

Correlation between the unit cell volume and bulk modulus with the average covalent radii for $A^I-B^{III}-C^{VI}_2$ and $A^{II}-B^{IV}-C^V_2$ chalcopyrite compounds

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Abstract

All the physical properties of a crystal are related to the virtual geometrical lattice and the real atomic basis associated to it. If the geometrical lattice is fixed (all the compounds under study belongs to the same space group), the physical properties, from a compound to another, will differentiate only by the real atomic basis. i.e. the physical properties can be compared as a function of structural parameters as the lattice parameter, bond length, atomic radii, or similar. In this work, we will study compounds that crystallize in the chalcopyrite structure (s.g. I42d) using as structural parameter, the average covalent radii (\bar{r}_c). We will show that a good correlation exists between the unit cell volume ($V = a^3 c$) and the isothermal bulk modulus (B_0) with \bar{r}_c , for $A^I-B^{III}-C^{VI}_2$ and $A^{II}-B^{IV}-C^V_2$ chalcopyrite compounds.

Key words: Bulk modulus; covalent radius; semiconductors.

Correlación entre el volumen de la celda unitaria y el módulo de volumen con el radio covalente promedio para compuestos calcopiríticos $A^I-B^{III}-C^{VI}_2$ y $A^{II}-B^{IV}-C^V_2$

Resumen

Todas las propiedades físicas de un cristal están relacionadas con la red geométrica virtual y la base atómica real asociada. Si la geometría de la red se fija (todos los compuestos bajo estudio pertenecen al mismo grupo espacial), las propiedades físicas, de un compuesto a otro, se diferenciarán solamente por la base atómica real, es decir, las propiedades físicas pueden compararse como una función de los parámetros estructurales, como el parámetro de la red, la longitud del enlace, radios atómicos, o similares. En este trabajo, estudiaremos compuestos que cristalizan en la estructura calcopirita (grupo espacial I42d) usando como parámetro estructural, el radio covalente promedio (\bar{r}_c). Demostraremos que existe una correlación entre el volumen de la celda unitaria ($V = a^3 c$) y el módulo isotérmico de volumen (B_0) con \bar{r}_c , para los compuestos calcopiríticos $A^I-B^{III}-C^{VI}_2$ y $A^{II}-B^{IV}-C^V_2$.

Palabras clave: Módulo de volumen; radio covalente; semiconductores.

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1. Introduction

Zunger et al (1) previously studied the dependency of the lattice parameters with the covalent radii for chalcopyrite materials. This model, based on the existence of bond alternation ($R_{AC} \neq R_{BC}$), allows calculation of the basic crystallographic parameters, α (the lattice parameter) and μ (the anion displacement) in agreement with experimental data, with the exception of η (the tetragonal distortion).

Respecting the isothermal bulk modulus (B_0) of chalcopyrite materials, Neumann (2) and Grima (3) have obtained semi empirical expressions for B_0 as a function of the unit cell volume and the average bond length, respectively. In both cases, the agreement with experimental values is relatively good, if we take into account the $\pm 10\%$ experimental error in average committed in the calculation of B_0 from experimental data.

The aim of this work is to use the average covalent radii (\bar{r}_c) as structural parameter, defined as $\bar{r}_c = (r_A + r_B + 2r_C) / 4$, where r_A , r_B and r_C are the individual atomic covalent radius (4) and produce simple empirical expressions for the volume of the unit cell and the isothermal bulk modulus of chalcopyrite compounds with equal (or better) agreement than previous models.

2. Correlation between the average covalent radii, \bar{r}_c and the volume ($V=a^2c$) of the unit cell

In Figure 1 and 2 it is shown the experimental unit cell volume, $V = a^2c$, as a function of the average covalent radii for chalcopyrite materials $A^I-B^{III}-C^{VI}_2$ and $A^{II}-B^{IV}-C^V_2$. The experimental lattice parameters, a and c , were obtained from literature (5). As it can be seen, V varies in a linear form with \bar{r}_c , and a linear fitting gives the empirical equations:

$$V [\text{\AA}^3] = (798 \pm 22) * \bar{r}_c [\text{\AA}] - (591 \pm 27) \quad \text{(for } A^I-B^{III}-C^{VI}_2) \quad [1]$$

$$V [\text{\AA}^3] = (722 \pm 41) * \bar{r}_c [\text{\AA}] - (513 \pm 51) \quad \text{(for } A^{II}-B^{IV}-C^V_2) \quad [2]$$

The fits are very good with a standard deviation of 7.9 and R-square (COD) of 0.993 for $A^I-B^{III}-C^{VI}_2$ and a standard deviation of 10.4 and R-square (COD) of 0.981 for $A^{II}-B^{IV}-C^V_2$.

These relations are very important for indexing purpose of x-ray diffraction patterns when the quantity of available peaks (or lines) are not enough. It reduces considerable the computing time and allows a more precise values for the tetragonal distortion, c/a .

3. Correlation between average covalent radii \bar{r}_c and the isothermal bulk modulus, B_0

In Figure 3 it is shown the experimental bulk modulus B_0 as a function of \bar{r}_c . In this case, experimental values of B_0 , for the same compound, have a relevant dispersion and are sometimes contradictory according to the accepted behavior that $B_{0(ABS2)} < B_{0(ABS2)} < B_{0(ABTe2)}$. Any way, we include all the experimental values available (unfortunately, the data for $A^{II}-B^{IV}-C^V_2$ compounds are very scarce) because although some bad point could deviate the fitting it is important to see as a whole the entire available experimental data.

It would be impulsive a linear fit over the experimental points but this is physically wrong. The variations of the bulk modulus with interatomic distance (or bond length), for covalent materials, follow a power law of the type $B_0 = mr^{-n}$ (6-8). The solid lines in Figure 3 fits experimental values for chalcopyrite materials whereas the broken lines is a fit using available date (experimental and *ab-initio* calculations) for covalent materials (9). The fitted curve for chalcopyrite materials (solid lines) seems to be shifted down from the more universal (broken lines)

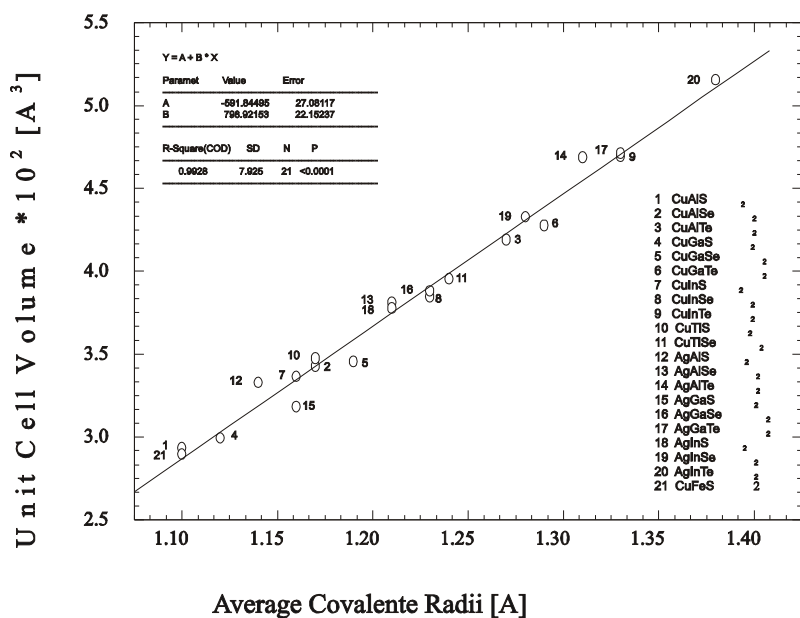


Figure 1. Experimental unit cell volume, $V = a^2c$ as a function of the average covalent radii for $A^I-B^{III}-C^{VI}$ chalcopyrite materials.

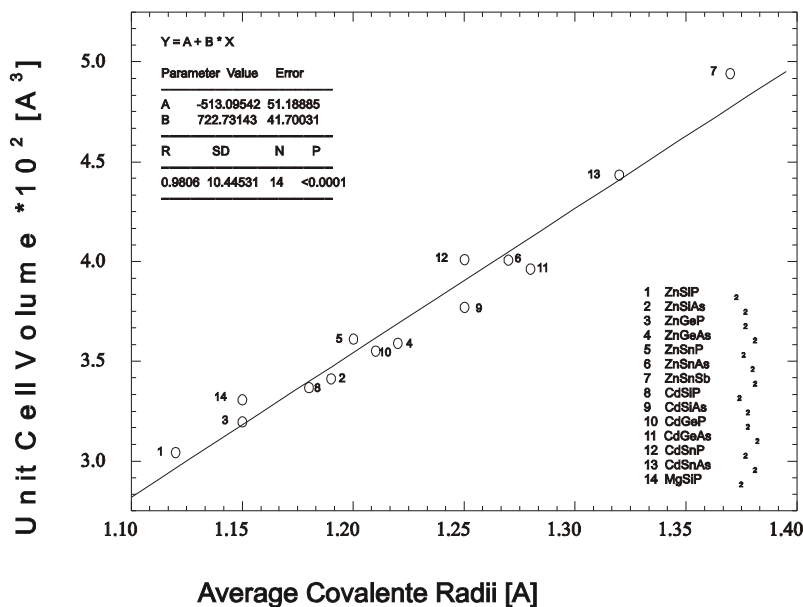


Figure 2. Experimental unit cell volume, $V = a^2c$ as a function of the average covalent radii for $A^{II}-B^{IV}-C^V$ chalcopyrite materials.

given by Grima et al. It could be explained if we take into account the order \rightarrow disorder phase transition that occurs in chalcopyrite

materials when temperature or pressure is applied. This “slow near second – order” transition “soft” gradually the frequency of

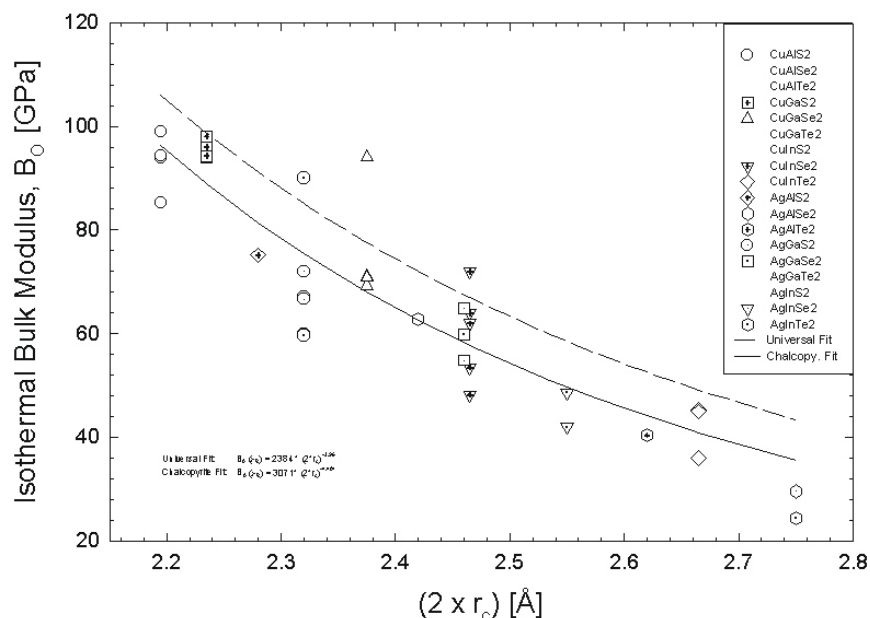


Figure 3. Isothermal bulk modulus vs two times the average covalent radii.

the phonon Γ_1 , in such a way that pretransitional (PT) effects are observed at pressure or temperature very much lower than the pressure or temperature transitions critical values (T_c , p_c). In the equation of state this PT effect is observed as a sub-linearity of the first derivative of B_0 ($B' = dB_0/dP$), which, generally, is taken as a constant near to 4 (10). Experimentally, it had been observed by *in-situ* energy dispersion diffraction measurements under pressure and temperature, on HgTe sample (11-12) which exhibits a transition under pressure at 1,5 GPa, that PT effects can be observed (and measured) even before the pressure begins to be applied i.e. at 0 GPa. The effect on the variation of B_0 with P is "to bent" the dependency as it is shown for HgTe (11). The experimental values are lower than the hypothetical values if the order \rightarrow disorder phase transition is omitted.

4. Conclusions

We obtain very simple relations for the unit cell volume as a function of the average covalent radii for $A^I-B^{III}-C^{VI}_2$ and $A^{II}-B^{IV}-C^V_2$

chalcopyrite materials in such a way that no experimental knowledge *a priori* is necessary to give the unit volume with a precision of ≈ 2 for both families of materials.

We suggest that chalcopyrite materials have an analogous PT behavior as observed previously for HgTe and that the observed experimental values for B_0 are shifted down because of the PT effects of disorder.

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