Lattice relaxation in $Zn_{1-x}Cd_xS$ binary alloy : An Extended X-ray Absorption Fine Structure (EXAFS) Study

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Introduction:-

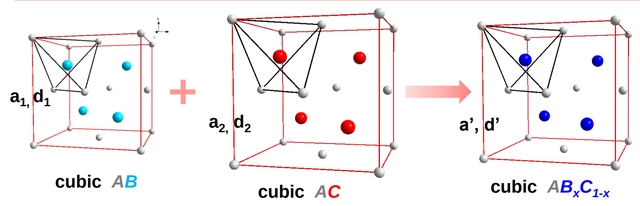
Vegard's Law :- *A linear relation exists, at constant temperature, between the crystal lattice parameter of an alloy and the concentrations of the constituent end members; Thus, lattice parameters (a) of an alloy of the type AB_xC_{1-x} can be explained as a linear sum of its constituent members (AB and AC) in respective proportions*

$$a_{AB_xC_{1-x}} = x.a_{AB} + (1-x).a_{AC}$$

Applicable to a wide range of alloys belonging to different crystal systems and different space groups

Background and Motivation :-

Virtual Crystal Approximation (VCA) :-

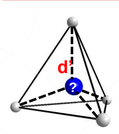


Global Structural Description :-

$a' = x.a_1 + (1-x).a_2$
$d' = x.d_1 + (1-x).d_2$
$a' = nd'$

Cell parameters Bond Distances

Origin of the problem :-



Any *local displacements* of atoms from their ideal positions in the unit cell completely ignored !

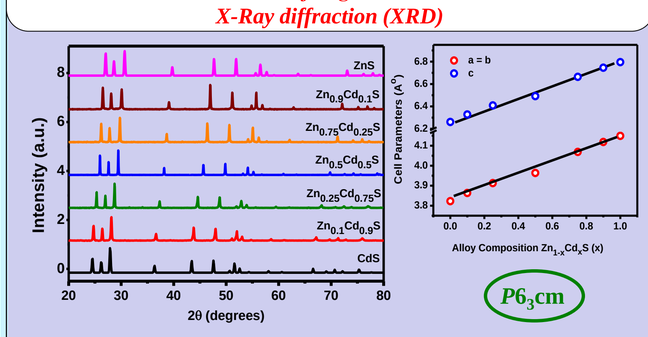
- Concept average bond length ?
- Distribution of atom-pair correlations ?
- Does the global crystal structure hold at the microscopic level ?

Aim of the study:-

- Detailed description of alloy structure at the atomic scale
- Is cationic substitution random in the alloy?
- Understand the nature of local alloying and relate it to the global description from diffraction

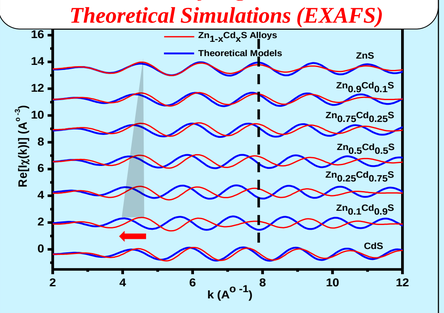
Results and discussion :-

Success of Vegard's Law X-Ray diffraction (XRD)



- $Zn_{1-x}Cd_xS$ alloys obey Vegard's Law

Failure of Vegard's Law Theoretical Simulations (EXAFS)

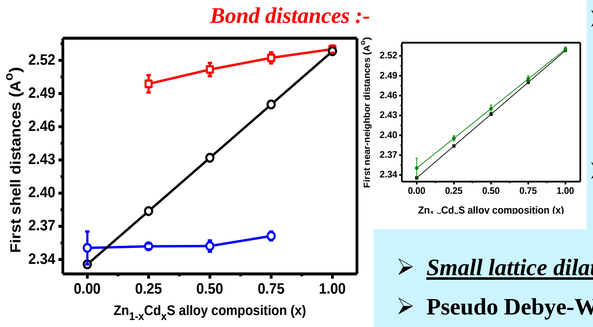


- Gradient Alloy Model *fails to describe* the local picture !

- *Local structure markedly different from global structure*
- *EXAFS studies* for local description of the alloy

First near-neighbor environment

Bond distances :-

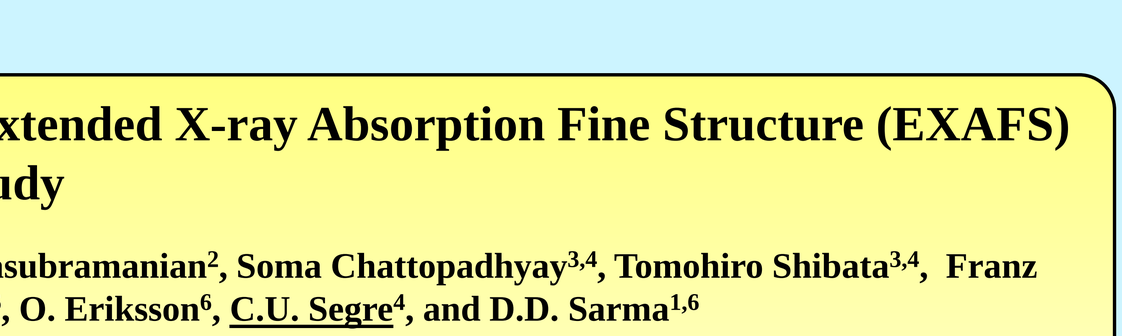


- *Bimodal* distribution of interatomic distances : Zn-S (*Red*) and Cd-S (*Blue*); Inset shows that average interatomic distance (*Olive*) closely approximates the virtual crystal line (*Black*)
- Bond lengths tend to retain their *ideal crystallographic value* and change only by 0.01-0.03 A°
- *Small lattice dilation* for by Zn-S (16.5%) and Cd-S (22.9%)
- Pseudo Debye-Waller factor (σ^2) dominated by *static component*

Atomic level scenario

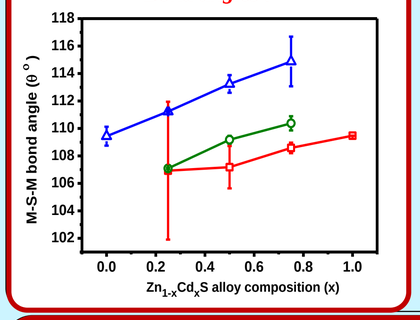
Second near-neighbor environment

Bond distances :- **Homogeneity :-** **Disorder :-**

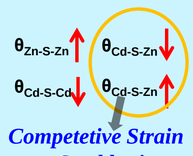


- *Trimodal* distribution of interatomic distances : Zn-S (*Red*), Zn-Cd (*Wine*) and Cd-S (*Blue*); Inset shows that average interatomic distance (*Olive*) closely approximates the virtual crystal line (*Black*)
- *Random Alloy* estimated from Zn:Cd ratio around Zn/Cd absorber; nominal Zn-Zn (*pink*), estimated Zn-Zn (*Blue*), nominal Cd-Cd (*Olive*) and estimated Cd-Cd (*Red*)
- σ^2 higher for alloys than pure end members due to competitive strain

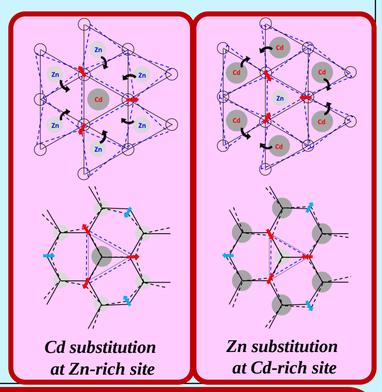
Bond angles :-



- *Trimodal* distribution of bond angles : Zn-S-Zn (*Red*), Zn-S-Cd (*Olive*); and Cd-S-Cd (*Blue*);

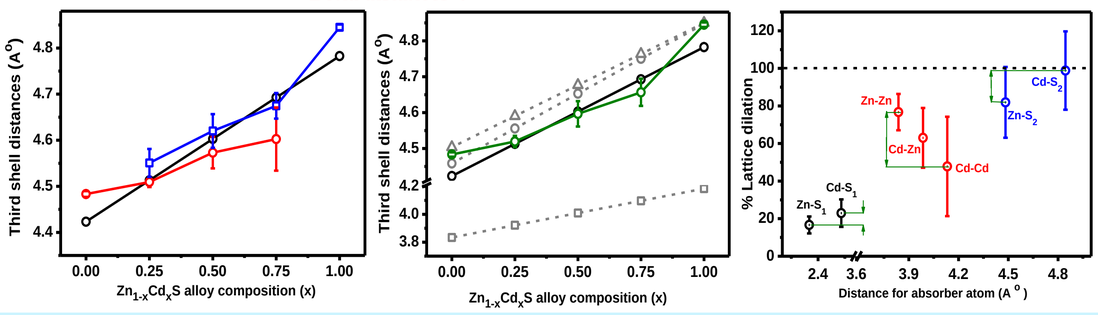


Competetive Strain on S sublattice



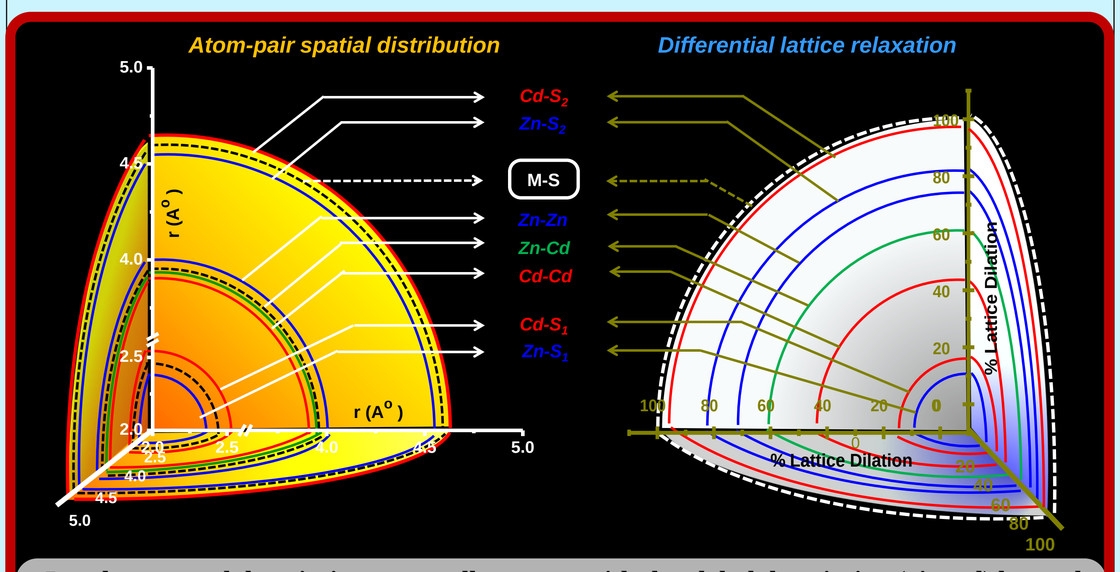
Third near-neighbor environment

Bond distances :- **Coordination shell relaxation :-**



- Zn-S (*Red*) and Cd-S (*Blue*) distances approach each other very closely and the average interatomic distance (*Olive*) closely *approximates the virtual crystal line* (*Black*) from XRD; grey lines represent different sets of M-S distances in virtual wurtzite crystal
- Large spatial separation for Zn-S and Cd-S intervened by a randomly substituted cationic sublattice yields *high σ^2 values*
- *% lattice dilation increases* with increasing distance from the absorber atom; differenertial atom-pair relaxation eventually merges with the virtual crystal relaxation line (Black dotted line)

Atom-pair spatial distribution **Differential lattice relaxation**



Local structural description eventually merges with the global description (virtual) beyond third coordination sphere

Conclusions :

- Bimodal bond distribution in the first near neighbor for binary alloys obeying Vegard's Law with slight dilation; end member components tend to retain their identities locally at the atomic scale
- Trimodal distribution of cation-cation distances and angles shows with much stronger relaxation towards the virtual wurtzite crystal lattice owing to random alloying at the substituted cationic sublattice
- Zn-S and Cd-S correlations in third shell approach each other very closely and extent of dilation almost coincides with the average crystal line
- Lattice relaxation differentially increases with increasing distance of the scattering atom from the absorbing atom, finally merging with the virtual description beyond the third coordination shell
- Results from *ab initio* calculations on the systems are in good agreement with EXAFS results

References :

L. Vegard, Z. Phys. 5, 17 (1921).
J. C. Mikkelsen, Jr. and J. B. Boyce, Phys. Rev. B 28, 7130 (1983).
A. Balzarotti, N. Motta, A. Kisiel, M. Zimnal-Starnawska, M. T. Czyzyk, and M. Podgorny, Phys. Rev. B 31, 7526 (1985).
Z. Wu, K. Lu, Y. Wang, H. Li, C. Li, and Z. Fang, Phys. Rev. B 48, 8694 (1993).

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