Elastic properties of chalcopyrite structured solids

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ABSTRACT

Elastic properties (i.e. six independent elastic stiffness constants, C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}) of chalcopyrite structured solids were evaluated. Values of C_{11}, C_{33}, C_{44}, C_{66}, of $A^IB^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ chalcopyrite semiconductors exhibit a linear relationship when plotted against the k_BT_m/Ω (k_B = Boltzmann's constant, T_m = melting temperature, Ω = atomic volume) normalization, but fall on two straight lines according to the product of ionic charges of the compounds. The calculated results are compared with available experimental data and previous calculations based on phenomenological models.

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1. Introduction

Chalcogenide and pnictide semiconductors with the formula $A^IB^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ have been widely studied because of their possible technological applications as photo-voltaic detectors, solar cells, light emitting diodes, modulators, filters and their use in nonlinear optics [1–5]. These semi-conductors crystallize in the chalcopyrite structure, which is deduced from that of zinc blende by the replacement of the cationic sublattice by two different atomic species. This induces the doubling of the zinc blende unit cell and introduces a tetragonal distortion characterized [6] by the parameter $\eta = c/2a$, where a and c are the lattice parameters, and by the anion displacement $u = 0.25 + (d_{A–C}^2 + d_{B–C}^2)/a^2$ from its position in the cubic cell, where $d_{A–C}$ and $d_{B–C}$ are the cation–anion distances. Because of the added structural (η; u) and chemical ($d_{A–C} \neq d_{B–C}$) degrees of freedom relative to their binary analogue, the ternary semi-conductors exhibit a wide range of interesting physical and chemical properties [2–4]. Although different methods of material preparation for these chalcopyrite ($A^IB^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$) compounds have been suggested [6], the knowledge of many of the physico-chemical properties that are essential for designing appropriate conditions for the growth of bulk single crystals and of high-quality epitaxial layers is still inadequate. The elastic properties of these compounds are characterized by six independent elastic stiffness constants C_{ij}: C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66} [7], because of this anisotropy of the elastic properties of these compounds it is evident that the availability of sufficiently large, single phase, homogeneous and defect-free single crystals is an essential precondition for reliable experimental determinations of the elastic constants independent of the specific method used. Table 1 presents the six deformation adapted to the tetragonal $I\bar{4}2d(D_{2d}^{12})$ space group (Laue class $\bar{4}2m$), that we have used to calculate the six elastic constants of chalcopyrite crystals. In general, the strain deformations reduce the symmetry of the cell, eventually increasing the number of degrees of freedom that have to be minimized. Deformations 4–6 in Table 1, for instance, have four internal coordinates of the atoms within the unit cell that are not fixed by symmetry and must be optimized for each deformed cell geometry.

Elastic constants of most of the chalcopyrite family of semiconductors have not been determined experimentally because of various difficulties in growing single crystals of these compounds [3,8]. Experimental determinations of elastic stiffness constants, compressibilities and bulk moduli for chalcopyrite compounds have been reported in the literature but the results are often contradictory [9]. Attempts have been made to fill this gap in the knowledge of the elastic properties of the chalcopyrites by theoretical calculations using different approaches, but mostly the results obtained differ considerably, and in many cases no satisfactory agreement has been achieved with existing experimental data. On the other hand, the availability of reliable elastic constant data is an essential prerequisite for any calculation or analysis of the influence of pressure, stress and strain on the properties of crystals and thin epitaxial layers.

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Table 1
Strains for the tetragonal chalcopyrite crystals phase.

Deformation	1	2	3	4	5	6
Strains	$\delta_1 = \delta_2 = x$	$\delta_1 = \delta_2 = x \, \delta_3 = \frac{-x(2+x)}{(1+x)^2}$	$\delta_3 = x$	$\delta_1 = \sqrt{\frac{1+x}{1-x}} - 1 ; \delta_2 = \sqrt{\frac{1-x}{1+x}} - 1$	$\delta_4 = \delta_5 = x \, \delta_3 = \frac{x^2}{4}$	$\delta_6 = x ; \delta_1 = \sqrt{1 + \frac{x^2}{4}} - 1 ; \delta_2 = \sqrt{1 + \frac{x^2}{4}} - 1$

In the past few years [10], a number of theoretical calculations based on empirical relations have become an essential part of material research. In many cases empirical relations do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of empirical relations allows a broader class of researchers to calculate useful properties, and often trends become more evident. Empirical concepts such as valence, empirical radii, ionicity and plasmon energy are then useful [11–15]. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids.

Recently, Verma and co-authors [15–18] have been evaluated the structural, electronic, mechanical and ground state properties of binary and ternary crystals with the help of valence electron theory of solids. In this paper, we explore the applicability of the $k_B T_m / \Omega$ (k_B = Boltzmann's constant, T_m = melting temperature, Ω = atomic volume) normalization for the elastic constants (i.e. six independent elastic stiffness constants, C_{11}, C_{12}, C_{13}, C_{22}, C_{33}, C_{44},) of chalcopyrite ($A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^{V}$) semiconductors. We note that Yonenaga and Suzuki have already used the parameter $G\Omega / k_B$ (G = shear modulus) to scale temperatures in a study of the elevated temperature mechanical properties of compound semiconductors. [19]. The proposed empirical relationship only the $k_B T_m / \Omega$ normalization and ionic charge are required as input, the computation of mechanical properties itself is trivial, and the accuracy of the results compares well with experimental values. The method turns out to be widely applicable.

2. Physical concepts

Several attempts have been made to estimate the elastic constants of chalcopyrite compounds using phenomenological models. In the first application of the rigid ion model to chalcopyrites [20], it has been shown that the frequencies of the infrared active zone-centre optical phonon modes can be well reproduced using an approximation for the inter-atomic forces which takes into account only interaction between nearest neighbours and two effective charge parameters. The Keating model, one of the valence-force-models, has been originally derived to describe he elastic properties of the covalently bonded semiconductors with diamond structure using two short-range force constants only, the bond-stretching force constant for the interaction between nearest neighbours and the bond-bending force constant for the interaction between second-nearest neighbours [21]. There are a number of ways to calculate the elastic coefficients of a material from theoretical methods.

Siethoff [22] suggested another basis for correlation of the elastic properties of materials and the activation energies of their transport properties, based on the Debye temperature, and presented data for cubic metals and compound semiconductors. However, Siethoff's empirical relations required quite dramatic changes in form for different crystal structures, which reduces their usefulness and questions whether they rest on any physical principles. Reeber and Wang [23] also used the Debye temperature but now used it to produce an empirical correlation for the temperature dependence of elastic properties. Correlations for elastic properties that require the Debye temperature also contain an inherent risk of circularity of argument, because many published estimates of the Debye temperature are themselves derived from measures used to determine crystal elastic properties (e.g., the speed of sound in a material).

Simple empirical methods of predicting the physical properties of materials are of interest to research communities other than that of compound semiconductors. An extensive study of the relationship between the transport properties of materials of different crystal structure and bond chemistry was undertaken by Brown and Ashby [24]. They found that a more reliable correlation for physical transport properties was provided by the melting temperature rather than the Debye temperature. This was further extended by Frost and Ashby [25], who presented evidence for a very strong correlation between the elastic properties of polycrystalline solids and their melting temperature T_m, with the following empirical relationships proposed for Young's modulus, E and shear modulus G:

$$E = \frac{100 k_B T_m}{\Omega} \tag{1}$$

$$G = \frac{44 k_B T_m}{\Omega} \tag{2}$$

Here, k_B is Boltzmann's constant and Ω is the atomic volume. Frost and Ashby further refined these empirical relations by studying the variation of the numerical parameter in the shear modulus correlation 44 in Eq. (2) with material class, which is determined by crystal structure and chemical bonding. This constant was found to be approximately constant for each material class and varied from 20 for alkali metals to 95 for simple oxides with the corundum (α-$Al_2 O_3$) crystal structure. From this they developed the concept of the isomechanical group, which is a group of materials that display identical or very similar mechanical and transport properties when described by the appropriate empirical normalization.

3. Concept of ionic charge theory

A chemical bond is formed when the atoms with incomplete valence shells combine. There are following main types of bonds:

1. Ionic or electrovalent bond.
2. Covalent bond.
3. Coordinate bond.
4. Mettalic bond.

The valence electrons refer to the electrons that take part in chemical bonding. These electrons reside in the outer most electron shell of the atom. The participation of valence shell electrons in chemical bonding may be explained on the basis of following grounds:

(i) The outermost-shell electrons are farthest away form the nucleus and therefore, are not very firmly bound to the nucleus.
(ii) The outermost-shell electrons of an atom are also close to any foreign atom that may approach them and are therefore the first to be attracted by the approaching atom.