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Dielectric properties of I-III-VI$_2$-type chalcopyrite semiconductors

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Dielectric properties of I-III-VI$_2$-type ternary chalcopyrite semiconductors, including linear and second order nonlinear optical susceptibilities at 10.6 μm, have been quantitatively studied from the chemical bond viewpoint. Contributions from each type of constituent chemical bond, i.e., I — VI and III — VI bonds, to the total linear and nonlinear optical properties of these compounds at 10.6 μm have been theoretically determined. The chemical bond method quantitatively expresses the trends in the dielectric properties of these compounds, which is helpful for carrying out modeling of their properties.

I. INTRODUCTION

For more than 20 years, chalcopyrite semiconductors with the formula I-III-VI$_2$ (where I, III, and VI represent elements in the corresponding columns of the periodic table) have attracted much attention due to their potential applications in nonlinear optical (NLO) devices, detectors, solar cells, etc.[1] As the chalcopyrite crystal structure is noncentrosymmetric, these compounds possess the essential property of a nonzero NLO tensor which can be quite large. Some chalcopyrite semiconductors that are part of the large family of I-III-VI$_2$ compounds, such as AgGaS$_2$, AgGaSe$_2$, etc., have become useful in NLO device applications with strong commercial possibilities. It is of interest to ask whether other materials in this class, or mixed crystals and alloys of two end compounds of this class, might offer excellent NLO responses. More generally, it is of interest to understand the origin of the NLO responses in these I-III-VI$_2$-type materials and to study the trends within this family of compounds. In the present work, our choice of I, III, and VI atoms allows us to consider the trends in the group I, group III, and group VI atoms separately in this class of materials with the general formula I-III-VI$_2$.

I-III-VI$_2$-type chalcopyrite semiconductors crystallize in the space group $I\overline{4}2d$ with four formula units in each unit cell, which is a ternary analog of the diamond structure and essentially a superlattice (or superstructure) of zinc blende. Like the atoms in diamond and zinc blende structures, each constituent atom in these ternary compounds, I, III, and VI, is tetrahedrally coordinated to four neighboring atoms. Thus there is much research interests in their hardness (e.g., Refs. 2–4) and pressure-induced behaviors (e.g., Refs. 5 and 6). Fundamental work has been done on various structurally similar III-V and II-IV-V$_2$ semiconductors.[7–9] Yet up to now there is no comprehensive work that concerns the second-order NLO behavior of these I-III-VI$_2$-type chalcopyrite semiconductors, although their potential NLO applications have been emphasized.

A comprehensive understanding of the origin of the optical nonlinearity of NLO crystalline materials is one of the most interesting subjects in the area of nonlinear optics, and has been intensively studied. Various theoretical methods starting from Miller's empirical rule up to the current first-principles calculations—at different approximation levels and from different starting points[10–15]—have been applied to this subject. In the current work, we will present a quantitative study on these interesting semiconductor compounds, which is based on the chemical bond method.

One of the most interesting aspects of these I-III-VI$_2$-type chalcopyrite semiconductors is the electronic configuration of the group I transition metal ion. Cu has the ground state electron configuration $[\mathrm{Ar}]3d^{10}4s^1$ (shell structure 2.8.18.1) and Ag the ground state electron configuration $[\mathrm{Kr}]4d^{10}5s^1$ (shell structure 2.8.18.18.1). Such electron configurations allow the d electrons to participate in the chemical bonding of the crystal. Hence, it is of great interest to know how many of the d electrons contribute to the bonds and in what manner they influence NLO responses in these I-III-VI$_2$-type compounds. Previous calculations[16–21] on this topic have shown important contributions from d electrons to the I — VI bonds in chalcopyrite compounds, yet these works have not given us an explanation of their NLO behaviors. In the present work we will follow the principal assumptions made previously[16–21] and treat d electrons as addition to the valence electrons of the type I ions that participate in the formation of I — VI bonds. The contributions from these modified I — VI bonds to the total linear (i.e., refractive indices n_o) and second-order nonlinear (i.e., nonlinear optical susceptibility tensor coefficients d_{36}) optical responses of these I-III-VI$_2$ type chalcopyrite semiconductors will be quantitatively scaled.

II. THE CHEMICAL BOND METHOD

The dielectric theory of solids proposed by Phillips and van Vechten (also referred to as PV theory),[22,23] the bond-charge model developed by Levine,[11,24] and the bond-valence model perfected by Brown[25,26] show us that chemical bonding behavior and related bond parameters of a crystal are the important indices that allow us to properly express complicated interactions among all constituent atoms or ions in a real crystal. The chemical bond is thus one of the effective starting points in understanding the complex relationship between composition, crystallographic structure and chemical and physical properties of solids.

The original PV theory can successfully deal with chemical bond properties of binary crystals, e.g., $A^N B^{8-N}$-type

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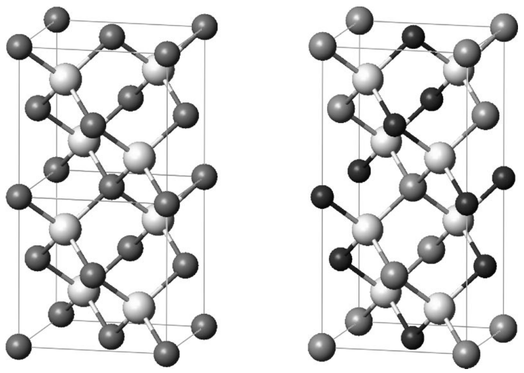

FIG. 1. Zinc blende (left) and chalcopyrite (right) crystallographic structures. Left: Two unit cells of the zinc blende lattice (dark gray, group II ion, light gray, group VI ion). Right: One unit cell of the chalcopyrite lattice (black, group I ion; dark gray, group III ion; light gray, group VI ion).

crystals[22,23] formed from A and B atoms with valencies N and $8-N$, respectively. Levine improved this theory and made it applicable for various types of multibond crystals.[11,24] As shown in previous publications,[15,27] the chemical bond method regards a complex crystal as the combination of all constituent chemical bonds. That means that a multibond crystal can be theoretically decomposed into a complete set of single bonds describing all constituent atoms or ions in their detailed chemical bonding structures. Any specific chemical bond A — B in a multibond crystal $A_aB_bD_dG_g\ldots$ can be expressed as a subformula

$$\frac{N(B-A)a}{N_{CA}}AB_{N(A-B)bN_{CA}/N(B-A)aN_{CB}} \tag{1}$$

where $A,B,D,G,\ldots$ represent different elements or different sites of an element in the crystal formula, and $a,b,d,g,\ldots$ represent the quantities of the corresponding element, $N(B-A)$ represents the number of B ions in the coordination group of the A ion, and N_{CA} represents the total number of ions that can be considered as bonded ions in the first coordination sphere of ion A. The prefix $N(B-A)a/N_{CA}$ represents the ratio between the number of B ions and the total number of ions bonded to the central A ion, and the subscript $[N(A-B)bN_{CA}]/[N(B-A)aN_{CB}]$ represents the ratio of the element B to A. Each type of bond has its specific subformula, and the sum of all subformulas equals the complete crystal formula (bond-valence equation). On the basis of this idea, physical properties can be calculated for simple single bonds and added up geometrically to yield the macroscopic properties of the crystal. During the decomposition of a multibond crystal into its constituent single chemical bonds, the charge-neutrality principle in any crystal formula must be obeyed; furthermore, each atom shares its valence as equally as possible among the bonds that it forms.[25] The following two network equations (with the same meaning as proposed by Brown[25]) should always be obeyed:

$$\sum_B s_{AB}=V_A\,,\quad \sum_{\text{loop}} s_{AB}=0, \tag{2}$$

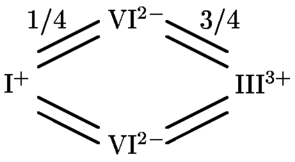

FIG. 2. Bond graph of I-III-VI$_2$-type ternary semiconductors. Valences of atoms and theoretical valences of the bonds are shown.

where each atom A in the corresponding lattice is assigned a formal charge equal to its atomic valence or oxidation state (V_A) and each bond between atoms A and B is assigned a bond valence (s_{AB}). The sum of the bond valences (each with appropriate algebraic sign according to the bond direction) at each node atom in the network equals its formal charge; the sum around any loop is zero.

The above idea allows PV theory and Levine's model to be successfully applied to any kind of multibond crystal. As shown previously,[15,27] the chemical bond method regards certain macroscopic physical properties of a crystal as the combination of the contributions of all constituent chemical bonds. Thus the linear and nonlinear optical properties of any crystal can be calculated by using the appropriate geometric sum of the corresponding properties of its constituent chemical bonds.

In a multibond crystal, the linear optical property χ can be ascribed to contributions χ^μ from the various types of bonds,

$$\chi=\sum_\mu F^\mu\chi^\mu=\sum_\mu N_b^\mu\chi_b^\mu, \tag{3}$$

where F^μ is the fraction of bonds of type μ composing the actual crystal. N_b^μ is the number of chemical bonds of type μ per cm^3. χ_b^μ is the susceptibility of a single bond of type μ.

$$\chi^\mu=(4\pi)^{-1}(\hbar\Omega_p^\mu/E_g^\mu)^2, \tag{4}$$

where Ω_p^μ is the plasma frequency, E_g^μ is the average energy gap between the bonding and the antibonding states, and $(E_g^\mu)^2=(E_h^\mu)^2+(C^\mu)^2$, where C^μ and E_h^μ are the average energy gaps due to ionic and covalent effects, respectively.[11,15,24,27] Furthermore, the fractions of ionic and covalent characteristics of the individual bonds, f_i^μ and f_c^μ, are defined by

$$f_c^\mu=(E_h^\mu)^2/(E_g^\mu)^2,\quad f_i^\mu=1-f_c^\mu. \tag{5}$$

Chemical bond nonlinearities are evaluated on the basis of linear results by means of a geometrical addition of nonlinear contributions d_{ij}^μ of all bonds μ.[11] The corresponding macroscopic property is the NLO tensor coefficient d_{ij} which can be expressed as

$$d_{ij}=\sum_{\mu}\left\{\frac{G^{\mu}_{ij}N^{\mu}_{b}(0.5)\{[(Z^{\mu}_{A})^{*}+n(Z^{\mu}_{B})^{*}]/[(Z^{\mu}_{A})^{*}-n(Z^{\mu}_{B})^{*}]\}f^{\mu}_{i}(\chi^{\mu}_{b})^{2}}{d^{\mu}q^{\mu}}+\frac{G^{\mu}_{ij}N^{\mu}_{b}s(2s-1)[r^{\mu}_{0}/(r^{\mu}_{0}-r^{\mu}_{c})]^{2}f^{\mu}_{c}(\chi^{\mu}_{b})^{2}\rho^{\mu}}{d^{\mu}q^{\mu}}\right\}, \tag{6}$$

where G^{μ}_{ij} is the geometrical contribution of chemical bonds of type μ, and $(Z^{\mu}_{A})^{*}$ and $(Z^{\mu}_{B})^{*}$ are the effective valence electron numbers of A (cation) and B (anion) ions, respectively. n is the ratio of numbers of the two elements B and A in the bond-valence equation.[27] d^{μ} is the bond length of the μ-type bond, q^{μ} is the bond charge of the μth bond, $s=2.48$, $r^{\mu}_{0}=d^{\mu}/2$, and $r^{\mu}_{c}=0.35r^{\mu}_{0}$ is the core radius. $\rho^{\mu}=(r^{\mu}_{A}-r^{\mu}_{B})/(r^{\mu}_{A}+r^{\mu}_{B})$ is the difference in the atomic sizes, where r^{μ}_{A} and r^{μ}_{B} are the covalent radii of atoms A and B. All the above parameters can be quantitatively deduced from the detailed chemical bonding structures of all constituent atoms, as described in previous publications.[15,27]

III. APPLICATION TO CHALCOPYRITES

The semiconductors of the I-III-VI$_2$ family are isoelectronic with the zinc blende II-VI compound semiconductors.

TABLE I. Chemical bond parameters and linear and second-order nonlinear optical contributions of all constituent bonds in I-III-VI$_2$-type chalcopyrite semiconductors at 10.6 μm.

Crystal	Bond	Bond length d^{μ} (AA)	Bond covalency f^{μ}_{c}	Bond susceptibility χ^{μ}	Bond charge q^{μ}/e	Geometry factor G^{μ}_{36}	NLO tensor contribution d^{μ}_{36} (pm/V)
CuAlS$_2$	Cu — S	2.380	0.323	5.212	0.761	0.191	–16.510
	Al — S	2.219	0.289	4.093	0.878	0.191	2.857
CuAlSe$_2$	Cu — Se	2.471	0.312	5.788	0.720	0.191	–18.703
	Al — Se	2.347	0.284	4.627	0.817	0.192	7.159
CuAlTe$_2$	Cu — Te	2.572	0.300	6.154	0.700	0.192	–16.159
	Al — Te	2.572	0.278	5.423	0.745	0.192	18.630
CuGaS$_2$	Cu — S	2.380	0.359	5.645	0.731	0.191	–21.051
	Ga — S	2.224	0.289	4.235	0.862	0.191	2.133
CuGaSe$_2$	Cu — Se	2.417	0.458	7.451	0.659	0.192	–37.444
	Ga — Se	2.417	0.281	5.047	0.777	0.192	7.220
CuGaTe$_2$	Cu — Te	2.590	0.307	6.394	0.682	0.192	–17.933
	Ga — Te	2.590	0.278	5.785	0.720	0.192	19.557
CuInS$_2$	Cu — S	2.288	0.379	5.480	0.746	0.189	–23.101
	In — S	2.517	0.282	5.338	0.755	0.190	0.625
CuInSe$_2$	Cu — Se	2.424	0.318	5.685	0.728	0.191	–20.555
	In — Se	2.598	0.279	5.892	0.714	0.191	6.046
CuInTe$_2$	Cu — Te	2.585	0.290	6.060	0.703	0.191	–17.273
	In — Te	2.763	0.277	6.732	0.665	0.191	21.127
AgAlS$_2$	Ag — S	2.530	0.281	5.481	0.747	0.186	–21.641
	Al — S	2.257	0.291	4.372	0.850	0.189	3.601
AgAlSe$_2$	Ag — Se	2.571	0.289	6.006	0.707	0.189	–26.921
	Al — Se	2.429	0.283	4.983	0.785	0.191	9.280
AgAlTe$_2$	Ag — Te	2.710	0.277	6.465	0.679	0.192	–27.423
	Al — Te	2.636	0.278	5.714	0.725	0.192	23.195
AgGaS$_2$	Ag — S	2.605	0.214	4.498	0.870	0.183	–10.853
	Ga — S	2.235	0.294	4.534	0.836	0.187	2.607
AgGaSe$_2$	Ag — Se	2.601	0.292	6.251	0.693	0.188	–29.601
	Ga — Se	2.416	0.284	5.183	0.769	0.191	8.346
AgGaTe$_2$	Ag — Te	2.714	0.288	6.766	0.662	0.192	–31.101
	Ga — Te	2.640	0.278	6.026	0.705	0.192	23.417
AgInS$_2$	Ag — S	2.505	0.320	5.813	0.716	0.192	–33.077
	In — S	2.505	0.280	5.177	0.765	0.192	0.795
AgInSe$_2$	Ag — Se	2.610	0.278	5.884	0.713	0.192	–29.028
	In — Se	2.610	0.278	5.879	0.714	0.192	6.875
AgInTe$_2$	Ag — Te	2.756	0.282	6.797	0.660	0.192	–33.978
	In — Te	2.756	0.276	6.622	0.669	0.192	22.561

TABLE II. Ordinary refractive indices n_o and second-order NLO tensor coefficients d_{36} at 10.6 μm. Some available experimental data are also presented here. d_{36} tensor elements are in pm/V. All refractive indices without citations are interpolated values (see text). The data listed in parentheses are experimental results.

Compound	Refractive index n_o	NLO tensor coefficient d_{36}	Compound	Refractive index n_o	NLO tensor coefficient d_{36}
$CuAlS_2$	2.378	–13.65	$AgAlS_2$	2.435	–18.04
$CuAlSe_2$	2.492	–11.54	$AgAlSe_2$	2.549	–17.64
$CuAlTe_2$	2.606	2.47	$AgAlTe_2$	2.663	–4.23
$CuGaS_2$	2.437 [a]	–18.92 (14.5±4.4 [a])	$AgGaS_2$	2.349 [a]	–8.25 (11.1±1.7 [c])
$CuGaSe_2$	2.692 [b]	–30.22 (30±3 [b])	$AgGaSe_2$	2.592 [b]	–21.25 (33±3.3 [b, c])
$CuGaTe_2$	2.663	1.62	$AgGaTe_2$	2.720	–7.68
$CuInS_2$	2.532 [a]	–22.48 (9.6±2.9 [a])	$AgInS_2$	2.549	–32.28
$CuInSe_2$	2.606	–14.51	$AgInSe_2$	2.623 [b]	–22.15 (37.6±3.8 [b])
$CuInTe_2$	2.720	3.85	$AgInTe_2$	2.777	–11.42

[a] From Boyd *et al.* (Ref. 28).
[b] From Boyd *et al.* (Ref. 29).
[c] From Dmitriev *et al.* (Ref. 30).

Both zinc blende and chalcopyrite crystallographic structures are sketched in Fig. 1 for comparison. From the crystallographic viewpoint, the tetragonal unit cell of chalcopyrite can be regarded as a concatenation of two cubic unit cells of the zinc blende structure stacked on top of each other along the *c* axis. The group II ions of the zincblende structure are alternately replaced by group I transition metal ions and group III ions. Furthermore, the structure suffers a tetragonal distortion: the unit cell is slightly strained in the *c*-axis direction. According to the following equation [derived using formula (1)], the chalcopyrite structure can be decomposed into two sorts of bonds:

$$\mathrm{I-III-VI_2=I-VI+III-VI.} \tag{7}$$

The macroscopic properties of the I-III-VI_2 compounds can be referred to the microscopic contributions from these two basic structural units—I-VI and III-VI—connected in an infinite network. For crystals, due to their periodicity, this infinite network can be reduced to a finite network consisting of only a single formula unit; the graph of this network for I-III-VI_2-type compounds is shown in Fig. 2. From this description we can derive the formal number of valence electrons—to be used in further calculations—of each of the ions. Considering the different bonds, for the group III and group VI ions we get the values $(Z_{\mathrm{III}}^{\mathrm{III-VI}})^*=3$, $(Z_{\mathrm{VI}}^{\mathrm{III-VI}})^*=9$, and $(Z_{\mathrm{VI}}^{\mathrm{I-VI}})^*=3$. However, for the group I ions, an additional complication shows up.

While the number of valence electrons for the group III and group VI ions can be treated as fixed, for the value of $(Z_{\mathrm{I}}^{\mathrm{I-VI}})^*$ a substantial portion of the *d* electrons of the transition metal must be formally included into the number of valence electrons. The amount depends on the specific compound. How to treat this ''*d*-electron problem'' is one of the key points and one of the most interesting aspects of the current calculations. Different approaches have been chosen in the past to account for this number. Neumann,[17] e.g., used a fixed value, including all of the *d* electrons, Merino *et al.*[21] derived values from band structure calculations of Jaffe and Zunger.[18,19] In the present work, we choose a different fitting

TABLE III. Effective number of valence electrons $(Z_{\mathrm{Cu}})^*$ and bond ionicities of Cu based I-III-VI_2-type semiconductors. In the evaluation of the bond ionicities of Cu — VI bonds, Neumann used a value of $(Z_{\mathrm{Cu}}^{\mathrm{Cu-VI}})^*=11$ (Ref. 17), which means that the Cu 3*d* electrons were considered to fully contribute to the Cu — VI bonds. For the bond ionicities of the III — VI bonds $(f_i^{\mathrm{III-VI}})$ Merino *et al.* (Ref. 21) used Neumann's data (Ref. 17).

	$(Z_{\mathrm{Cu}}^{\mathrm{Cu\text{-}VI}})^*$		$f_i^{\mathrm{Cu\text{-}VI}}$			$f_i^{\mathrm{III\text{-}VI}}$	
Compound	Ref. 21	This work	Ref. 17	Ref. 21	This work	Ref. 17	This work
$CuAlS_2$	7.39	8.33	0.78	0.58	0.677	0.62	0.711
$CuAlSe_2$	8.06	8.46	0.79	0.55	0.688	0.65	0.716
$CuAlTe_2$	8.25	8.61	0.75	0.52	0.700	0.56	0.722
$CuGaS_2$	8.05	7.83	0.77	0.60	0.641	0.55	0.711
$CuGaSe_2$	8.60	6.73	0.76	0.54	0.542	0.55	0.719
$CuGaTe_2$	8.56	8.47	0.81	0.47	0.693	0.51	0.722
$CuInS_2$	8.64	7.64	0.77	0.53	0.621	0.60	0.718
$CuInSe_2$	8.74	8.39	0.77	0.46	0.682	0.60	0.721
$CuInTe_2$	8.96	8.80	0.76	0.30	0.710	0.57	0.723

TABLE IV. Values of the ionic and covalent contributions of the individual bonds to the nonlinear susceptibility [first and second terms in Eq. (6)] for I-III-VI$_2$-type semiconductors.

Compound	Bond	Ionic	Vovalent	Compound	Bond	Ionic	Covalent
		contribution				contribution	
CuAlS$_2$	Cu — S	−10.598	−5.911	AgAlS$_2$	Ag — S	−12.077	−9.563
	Al — S	6.005	−3.148		Al — S	7.667	−4.065
CuAlSe$_2$	Cu — Se	−15.458	−3.245	AgAlSe$_2$	Ag — Se	−17.842	−9.079
	Al — Se	9.092	−1.932		Al — Se	11.770	−2.490
CuAlTe$_2$	Cu — Te	−21.366	5.207	AgAlTe$_2$	Ag — Te	−25.483	−1.940
	Al — Te	15.421	3.209		Al — Te	19.206	3.990
CuGaS$_2$	Cu — S	-12.999	−8.051	AgGaS$_2$	Ag — S	-6.711	−4.142
	Ga — S	6.583	−4.450		Ga — S	8.539	−5.931
CuGaSe$_2$	Cu — Se	−28.472	−8.972	AgGaSe$_2$	Ag — Se	−19.543	−10.058
	Ga — Se	11.255	−4.034		Ga — Se	13.111	−4.765
CuGaTe$_2$	Cu — Te	−23.897	5.963	AgGaTe$_2$	Ag — Te	−28.827	−2.274
	Ga — Te	18.429	1.129		Ga — Te	22.066	1.350
CuInS$_2$	Cu — S	−13.915	−9.186	AgInS$_2$	Ag — S	−17.508	−15.568
	In — S	12.001	−11.376		In — S	12.927	−12.132
CuInSe$_2$	Cu — Se	−16.925	−3.629	AgInSe$_2$	Ag — Se	−19.498	−9.529
	In — Se	17.308	−11.262		In — Se	19.450	−12.575
CuInTe$_2$	Cu — Te	−22.622	5.349	AgInTe$_2$	Ag — Te	−31.542	−2.435
	In — Te	27.656	−6.528		In — Te	29.480	−6.919

approach using experimental data of the ordinary refractive index n_o as a reference.

In the calculation of the average energy gap due to the ionic effect,[11,15,24,27]

$$C^{\mu}=14.4b^{\mu}\exp(-k_s^{\mu}r_0^{\mu})[(Z_A^{\mu})^{*}-n(Z_B^{\mu})^{*}]/r_0^{\mu}, \quad (8)$$

we follow Levine's conclusion that the structural factor $b^{\mu}=0.089$ yields satisfactory results for a wide range of crystal classes, including zinc blende and wurtzite.[11,24] From the fit, using Eqs. (3)–(6) and (8), proper values for $(Z_{\mathrm{I}}^{\mu})^{*}$ can be derived.

Unfortunately, up to date there are only few experimental data available concerning the dielectric properties of the I-III-VI$_2$-type compounds.[28–30] Therefore, we deduce the missing values of the refractive indices using a linearized interpolation scheme based on the average atomic number of the compound.[31]

Crystallographic structure data for all I-III-VI$_2$ compounds we studied here are taken from Ref. 19. From these data the bond geometries can be derived. On the basis of this structural information and following the decomposition formula Eq. (7), the macroscopic optical properties for each I-III-VI$_2$ crystal can be calculated by summing up the microscopic contributions of its corresponding constituent chemical bonds.

IV. RESULTS AND DISCUSSION

Starting from the chemical bonding structures of all constituent atoms in the I-III-VI$_2$ compounds, we have quantitatively calculated chemical bond parameters of all constituent chemical bonds, and further their quantitative contributions to the total linear and nonlinear optical properties of the whole crystal. Calculated results are summarized in Table I.

The restrictions imposed by the crystal symmetry[32] and the so-called Kleinman symmetry conditions on NLO tensor coefficients,[33] yield only one independent nonzero NLO tensor coefficient—d_{36}—for the I-III-VI$_2$-type chalcopyrite semiconductors. On the basis of the geometrical sum of all nonlinear contributions of constituent chemical bonds d_{36}^{μ}, the total NLO tensor coefficient d_{36} can be quantitatively calculated. The final results and available experimental data, as well as the interpolated refractive indices at 10.6 μm, are listed in Table II. A comparison between calculated and experimental data shows that the current work reasonably explains the nonlinear dielectric behavior of the I-III-VI$_2$ family of semiconductors.

A comparison of the bond ionicities calculated in the

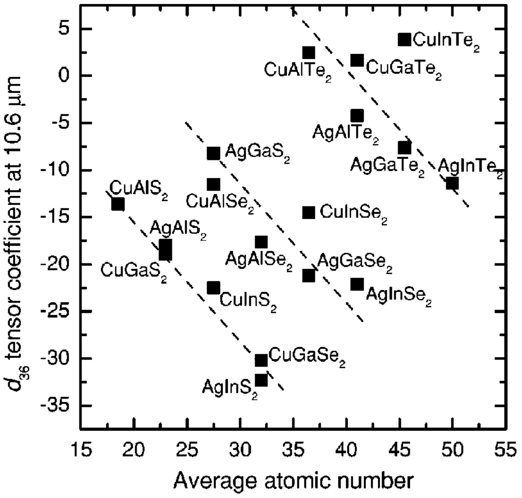

FIG. 3. Calculated second-order nonlinear optical susceptibilities of various I-III-VI$_2$-type ternary semiconductors plotted as a function of the crystal composition (average atomic number) of the compound (dashed lines are guides for the eye).

present work with previously calculated results for Cu-based I-III-VI$_2$-type compounds,[17,21] is summarized in Table III. The large differences between the results calculated by different authors can be ascribed to the following facts.

(1) Different approaches are used to determine the *d*-electron contribution to the formal valence of the group I transition metal ions.

(2) Dielectric responses at different wavelengths are concerned; the current work studies properties at 10.6 μm, while in other works static conditions are assumed.[17,21]

(3) Different methods are used to treat $(Z_{\mathrm{VI}})^*$. The present work determines the value for $(Z_{\mathrm{VI}})^*$ on the basis of its bond graph; the two types of bonds are treated differently. The other work[17,21] uses a fixed value of 6.0 (due to the outer shell electronic configuration s^2p^4). In fact, as shown in Fig. 2, the four bonds of the group VI ions are not equal; therefore, it is reasonable to deduce the effective valence electron number of ions from the corresponding bond graph.

The ionicity values show that the I — VI bonds are more covalent than the III — VI bonds (due to the strong *d*-electron effect of the I ions). This agrees well with previous conclusions of Jaffe and Zunger.[18,19]

Table I shows that there are differences in the contributions of the I — VI and III — VI bonds to the dielectric response, especially the nonlinear optical properties, of the I-III-VI$_2$-type compounds. In order to understand the property-changing trends in these materials more thoroughly, we compared the ionic and covalent contributions of the individual bonds. The ionic contribution is calculated from the first term in Eq. (6) (based[11] on the electronegativity difference of the two bonded atoms A and B), the covalent contribution from the second term (based on the atomic size difference of the two atoms[11]). The results are detailed in Table IV. Several trends can be derived: (1) The ionic contributions are always larger than the covalent ones. (2) The ionic contributions of the two different bonds in a compound tend to cancel. (3) In Te compounds the covalent contributions tend to a further cancellation of the remaining ionic contributions. These and other trends can also be found in the plot of the total second-order nonlinear optical susceptibilities of the compounds considered plotted as a function of the crystal composition (Fig. 3).

V. CONCLUSION

From the chemical bond viewpoint, we have analyzed second-order nonlinear optical properties of several Cu and Ag based I-III-VI$_2$-type semiconductors, which are potential candidate materials for frequency-doubling applications. Calculations of the contributions of the different constituent chemical bonds to the total dielectric response of the crystals demonstrate their individual role. The present work also quantitatively shows that the *d* electrons of the group I transition metal ions are one of the important factors that dominate the contributions of the I — VI bonds to the total optical response of the compound. The trends found in the chalcopyrite compounds investigated here provide important guidelines for future improvement of the nonlinear optical properties of these and similar materials. Furthermore, the present work shows that the I-III-VI$_2$-type compounds have predominantly ionic character of the chemical bond.

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