Calculation of Refractive Indices of Triple Chalcogenide Crystals

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$AgGaS_2$, $CdGa_2S_4$, $CdGa_2Se_4$ crystals belong to the large class of triple chalcogenide compounds. These crystals are widely used in various nonlinear optical devices. Therefore calculation of optical properties of these compounds is important.

In this work high frequency refractive indices are calculated by using Harrison's bond-orbital method.

For investigation of crystal properties, the calculated energies of the V_2 covalent bond and V_3 ionic bond are used. Using the above mentioned theory, it is possible to find out that the interaction of *s* and *p* orbitals of the cation and the anion is represented by the energy

$$\varepsilon_k = \frac{\varepsilon_s + \varepsilon_p}{2} \pm \sqrt{\left(\frac{\varepsilon_s - \varepsilon_p}{2}\right)^2 + f(k)^2 V_{sp\sigma}^2} \qquad (1)$$

where $f(k)^2$ depends on phases and orientations of neighboring orbitals and coincides with the number of neighbors around the given atom (coordination number N_c). The first and the second terms under the square root represent V_3 and V_2 energies, respectively. Because of the interaction of *p* orbitals of both the cation and the anion, energy ε_s of the cation in (1) is replaced by ε_p, and the energy V_2 will represent the interaction of these orbitals. Table 1 contains the values of Hartree–Fock terms for atoms of $AgGaS_2$ and $CdGa_2S(Se)_4$ crystals [1]. The method of calculation is presented in [2].

Table 1. Hartree–Fock values for the valence levels

Energy level	Ag	Cd	Ga	S	Se
ε_s, eV	-5.99	-7.21	-11.55	-24.02	-22.86
ε_p, eV	-3.29	-3.89	-5.67	-11.60	-10.68

For comparison with experimental data, we calculated the dielectric susceptibility χ. Experimental data are taken from [3, 4, 5], where the dielectric susceptibility was defined as the squared high frequency refractive index at $\omega \rightarrow 0$ [6]. The results of calculations are presented in Table 2.

Table 2. Calculated parameters of $AgGaS_2$ and $CdGa_2S(Se)_4$ crystals

Bond type	N_c	d, Å	V_2, eV	V_3, eV	α, Å^3	X	γ	N_{theor}	N_{exp}
$AgGaS_2$									
Ag-S (s-p)	4	2.556	3.31	2.80	5.847	0.044	0.5	1.97	2.37
Ga-S (p-p)	4	2.276	4.06	2.97	17.717	0.188	1.5		

$CdGa_2S_4$									
Cd-S (s-p)	4	2.52	3.41	2.19	12.552	0.098	0.5	2.25	2.34
Cd-S (p-p)	4	2.52	3.31	3.85	6.575	0.051	1.5		
Ga-S (p-p)	4	2.31	3.94	2.96	17.199	0.174	1.5		
$CdGa_2Se_4$									
Cd-Se (s-p)	4	2.59	3.23	1.73	24.061	0.173	0.5	2.46	2.53
Cd-Se (p-p)	4	2.59	3.14	3.39	9.113	0.066	1.5		
Ga-Se (p-p)	4	2.59	3.14	2.50	22.687	0.163	1.5		

By determining the polarizability of $AgGaS_2$ and $CdGa_2S(Se)_4$ crystals and susceptibility χ, it is possible to write the refraction index as $n^2 = 1 + 4\pi\chi$. In such a way, we obtain the values presented in Table 2. The performed calculation shows a satisfactory agreement with experiment: 96 and 97% for $CdGa_2S_4$ and $CdGa_2Se_4$, respectively, and 83% for $AgGaS_2$.

Thus, the results obtained in the present work confirm the possibility of application of this approximation for analysis of optical properties of complex crystalline compounds with a large number of atoms in a unit cell.

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