Band Gap Anomaly in Ternary Chalcopyrite Semiconductors, the Role of p-d Hybridization.

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Summary. — The anomalous reductions in the energy band gap of the chalcopyrite semiconductors as compared to their relative binary analogs are estimated quantitatively by using a simple relation that involves quantum defect electronegativity scale and the average principal quantum number. The chemical and the structural contribution to this anomaly is discussed in details and it is shown that the relation can be easily extended to explain the variation in the band gap of some cross-substitutional alloys.

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1. - Introduction.

The crystal structure of a ternary I-III-VI$_2$ and II-IV-V$_2$ compound is related to its respective II-VI and III-V zincblende arrangement, the former being a logical extension of the latter. This structural resemblance can provide valuable information regarding the quantitative predictions of various physical properties of the ternary compounds from those of the binary analogs (1). The chalcopyrite may be considered as a superlattice of the zincblende in which the two kinds of cations cause the doubling of the unit cell along the c-axis. The two structures differ in that the chalcopyrite has a $c/a$ ratio generally different from 2 (unit cell distortion) and an anion sublattice, which is slightly distorted with respect to the f.c.c. zincblende sublattice (internal $u$ distortion, $u \neq 0.250$).

Furthermore, the band gaps of the ternary compounds are substantially smaller than those of the binary parents.

Recently, JAFFE and ZUNGER have proposed a theory of the band gap anomaly in the I-III-VI$_2$ chalcopyrite semiconductors relative to their II-VI zincblende analogs (2). Their approach is based on calculating self-consistently the electronic band structure of these materials in the local-density approximation using the potential-variational-mixed-basis scheme (3,4).

They have shown that the problem can be analysed in terms of a chemical factor, $\Delta E_{chm}^b$, and a structural factor, $\Delta E_u^s$, such that the total downshift in the band gap is given by

$$\Delta E_g^{tot} = \Delta E_{chm}^b + \Delta E_u^s.$$ 

The chemical contribution consists of a hybridization of the noble metal $d$ levels with $p$ levels of the anions and a cation electronegativity part. The structural contribution to the downshift in energy is due to the existence of bond alteration, resulting from the nonideal anion displacements ($u - \frac{1}{2} \neq 0$) and, to a lesser extent, from the tetragonal distortion ($2 - c/a \neq 0$). They further establish the relationship between these band gap anomalies and structural deformations. Notwithstanding the importance of quantum-mechanical sophisticated calculations, there is still need for semi-empirical relations, which are interesting to look for systematics in the available experimental data.