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Distortion in the $\text{CdS}_{1-y}\text{Se}_y$ Lattices: an Example of Relaxation in Wurtzite Compounds

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Abstract

Relaxation in pseudobinary wurtzite lattices is predicted using the valence force field (VFF) approach.

In this hexagonal packing structure, the computer simulation of the quasi-tetrahedral alloy lattice at an arbitrary composition is carried out by searching atomic positions at which the elastic forces acting

upon every atom vanish. The VFF model is applied to the II–VI compound $\text{CdS}_{1-y}\text{Se}_y$: the bimodal distribution of the distances between first neighbouring atoms is split, taking into account the type of chalcogen atom bound to the Cd one and the distortion of tetrahedra in the non-ideal wurtzite structure. The values of interatomic distances up to the second neighbours agree with the published extended X-ray absorption fine-structure spectroscopy (EXAFS) data. The natural distortion ($\pm 0.42^\circ$ for CdS and $\pm 0.16^\circ$ for CdSe) around the regular tetrahedral angle value remains present in the alloy. The calculated mixing enthalpy follows a subregular law: $\Delta^M H = y(1-y)[2803 - (2y-1)125] \text{ J mol}^{-1}$.

Introduction

The local atomic arrangements in zinc-blende alloys are now well known (Van Vechten, 1969a, 1969b, 1973). Experimental extended X-ray absorption fine-structure spectroscopy (EXAFS) studies of the local structure have been performed on a large number of systems (Mikkelsen & Boyce, 1983; Balzarotti, Motta, Kisiel, Zimnal-Starnawska, Czyzyk & Podgorny, 1985; Motta, Balzarotti, Letardi, Kisiel, Czyzyk, Zimnal-Starnawska & Podgorny, 1985; Marbeuf, Karouta, Dexpert, Lagarde & Joullié, 1986; Bunker, 1987; Marbeuf, Ballutaud, Triboulet, Dexpert, Lagarde & Marfaing, 1989; Boyce & Mikkelsen, 1989). These studies have evidenced great lattice relaxations related to the difference between the atomic sizes in the mixed sublattice. These important results show the non-validity of the virtual crystal approximation (VCA) for the description of the local properties of the pseudobinary semiconductor alloys. On the other hand, the relaxation in the zinc-blende structure has been modelled by Zunger & Wood (1989) and Wei, Ferreira & Zunger (1990) as a consequence of *ab initio* calculations or by using the valence force field (VFF) approach (Podgorny, Czyzyk, Balzarotti, Letardi, Motta, Kisiel & Zimnal-Starnawska, 1985), in which the elastic properties are described by the tetrahedral potential expression of Keating (1966) and Martin (1970). These calculations lead to a model of distorted structure. The validity of this model has been checked by comparing the calculated local environment to that obtained experimentally by EXAFS.

A large number of semiconductor alloys, especially some sulfides and selenides, do not crystallize in the cubic zinc-blende structure but in the hexagonal wurtzite structure (Roth, 1967; Mills, 1974; Kikuma & Furukoshi, 1985). For the local environment in pseudobinary systems with these significantly more complicated structures, very little experimental information is available. The few existing EXAFS studies (Levelut, Ramos, Petiau & Robino, 1991;

Ramos, Levelut, Petiau & Villain, 1993)* show that strong relaxation related to the lattice difference is present in these pseudobinary systems as well. However, more distant neighbour information is very limited.

As the VFF model is valid for any local tetrahedral environment, it is assumed to work for a hexagonal close packing structure. Calculations applied to hexagonal wurtzite could be very helpful to predict the local distortion in these systems where experimental information is scarce and difficult to interpret. As far as we know, such an approach does not yet exist.

The purpose of this paper is to compare the local structure in $\text{CdS}_{1-y}\text{Se}_y$ wurtzite semiconductor obtained from the calculations in the VFF model to the experimental structure deduced from EXAFS analysis. The $\text{CdS}_{1-y}\text{Se}_y$ system is the only pseudobinary system with the wurtzite structure for which EXAFS data are available up to the fourth neighbouring shells and for y varying between 0 and 1 (L, R). Because the local environment in CdS and CdSe is close to a perfect tetrahedron, $\text{CdS}_{1-y}\text{Se}_y$ is then a good candidate to test the model in wurtzite structure and to see to what extent we can use these calculations to predict the local distortions in this type of structure. The characteristics of the wurtzite structure are given at first. A simplified VFF formalism is established for the binary (CdS and CdSe) and the pseudobinary ($\text{CdS}_{1-y}\text{Se}_y$) alloys. The relaxed structure is then calculated for CdS, CdSe and $\text{CdS}_{1-y}\text{Se}_y$ for various y values and the results are compared with the available EXAFS data. Some conclusions are then derived on the perspectives of the method.

The wurtzite structure

The ideal wurtzite structure is described by two hexagonal perfect identical close-packed sublattices [$c/a = (8/3)^{1/2}$] shifted along the c axis by $u = 3/8$ (Fig. 1). In this structure, an atom of one sublattice is surrounded by four atoms of the other sublattice, forming a perfect tetrahedron. Real systems show deviation from this ideal model: c/a is usually lower than $(8/3)^{1/2}$. Table 1 gives the a , c and u values in CdS and CdSe. These deviations yield a distortion of the structure along the c axis. Thus, one may distinguish between axial distances $d^{(ax)}$ for the bonds between atoms with the same x and y coordinates (atoms 1 and 4 on Fig. 1),

$$d^{(ax)} = d_{14} = uc, \quad (1a)$$

and equatorial distances $d^{(eq)}$ for the bonds between

* These references will be referred to hereafter as L and R, respectively.

atoms having at least different x or y coordinates (l and i),

$$d^{(eq)} = d_{li} = [a^2/3 + (1/2 - u)^2 c^2]^{1/2} \quad (i = 1, \dots, 3). \quad (1b)$$

Expressions giving the distance values to the first, second, third and fourth neighbouring shells in a non-ideal wurtzite structure are reported in Table 2. Distortion is found for the corresponding polyhedra, except for the third shell.

In the same way, angles are not strictly equal to $\arccos(-1/3) = 109.47^\circ$. The wurtzite structure shows two angle types: angles around l atoms involving neighbours at different z values [$\theta^{(ax)}$],

$$\theta^{(ax)} = \theta_{4li} = \arccos[(u - \frac{1}{2})c/d^{(eq)}], \quad (2a)$$

and angles with neighbours at the same z coordinate [$\theta^{(eq)}$],

$$\theta^{(eq)} = \theta_{lil} = \arccos[1 - a^2/2d^{(eq)}]. \quad (2b)$$

The lattice parameters (a , c), the compacity ratio (c/a) and the position parameter (u) corresponding to CdS and CdSe (National Bureau of Standards, 1954, 1955; Stevenson, Milanko & Barnea, 1984; Stevenson & Barnea, 1984) (Table 1) show that the structure of these two binaries is close to an ideal wurtzite structure. The distances $d^{(eq)}$ and $d^{(ax)}$ differ only by 0.006 Å in both cases, whereas for CdS, which presents the greatest angular distortion, $\theta^{(eq)} = 109.89^\circ$, $\theta^{(ax)} = 109.05^\circ$.

In a pseudobinary wurtzite crystal described by VCA, all atoms are assumed to be located at the exact positions of the space group [(2b) positions of $C_{6v}^4 - C6mc$]. In fact, the local strain generated by the difference between the interatomic distances given by the Vegard law and the natural interatomic distances cannot be accommodated and induces atomic displacements: this is the so-called lattice relaxation.

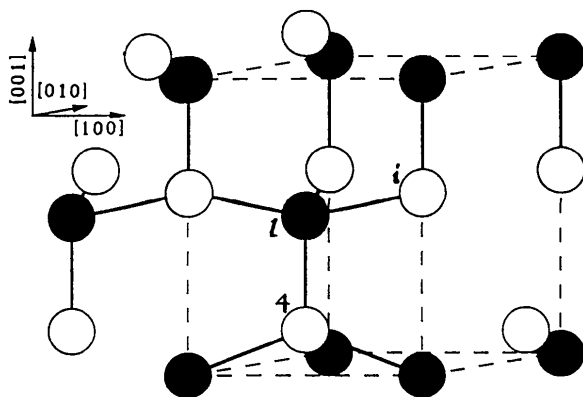


Fig. 1. Ideal wurtzite structure. For a given atom (l), one may distinguish bonds with atoms having the same x and y coordinates (atoms labelled 4) and with atoms having at least different x or y coordinates (atoms labelled i).

Table 1. Lattice parameters (a , c) and sublattice translation parameter (u)

	CdS*	CdSe†	Ideal wurtzite
a (Å)	4.136	4.299	
c (Å)	6.713	7.010	
c/a	1.623	1.631	1.633
u	0.377	0.376	0.375

* National Bureau of Standards (1954); Stevenson *et al.* (1984).

† National Bureau of Standards (1955); Stevenson & Barnea (1984).

The valence force field model in the wurtzite structure

Binary lattice case (CdS and CdSe)

Keating (1966) first gave a useful expression accounting for the elastic properties of the diamond structure. Small local atomic displacements are considered, and then Hooke's law remains valid; the local environments are not far from the regular tetrahedra.

The local potential for an l atom centred in a tetrahedral environment is then,

$$V = \sum_{i=1}^4 (\alpha/8a^2)(r_{li}^2 - 3a^2)^2 + \sum_{i,j>i}^4 (\beta/4a^2)(r_{ij} + a)^2 \quad (3)$$

where $\|r\|$ is an interatomic distance, $4a$ the lattice parameter, α the central first-neighbour constant of the corresponding li bond and β the non-central second-neighbour constant involved in the ilj angle. In this covalent description, α and β are calculated from the stiffness constants C_{mn} .

In order to extend this purely covalent description to the partly ionic zinc-blende structure, Martin (1970) added effective point-ion Coulombic forces. (3) remains valid, but the relations giving force constants also contain an electrostatic term involving the dynamic effective charge Ze^* . Then, the β/α ratio reflects the ionic character of bonds in a binary compound.

Because of the previous assumptions (Hooke's law, small tetrahedral distortions), the VFF model may be applied to the nearly tetrahedral structure such as wurtzite. To account for the differences between axial and equatorial geometrical parameters in the wurtzite structure, the V potential (3) is written as

$$V = \sum_{i=1}^3 \frac{3\alpha^{(eq)}}{8d^{(eq)2}} [r_{li}^2 - d^{(eq)}]^2 + \frac{3\alpha^{(ax)}}{8d^{(ax)2}} [r_{l4}^2 - d^{(ax)}]^2 + \sum_{i=1}^3 \left\{ \sum_{j>i}^3 \frac{3\beta^{(eq)}}{8d^{(eq)2}} [r_{ij} - d^{(eq)} \cos \theta^{(eq)}]^2 \right\} + \sum_{i=1}^3 \frac{3\beta^{(ax)}}{8d^{(eq)}d^{(ax)}} [r_{ij}r_{i4} - d^{(eq)}d^{(ax)} \cos \theta^{(ax)}]^2. \quad (4)$$

This expression may be simplified

$$(i) \alpha^{(eq)} = \alpha^{(ax)} = \alpha$$

$$(ii) \beta^{(eq)} = \beta^{(ax)} = \beta.$$

(i) and (ii) are based on the assumption that tetrahedra are weakly distorted.

In a hexagonal lattice, the constants α and β cannot be as simply derived from the elastic constants as in the cubic lattice. However, the calculated lattice relaxation shows very little dependence to the absolute values of α and β . These constants are then reasonably approximated by interpolation between values of known blende constants (Martin, 1970; Martins & Zunger, 1984). One obtains $\alpha = 43.1$ and $\beta = 4.2$ for CdS, $\alpha = 35.8$ and $\beta = 3.4$ for CdSe (in N m^{-1}).

Pseudobinary lattice case ($\text{CdS}_{1-y}\text{Se}_y$)

If the VFF model is extended to the pseudobinary $\text{CdS}_{1-y}\text{Se}_y$ compounds, one must distinguish the nature of the atoms in the chalcogen sublattice. The final form of V is derived by introducing binary constants into (4),

$$V = \sum_{i=1}^3 \frac{3\alpha_{li}}{8d_{li}^{(eq)^2}} [r_{li}^2 - d_{li}^{(eq)^2}]^2 + \frac{3\alpha_{l4}}{8d_{l4}^{(ax)^2}} [r_{l4}^2 - d_{l4}^{(ax)^2}]^2 \\ + \sum_{i=1}^3 \left\{ \sum_{j>i}^3 \frac{3\beta_{ij}}{8d_{li}^{(eq)}d_{lj}^{(eq)}} [\mathbf{r}_{li}\mathbf{r}_{lj} - d_{li}^{(eq)}d_{lj}^{(eq)} \cos \theta_{ij}^{(eq)}]^2 \right\} \\ + \sum_{i=1}^3 \frac{3\beta_{i4}}{8d_{li}^{(eq)}d_{l4}^{(ax)}} [\mathbf{r}_{li}\mathbf{r}_{l4} - d_{li}^{(eq)}d_{l4}^{(ax)} \cos \theta_{ij}^{(eq)}]^2. \quad (5)$$

This expression may be compared with that established for a pseudobinary zinc-blende lattice (Podgorny *et al.*, 1985; Martin, 1970; Martins & Zunger, 1984). α_{li} is the central first-neighbour constant in the li binary (CdS or CdSe). For i and j atoms of the same nature, β_{ij} represents the non-central second-neighbour constant of the same binary. In the other cases, as for zinc-blende, β_{ij} – which is specific to the mixed compound – is evaluated as,

$$\beta_{ij} = (\beta_{iii}\beta_{jii})^{1/2}.$$

Relaxation procedure

The relaxation procedure is carried out by searching for the configurations at which the elastic forces acting upon every atom vanish. An infinite crystal has been simulated by setting periodic limiting conditions to a large cluster (12^3 cells). This cluster is built by putting on a mixed sublattice a random distribution of S and Se atoms, according to the x composition. The assumption of a random distribution for

the chalcogen atoms is supported by the EXAFS data (L) and will be checked by calculating the thermodynamic mixing functions. Before relaxation, atomic positions (x_i^0) are those of the VCA crystal. At each calculation loop of the relaxation procedure, the displacements δx_i of each l atom are calculated by equating to zero the resulting elastic forces acting upon this l atom. The new position set,

$$x_l = x_l^0 + \delta x_l,$$

decreases the remaining strain energy E . The procedure is achieved when the variation of the resulting energy $\Delta E/E$ is less than 10^{-8} .

Radial distribution $P(\mathbf{r})$ around a type of atom (Cd, S or Se) is then calculable. In the range 0–6 Å, the distances between these atoms with the first, second, third and fourth neighbours [$d^{(1)}$, $d^{(2)}$, $d^{(3)}$ and $d^{(4)}$] are obtained. Angular distribution $P(\theta)$ is also deduced. The reference state for the energy of the solid solution is the binary li for which $E_{li} = 0$ and the calculations are performed without entropic terms. E represents then the strain contribution to the mixing enthalpy $\Delta^M H$.

Results and discussion

Mixing enthalpy of $\text{CdS}_{1-y}\text{Se}_y$

The mixing enthalpy of the $\text{CdS}_{1-y}\text{Se}_y$ solid solution $\Delta^M H$ has been deduced as being equal to the total strain energy ΔE remaining after the complete lattice relaxation. The resulting $\Delta^M H(y)$ function follows a subregular law as shown by Fig. 2,

$$\Delta^M H = y(1-y)[2803 - (2y-1)125] \text{J mol}^{-1}.$$

The slight asymmetry corresponding to the weak value of the $(2y-1)$ term is a general feature in III–V and II–VI pseudobinary alloys (Wei *et al.*, 1990). The substitution of small S atoms by greater Se atoms in a S-rich lattice requires more energy than the substitution of great Se atoms by smaller S atoms in a Se-rich lattice. The constant term has a value (2803 J mol^{-1}) very close to the corresponding one in $\text{Cd}_{1-y}\text{Hg}_y\text{Te}$ [2320 J mol^{-1} (Marbeuf, Druilhe, Triboulet & Patriarche, 1992)]. We have tested the validity of the random distribution of the $\text{S}_{4-n}\text{Se}_n$ tetrahedrons by using a quasi-chemical description of the II–VI solid solution (Marbeuf & Guillaume, 1984). The short-range order parameter $p_{(S,Se)}$ may be deduced from $\Delta^M H$,

$$p_{(S,Se)}[1 - p_{(S,Se)}] = \Delta^M H / (6RT). \quad (6)$$

This parameter has a very low value (0.04₇) at $T = 300 \text{ K}$ for $y = 1/2$. This result is in agreement with R and shows that chalcogen atoms can be considered as randomly distributed in the structure.

The valence force field model in binaries

The following results are used to check the relaxation procedure by comparison with the crystallographic structure. For a defined type of atom (Cd and S in CdS, Cd and Se in CdSe), the maxima of $P(r)$ in the range 0–6 Å give successively the distances with the first, second, third and fourth neighbours [$d^{(1)}$, $d^{(2)}$, $d^{(3)}$ and $d^{(4)}$]: as an example, Fig. 3(a) shows such a calculation for CdSe by taking Cd as the central atom. The first peak corresponds to the $d_{\text{Cd-Se}}^{(1)}$ distances, which are in fact split into equatorial and axial types (see the insert in the 2.4–2.9 Å range): $d_{\text{Cd-Se}}^{(\text{eq})} = 2.630$ Å and $d_{\text{Cd-Se}}^{(\text{ax})} = 2.636$ Å are equal to those reported in Table 2. The intensity ratio $I_{(\text{ax})}/I_{(\text{eq})}$ reflects the corresponding bond ratio 1/3. Table 3 shows the comparison between the EXAFS (L; R) values and those calculated for $d^{(1)}$.

In $P(r)$, two main maxima are observed in the range 4–4.5 Å (Fig. 3a). The positions of these maxima (4.295 and 4.375 Å) are in good agreement with $d_{\text{Se-Se}}^{(2)} = 4.294$ and $d_{\text{Se-Cd}}^{(3)} = 4.384$ Å (R), respectively, and corresponding values in Table 2. The ratio between the height of the second and third peaks [labelled $d^{(2)}$ and $d^{(3)}$ in Fig. 3a] corresponds to the fact that Cd atoms are surrounded by 12 Cd and one Se atoms. The peak located at 5.040 Å may be obviously attributed to the $d_{\text{Cd-Se}}^{(4)}$ distances (diffraction values are 5.040 and 5.043 Å, Table 2): as shown in Table 4, EXAFS values (R) are close to the present calculated $d^{(2)}$, $d^{(3)}$ and $d^{(4)}$ ones.

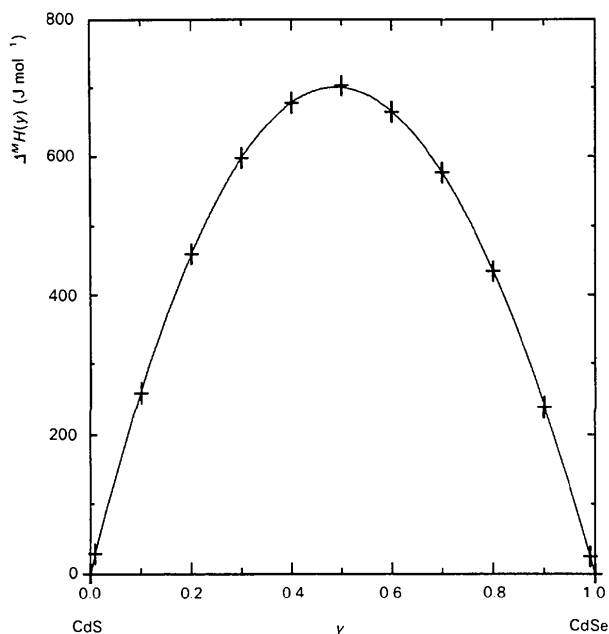


Fig. 2. Mixing enthalpy $\Delta^M H(y)$ of CdS_{1-y}Se_y referred to CdS and CdSe. The calculated points (+) are fitted by a subregular law (—).

Table 2. Relations between the distances of the first four shells and the lattice parameters a , c and u

Shell	N	d	CdS d (Å)	CdSe d (Å)
1	3	$[a^2/3 + (1/2 - u)^2 c^2]^{1/2}$	2.527	2.630
	1	uc	2.531	2.636
2	6	$(a^2/3 + c^2/4)^{1/2}$	4.119	4.295
	6	a	4.136	4.299
3	1	$(1 - u)c$	4.185	4.374
4	3	$[4a^2/3 + (1/2 - u)^2 c^2]^{1/2}$	4.847	5.040
	6	$(a^2 + u^2 c^2)^{1/2}$	4.849	5.043

Table 3. Comparison between EXAFS data (Levelut *et al.*, 1991; Ramos *et al.*, 1993) and relaxed distances (Å) deduced from the model (first shell)

y	Atom	EXAFS	Model
0	S	2.52 (0.01)	2.526 (eq)
			2.532 (ax)
0.2	S	2.53 (0.01)	2.528 (eq)
			2.532 (ax)
	Se	2.617 (0.005)	2.615 (eq)
			2.620 (ax)
0.5	S	2.53 (0.005)	2.533 (ax)
			Se
0.8	S	2.53 (0.01)	2.530 (eq)
			2.536 (ax)
	Se	2.630 (0.005)	2.628 (eq)
1	Se	2.634 (0.005)	2.630 (eq)
			2.636 (ax)

Table 4. Comparison between EXAFS data at SeK (Ramos *et al.*, 1993) and relaxed distances (Å) deduced from the model (second, third and fourth shells)

y	$d^{(n)}$	Atom	EXAFS	Model	
0.2	2nd peak	$n = 2$	S	4.12 (0.015)	4.175
			Se	4.22 (0.015)	4.195
			Cd	4.29 (0.015)	4.240
	3rd peak	$n = 4$	Cd	4.88 (0.02)	4.870
0.5	2nd peak	$n = 2$	S	4.16 (0.015)	4.19
			Se	4.24 (0.015)	4.23
			Cd	4.33 (0.015)	4.275
	3rd peak	$n = 4$	Cd	4.93 (0.015)	4.935
0.8	2nd peak	$n = 2$	S	4.21 (0.015)	4.235
			Se	4.27 (0.015)	4.265
			Cd	4.35 (0.015)	4.295
	3rd peak	$n = 4$	Cd	5.008 (0.01)	5.025
1	2nd peak	$n = 2$	Se	4.294 (0.01)	4.295
			Cd	4.384 (0.01)	4.375
			Cd	5.051 (0.005)	5.040

From this comparison, it may be concluded that the relaxation procedure of a binary wurtzite lattice yields the unrelaxed structure where the equatorial and axial distances coexist. Discrimination may also be made between $\theta^{(\text{ax})}$ and $\theta^{(\text{eq})}$ angle values: the $P(\theta)$ for CdS is given in Fig. 4 and shows that the mean angle values $\bar{\theta}^{(\text{ax})}$ and $\bar{\theta}^{(\text{eq})}$ differ from $\sim 0.8^\circ$.

The model in the pseudobinary case

In order to test the comparison between EXAFS data and calculations, the relaxed lattices for $y = 0.2$, $y = 0.5$ and $y = 0.8$ for which experiments are available (R) are searched. In the case of $\text{CdS}_{0.2}\text{Se}_{0.8}$, the

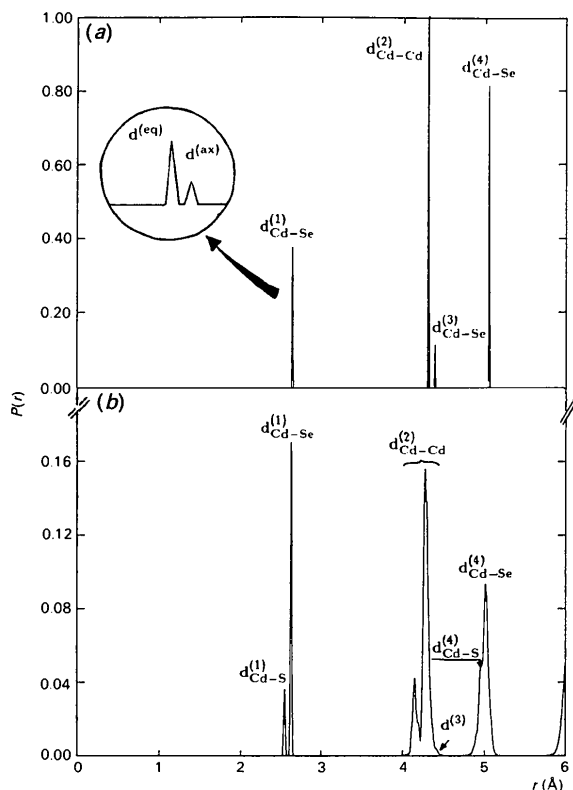


Fig. 3. Radial distribution around Cd atoms in (a) CdSe and (b) $\text{CdS}_{0.2}\text{Se}_{0.8}$ with peaks corresponding to the distances between first, second, third and fourth neighbours. The insert shows the tetrahedron distortion [$d^{(eq)} \neq d^{(ax)}$] in the CdSe wurtzite lattice.

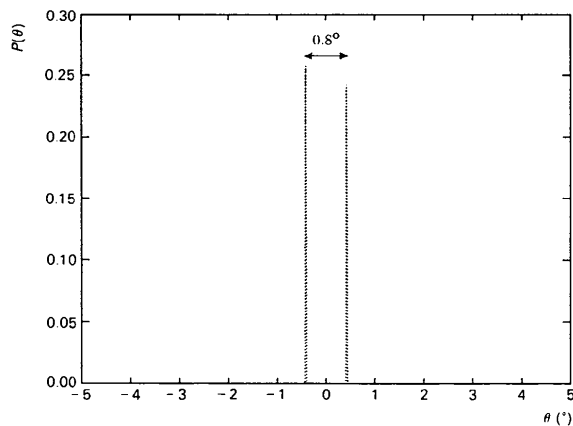


Fig. 4. Angular distribution $P(\theta)$ in CdS showing the angular distortion of the S_4 tetrahedra (the angle values are reported relative to the perfect tetrahedral angle $\theta = 109.47^\circ$).

$P(r)$ around the Cd atoms is reported in Fig. 3(b). A large splitting appears at the $d^{(1)}$ position: owing to the molar ratio S/Se, the most intense peak located at 2.628 Å corresponds to $d_{\text{Cd-Se}}^{(1)}$ and the smaller one (2.530–2.536 Å) to $d_{\text{Cd-S}}^{(1)}$. EXAFS measurements [$d_{\text{Cd-S}}^{(1)} = 2.53$, $d_{\text{Cd-Se}}^{(1)} = 2.634$ Å] agree very well with our calculated values (Table 3). Therefore, as by EXAFS, a bimodal distribution of $d^{(1)}$ distances is found in the pseudobinary structure. The peaks corresponding to $d_{\text{Cd-S}}^{(1)}$ and to $d_{\text{Cd-Se}}^{(1)}$ are broadened, as a consequence of the existence of $d^{(eq)}$ and $d^{(ax)}$ distances. Even when the atomic displacements are important, the natural distortion of the hexagonal close packing wurtzite structure subsists in the $\text{CdS}_{1-y}\text{Se}_y$ lattice. As for CdSe, (2a) and (2b) allow one to distinguish between $\theta^{(ax)}$ and $\theta^{(eq)}$ angle values. It is not surprising then to find a split angular distribution $P(\theta)$ accounting for the original displacement of Cd atoms in $S_{4-n}\text{Se}_n$ tetrahedra. The mean angle values $\theta^{(ax)}$ and $\theta^{(eq)}$ differ by $\sim 1^\circ$.

The same $P(r)$ calculations are achieved for other compositions ($y = 0.01, 0.1, 0.3, 0.4, 0.6, 0.7, 0.9$ and 0.99). Calculations and EXAFS data (L; R) for distances with first neighbours are compared in Fig. 5. The importance of the relaxation means that, as for other III-V or II-VI alloys, the $\text{CdS}_{1-y}\text{Se}_y$ lattice is considerably closer to the Pauling limit (Pauling, 1967) than to the VCA limit. The stiffness of the essentially covalent lattice does not allow great angular distortions: the standard deviation of θ resulting from the relaxation is reported in Table 5 with a maximum at $y = 0.5$ [$\sigma(\theta) = 1.55^\circ$].

For the second, third and fourth shells, it is more interesting to look at the $P(r)$ function around Se, which may be directly compared with EXAFS data at SeK (Table 4). Fig. 6 represents such a function for $\text{CdS}_{0.2}\text{Se}_{0.8}$. Even if the distance distribution is

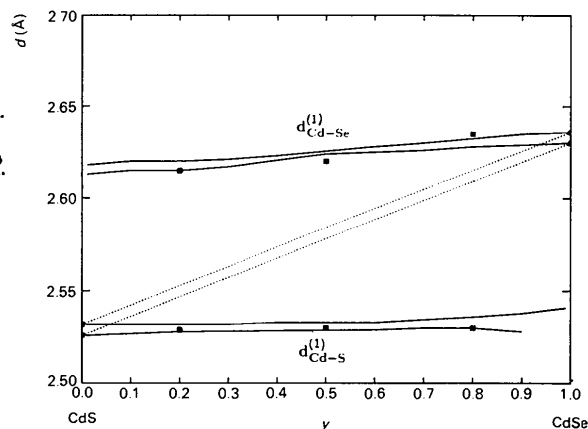


Fig. 5. Comparison between EXAFS data (■, Levelut *et al.*, 1991; Ramos *et al.*, 1993) and relaxed distances deduced from calculations (—). Distances between first neighbour atoms from Vegard's law (···) are also given.

Table 5. Standard deviations of θ ($^\circ$) versus composition

y	$\sigma(\theta)$
0	0
0.1	0.94
0.2	1.26
0.3	1.44
0.4	1.53
0.5	1.55
0.6	1.52
0.7	1.42
0.8	1.24
0.9	0.92
1	0

broadened by an alloying effect and is more complicated, two main maxima appear in the $d^{(2)}$ region at 4.235 and 4.265 Å [$d_{\text{Se-S}}^{(2)} = 4.21$ and $d_{\text{Se-Se}}^{(2)} = 4.27$ Å respectively (R)]. The small structure on the right side of the peak (4.295 Å) corresponds to the $d_{\text{Se-Cd}}^{(3)}$ distances [EXAFS yields $d_{\text{Se-Cd}}^{(3)} = 4.35$ Å, (R)]. The peak located at 5.025 Å is clearly attributed to the fourth neighbours [$d_{\text{Se-Cd}}^{(4)} = 5.008$ Å, (R)].

Concluding remarks

Wurtzite lattices in II-VI compounds are hexagonal close packing networks with nearly tetrahedral local structure. A modified 'valence force field' model in the Keating scheme, taking into account the natural tetrahedral distortion, has been established for the wurtzite structure, allowing the study of the relaxation to CdS_{1-y}Se_y lattices. As in 'blende' pseudobinary crystals, a bimodal distribution of the distances between first neighbouring atoms has been found, but it is split: this pseudotetramodal distribution is the consequence of the different atomic sizes

between S and Se atoms and of the distortion of tetrahedra in a non-ideal wurtzite structure. Values and evolution of interatomic distances up to the fourth neighbours agree very well with the published EXAFS data. The natural distortion around the regular tetrahedral angle value remains present in the alloy. The calculated mixing enthalpy follows a classical subregular law.

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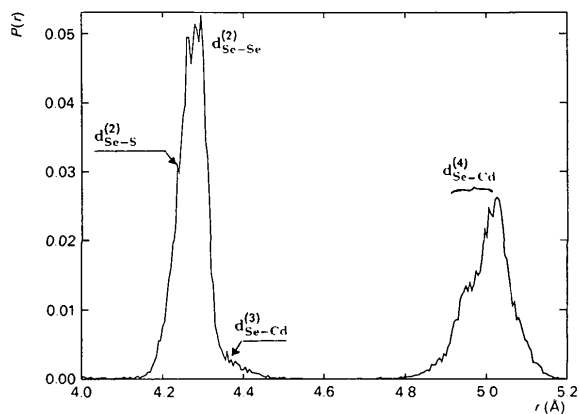


Fig. 6. Radial distribution around Se atoms in CdS_{0.2}Se_{0.8}, showing the distances between second, third and fourth neighbours.