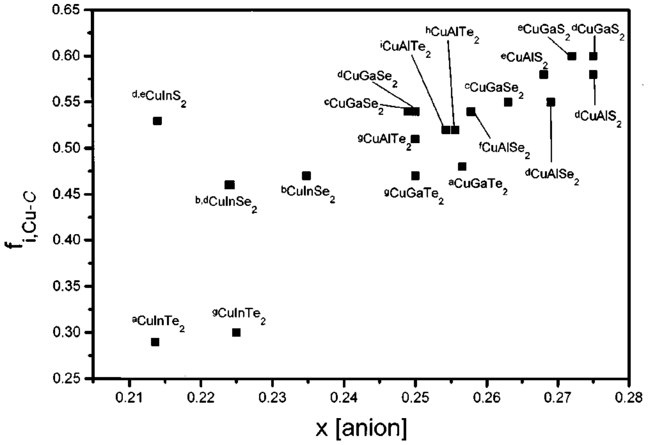

FIG. 2. Cu-C bond ionicities $f_{i,\text{Cu-}C}$, vs the anion fractional coordinate values x[anion], taken from (a) Ref. 13, (b) Ref. 14, (c) Ref. 15, (d) Ref. 16, (e) Ref. 17, (f) Ref. 18, (g) Ref. 19, (h) Ref. 20, and (i) Ref. 21.

dance with Z_{Cu}, and indicating that the anion position in the lattice can be taken as a good estimation of the Cu-C bond ionicity.

V. CONCLUSIONS

The bond ionicities of several CuBC_2 (B = Al, Ga, In and C = S, Se, Te) chalcopyrite compounds were estimated. The effective number of Cu valence electrons has been estimated by means of the α_d character considering Jaffe and Zunger's band-structure calculations in chalcopyrite compounds, and performing a simple extrapolation for Te compounds. To evaluate the bond ionicities, a set of Cu-C bond susceptibilities has been proposed. The $f_{i,\mathrm{Cu}\text{-}C}$ bond ionicities were found to increase with the atomic fractional coordinate of the C atom, x[anion], indicating that the anion position is a good estimation of the Cu-C bond ionicity.

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