Local crystalline structure of multinary semiconducting alloys: Random *vs.* ordered distributions

A. Kisiel [a,*], B.V. Robouch [b], A. Marcelli [b,c]

[a] *Instytut Fizyki im.Mariana Smoluchowskiego, Uniwersytet Jagielloński, ul. S. Łojasiewicza 11, 30- 348, Cracow, Poland*
[b] *INFN − Laboratori Nazionali Frascati, via E. Fermi 40, CP 13, 00044 Frascati (RM), Italy*
[c] *Rome International Center for Materials Science Superstripes (RICMASS), Via dei Sabelli 119A, 00185, Roma, Italy, Italy*

A B S T R A C T

A description of the status of the art of experimental and theoretical investigations of local crystalline structures of tetrahedron ordered ternary and quaternary semiconducting alloys is presented. Experimental EXAFS data and FTIR analysis are summarized and analyzed using both the *Rigid Network Cations* theoretical model and the *Strained-tetrahedra* model. Internal preferences of ion pairs in ternary and quaternary alloys are discussed. Several ternary systems of different structures show ideal quasi-canonical Bernoulli distributions, while others are characterized by extreme preferences in which one, several or even all configurations are depressed or even lacking. The results demonstrate that the validity of the Bernoulli distribution is limited and not fulfilled in many systems. This article is an expanded version of the scientific reports presented at the International Conference on Semiconductor Nanostructures for Optoelectronics and Biosensors 2016 ICSeNOB2016, May 22–25, 2016, Rzeszow, Poland.

Contents

1. Introduction

Melting and subsequently crystallizing two or more miscible chemical compounds lead to solid solutions or alloys. Combining in various proportions two binary compounds containing cations (A, B and/or C) and anions (X, Y and/or Z) result in an unlimited number of ternary (ABX or AXZ) or quaternary (ABXY, ABCX or AXYZ) alloys with continuously varying physical properties of particular interest for semiconductor physics. Binary semiconductor compounds with cations from Column II or III of the Mendeleev table and anions from Column VI or V usually crystallize as tetrahedron coordinated *fcc* cubic zincblende B3 (sphalerite) or hexagonal

wurtzite B4 structures. Both structures are characterized by the tetrahedral spatial ordering: a cation\anion at the center of the tetrahedron surrounded by four atoms anions\cations at the four corners of the tetrahedron. The ternary alloys contain five distinct elementary tetrahedra $(T_k)_{k=0,4}$ each. The unit cell of their binary compounds is diatomic. Each atom in the crystal lattice in the first zone of nearest neighbours (NN) with coordination number N_1 of four and in the second zone of next nearest neighbours (NNN) N_2 of 12 atoms, and in subsequent zones with $N_j = 12$ atoms. The NN bond distance (R_1) and coordination numbers N_1, as well as the NNN bond distance (R_2) and coordination numbers N_2 can be determined using EXAFS analysis. However, we have to underline here that for coordination numbers greater, then 6 the error induced by EXAFS can be large and XANES models are more suitable to identify such large coordination numbers.

When the starting two or more binary compounds crystallize in a common B3 or B4 structure, the resulting multinary alloy retains

* Corresponding authors.
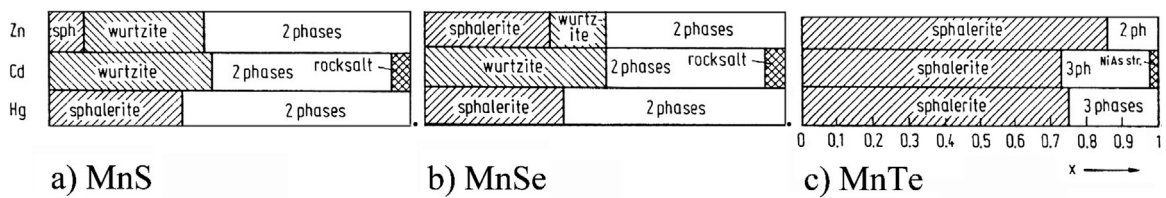 *E-mail address:* andrzej.kisiel@uj.edu.pl (A. Kisiel).

Fig. 1. a) MnS; b) MnSe; c) MnTe solubility of Mn in II–VI for Zn, Cd, and Hg.
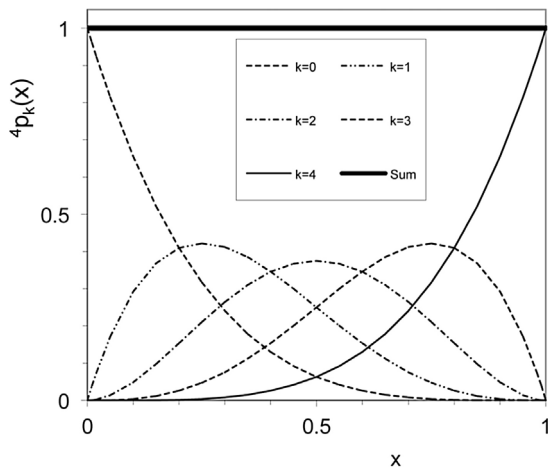

Fig. 2. Bernoulli random distribution $^4p_k(x)$ of elementary configuration tetrahedra in a ternary $A_{1-x}B_xC$ crystal.

the same crystalline structure. If the binary constituents have different crystalline structures, the resulting structure retains the starting structure until a relative content exceeds a value beyond which a structural phase transition occurs, eventually ending with another structure or with a mixture of different structures. This is the typical behaviour of alloys of binary Group II–VI with transition metal (e.g., Mn, Fe, etc.). Transition metal chalcogenides (S, Se, and Te) crystallize in either a six fold coordinated cubic rock salt structure (MnS, MnSe) or in NiAs hexagonal structures (MnTe, FeS, FeSe, and FeTe) (Fig. 1) [1].

For more complex alloys such as quaternary alloys Q_{xy}, we may distinguish two families. The first that we identified as *truly* quaternary with ABCX (Q_{31}) or AXYZ (Q_{13}) formulas consists of fifteen different tetrahedron configurations: 3 binary, 9 ternary, and 3 quaternary while the second described as ABXY(Q_{22}) consists canonically of 4 binary, 12 ternary configurations, and ruling out the presence of antisites has no quaternary. The latter are referred in the next as **pseudo**-quaternary alloys [2].

2. Analysis of ternary and quaternary semiconductor alloy crystal local structures

Mikkelson and Boyce [3,4] were among the first to investigate semiconductor ternary alloys using EXAFS. They started with the $In_{1-x}Ga_xAs$ ternary zincblende solutions obtained from InAs, successively replacing In by Ga atoms. Using the powder diffraction they observed that the $In_{1-x}Ga_xAs$ lattice constant is linearly dependent on x (Fig. 2a). However, experimental results of EXAFS show that Ga atoms were not substituted at the In atomic positions at the typical distances of the InAs, but were located at distances characteristic of the GaAs binary compound. This surprising behaviour was later explained as the formation of a bi-modal structure in which the different ionic radii of Ga and In cause different R_1's for In-As and Ga-As pairs. In their *Rigid Network Cations* theoretical model Balzarotti et al. [5,6] arbitrarily assumed, the presence

in these alloys of a rigid elementary tetrahedron. Cations A and B were rigidly fixed at the corners of the tetrahedron, while the C-anions shifted to a position within the tetrahedron determined by the interactions of AC and BC ions as per the *Force Field Valence* of Keating [7] and Martin [8]. Accordingly, the positions in the elementary tetrahedra named T_0 (4AC), T_1 (3A1BC), T_2 (2A2BC), T_3 (1A3BC) and T_4 (4BC) become a function of the relative content of the alloy (see Fig. 3). Moreover, the model assumes that ions are randomly distributed according to the Bernoulli binomial distribution (Fig. 4) within the five elementary tetrahedra in the crystal. The model was applied to analyze EXAFS data of $In_{1-x}Ga_xAs$ [3,4] $Cd_{1-x}Mn_xTe$ (Fig. 4) [5,6], and $Cd_{1-x}Zn_xTe$ and $HgSe_{1-x}Te_x$ [9]. However, the *Rigid Network Cations* model does not allow a complete description of the EXAFS experimental results of tested ternary alloys. This may be attributed to the fact to the fact that this model disregards obvious deformations of the configuration tetrahedra, due to differences in lattice constants of the two binary components. Part of the shortcomings was removed in the Monte Carlo simulations and in the Modified Quasi Chemical Approximation [10]. Using this model Wiedmann et al. [11] developed the elements of the theory of the *Elastic Stress Relaxation* for ternary alloys $A_{1-x}B_xC$ adding the relaxation of the elemental tetrahedra by the introduction of elementary clusters in the scheme of *Iterative Random Cluster* model.

The statistical *Strained-tetrahedra* model [12,13] is a more precise approach providing an improved description of the structure of ternary and quaternary alloys. The model with its seven axioms covers simultaneously the model of *Rigid Network Cations* and *Cluster* model.

The statistical *Strained-tetrahedron* model was developed to overcome two common assumptions of previous models: 1) rigid undistorted ion sublattice of regular tetrahedra throughout all five configurations and 2) random ion distribution. These simplifying assumptions restrict the range of applicability of the models to a narrow subset of ternary alloys for which the constituent binaries have their lattice constants and standard molar enthalpies of formation ($\Delta_f H_0$) equal or quasi-equal. Beyond these limits predictions of such models become unreliable, in particular, when the ternary exhibits site occupation preferences (SOP).

The seven basic assumptions of the model are:

1) Elemental tetrahedra are free to have different sizes and shapes;
2) All possible (19) elemental inter-ion ternary distances are tetrahedron constrained;
3) Elemental volumes of the two sublattices, for each of the three strictly ternary configurations, pair-by-pair relax to common values, i.e., the three constraints on the distance parameters;
4) Bernoulli binomial polynomials with preference weight coefficients describe configuration populations. ^Np_k (for ternary), $^Np_{kj}$ (for quaternary);
5) All NNN and further fills are determined by NN preferences;
6) Total coordination number is conserved as dilution varies imposing bonds on the coefficient values;
7) The formation of each ternary configuration is carried out until the full consumption of one of the corresponding binary ingredients, or both simultaneously as in the random case, is achieved.