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Distribution of chalcogen atoms in the wurtzite CdS_xSe_{1-x} solid solution: experimental study by x-ray absorption

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Abstract. The assumption of a random distribution of chalcogen atoms in the wurtzite structure is usually made to interpret the properties of ternary CdS_xSe_{1-x} compounds. However, there has not yet been any experimental evaluation of this distribution. We report here the results of low-temperature x-ray absorption measurements (4.5 K) at the selenium K edge in CdS_xSe_{1-x} compounds for $x = 0$, 0.2, 0.5 and 0.8. These measurements make a quantitative analysis of the next-nearest neighbours up to the fourth-neighbour shell around selenium atoms possible. The numbers of sulphur and selenium second neighbours of selenium atoms for each ternary compound are found to be proportional to the respective molar ratio. The analysis can be made with the best accuracy for $x = 0.5$, and no clustering is observed. As maximum clustering is expected for this value of x, it is concluded that deviation from the random distribution of selenium atoms is very small in CdS_xSe_{1-x}.

1. Introduction

The ternary compounds CdS_xSe_{1-x} have band gap energies which make them potentially suitable material for visible optoelectronics [1, 2]. The electronic and excitonic properties of these ternary compounds compared with those of the binary compounds have given rise to important studies [3–6]. In these studies the assumption is made that the chalcogen atoms sulphur and selenium are randomly distributed in the structure. However, there is no direct experimental evidence of chemical disorder.

Under the standard conditions of growth, CdS_xSe_{1-x} compounds crystallize in the hexagonal wurtzite structure [7]. The lattice parameters of the ternary compounds obey Vegard's [8] law, i.e. they vary almost linearly with the parameter x. On the other hand for the ternary compounds the distances R_{Cd-S} and R_{Cd-Se} are very close to the distances in the binary compounds over the whole composition range [9]. This relaxation of the coordination shell has already been observed in a large number of II–VI and III–V compounds [10, 11] and can be understood from simple models of bond relaxation [12, 13]. It could also be the result of partial clustering of the chalcogen atoms in the structure. Clustering in ternary compounds can be characterized by the parameter β [14]. This parameter is defined for a compound $A_xB_{1-x}C$ as the probability of finding an atom A as the second neighbour next to another atom A: $P_{AA} = x + \beta(1 - x)$. The limiting values $\beta = 1$ and $\beta = 0$, respectively, correspond to total clustering and to the random distribution of atoms A and B in the structure. It has been shown that thermodynamic studies are able to predict the value of the clustering parameter in ternary zincblende compounds [15–18]. β has been found to

be a maximum at around $x = 0.5$ and is correlated with the lattice mismatch between the two binary compounds [18]. Data for various III–V zincblende systems have been reviewed by Yamazaki *et al* [18]. For systems with a lattice mismatch smaller than 5% the clustering parameter does not exceed 0.1 for $x = 0.5$ [18]. In 1967, Verleur and Barker [19] took into account the possibility of clustering to interpret the infrared reflectivity spectra of mixed crystals of CdS_xSe_{1-x}. The value of β giving the best fit was 0.4. This value is very high with regard to the small lattice mismatch (about 4%) between CdS and CdSe (table 1).

Table 1. Lattice parameter of CdSe [29, 30] and CdS [31, 32]. The lattice mismatch between the two compounds is small ($\delta a/a \simeq \delta c/c \simeq 4\%$).

Compound	a (Å)	c (Å)	c/a	u
CdS	4.136	6.713		0.377
CdSe	4.299	7.010		0.376
Ideal wurtzite			1.633	0.375

In the present work the local environmment of selenium atoms in CdS_xSe_{1-x} has been investigated using the extended x-ray absorption fine structure (EXAFS) up to the fourth-neighbour shell. Analysis of the EXAFS data gives information about the local organization around selenium. This information has been compared with that obtained for the binary compound CdSe. Direct evaluation of the clustering parameter β is obtained from the number and nature of second neighbours. EXAFS data reduction, samples and measurements are presented in section 2. The results are then given and discussed in sections 3 and 4.

2. Data analysis, samples and measurements

2.1. EXAFS analysis

Structural information is obtained using simple scattering theory [20, 21]. The EXAFS signal $\chi(k)$ consists of the modulation of the absorption rate above a core level, normalized to a structureless background. On the assumption that the back-scattered waves are plane and that the atoms are spherical, $\chi(k)$ is given for the K edge of an isotropic sample by

$$\chi(k) = (-1) \sum_j N_j \frac{f_j(k)}{kR_j^2} \exp\left(-\frac{2R_j}{\lambda_j(k)}\right) \exp(-2k^2\sigma_j^2) \sin[2kR_j + \phi_j(k)]. \tag{1}$$

k is the photoelectron wavevector given by

$$k = [(2m/n^2)(E - E_0)]^{1/2} \tag{2}$$

where E is the energy of the photon, E_0 is the energy of the photoabsorption threshold, m is the mass of the electron and $n = h/2\pi$ (h is Planck's constant). N is the number of neighbours in the shell j at the distance R_j. $|f_j(\pi, k)|$ and $\phi_j(k)$ are the phase and the amplitude functions, respectively, relative to the absorber–back-scatterer pair j. The exponential damping term $\exp[-2R_j/\lambda_j(k)]$ describes the inelastic losses. $\lambda_j(k)$ is the electron mean free path resulting from the finite lifetime of the excited state. Over the EXAFS region, $\lambda_j(k)$ can be taken to be of the form $\lambda_j(k) = k/\Gamma_j$ [22], where Γ_j is a constant independent of k. $\exp(-2k^2\sigma_j^2)$ is a Debye–Waller-type term used to account for the effects

of the atomic disorder. σ_j^2 is the mean square relative deviation of the absorber–back-scatterer distance from its average value. The Debye–Waller factor accounts for both thermal (vibrational) and structural (static) disorder contributions ($\sigma_j^2 = \sigma_j^2$ static $+ \sigma_j^2$ vibrational). The use of this kind of Debye–Waller term assumes harmonic vibrations and a Gaussian distribution of static interatomic distances. The harmonic approximation becomes more valid, the lower the temperature of the measurement [21]. It is fully justified for measurement at 4.5 K. The Gaussian model for static disorder corresponds to the first-order development of the distribution function. It is valid for systems where the static disorder is small. A value of σ_j static $= 0.1$ Å is conventionally considered as an upper limit for this approximation to be correct [23].

The EXAFS analysis is performed using a standard procedure for data reduction [24, 25]: extraction of the oscillatory part of the absorption coefficient $\chi(k)$, Fourier filtering of the contribution of each atomic shell and a fitting procedure.

The extraction of $\chi(k)$ is performed with a Victoreen fit at energies below the absorption edge and extrapolation over the whole energy range. A Fourier transform is performed, the EXAFS signal corresponding to the imaginary part of this Fourier transform. Fourier filtering of the contribution of each atomic shell is performed on the $k\chi(k)$-function using Kaiser window functions. The fitting procedure is performed in k-space, with Fourier-filtered data corresponding to separated shells. The experimental function is compared with a calculated function for a hypothetical structural model for the shell. For each back-scattered atom, tabulated phase and amplitude functions $|f_j(\pi, k)|$ and $\phi_j(k)$ are used [26]. The period of the sine function is determined by the distance R. A shift of the origin of the energy used on the k-scale is allowed to compensate uncertainties in the calculated phase shift and in the initial E_0 assignment. The refined value of the photoabsorption threshold is then $E_0 + \Delta E_0$. In a single-shell analysis, two parameters, R and ΔE_0 are required to fit the period of the EXAFS signal. However, a variation in the value of ΔE_0 is mostly sensitive at low k, whereas errors in the distance R are especially obvious at high k. Therefore the solution is usually unique in the case of a one-shell fit. The amplitude of the EXAFS function is determined by the coordination number and the two damping terms. The three parameters N, Γ and σ are strongly correlated. The number of neighbours is a scale factor over the whole k-range. The two damping terms attenuate the EXAFS magnitude in different k-domains. The amplitude attenuation due to the mean free path is mostly felt at low k-values, unlike σ [21]. This partly allows the contributions of the two damping terms to be separated.

The contribution of one shell is finally characterized by the five parameters R, ΔE_0, N, Γ and σ. On the other hand the number of degrees of freedom is limited owing to the limited k-range in the Fourier transform. According to the classical information theory [27] the number of significant parameters is given by $N_s \approx 2\Delta r \Delta k / \pi$. ($\Delta r$ is the width of the filter window in the real space; Δk is the length of the data set: $\Delta k = k_{max} - k_{min}$.) When the contributions of several shells cannot be isolated from each other, the number of parameters to be taken into account in the analysis is *a priori* multiplied by the number of shells. In order to obtain a meaningful analysis, the limitation of the number of significant parameters must be borne in mind.

The quality of the adjustments is evaluated from a reliability-on-fit parameter ζ. The accuracy of each parameter is estimated from the variation in ζ. If the best fit (x_0, y_0, z_0, ...) corresponds to a value ζ_{min} for the reliability-on-fit parameter, the accuracy of the parameter x is the variation Δx from x_0, giving a fit with a reliability-on-fit parameter $2\zeta_{min}$, all other parameters being maintained constant.

2.2. Samples

The preparation and the characterization of the samples have been reported in a previous paper [9].

The space group for the wurtzite structure is $P6_3mc$. The hexagonal unit cell contains four atoms at the special positions 2b [7]. The cadmium atoms occupy the sites $(\frac{1}{3}, \frac{2}{3}, 0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$, while the chalcogen atoms are at $(\frac{1}{3}, \frac{2}{3}, u)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + u)$ (figure 1).

In the ideal wurtzite structure AB the two sublattices of atoms A and B are prefect hexagonal close-packed lattices (i.e. $c/a = (\frac{8}{3})^{1/2} = 1.633$). The two lattices are shifted from each other in the direction [001] by a distance uc so that the coordination polyhedron around each atom is a perfect tetrahedron (i.e. $u = (\frac{1}{3})(a/c)^2 + \frac{1}{4} = \frac{3}{8}$) [28]. In a non-ideal wurtzite structure the atomic shells are split along the [001] axis. The distances to the first four neighbours are related to the lattice parameters a and c and to the parameter u. These relations are given in table 2 for ideal and non-ideal wurtzite structure. The lattice parameters of CdS and CdSe are given in table 1. The two conditions for an ideal wurtzite structure are fulfilled to better than 0.2% for CdSe [29, 30] and to better than 0.6% for CdS [31, 32]. The split due to deviation from the ideal wurtzite structure is small for each shell in both compounds (table 2). As a first approximation the structures of CdSe and CdS have been considered as ideal wurtzite structures. In the EXAFS analysis the deviation from this ideal structure results for each shell in a contribution σ_{ni} to the static disorder. σ_{ni} is related to the root mean square standard deviation from the 'ideal' value of the distance. For a shell made of two subshells of m atoms at d_m and n atoms at d_n, with $d_m - d_n = \Delta r$, σ_{ni} is $(mn)^{1/2}\Delta r/m + n$ [21]. These values are given in table 2 for CdS and CdSe.

Table 2. Relations between the distances of the first four shells and the lattice parameters c, a and u in wurtzite structures. Calculated values for CdS and CdSe, and split s with respect to the ideal wurtzite structure are also given.

			CdS		CdSe	
	N	d	d (Å)	s (Å)	d (Å)	s (Å)
First shell	1	uc	2.531		2.636	
				0.002		0.003
	3	$[\frac{1}{3}a^2(u - \frac{1}{2})^2c^2]^{1/2}$	2.527		2.630	
Second shell	6		4.136		4.299	
				0.009		0.003
	6	$[\frac{1}{3}a^2 + \frac{1}{4}c^2]^{1/2}$	4.119		4.295	
Third shell	1	$(1-u)c$	4.185		4.374	
Fourth shell	6	$[a^2 + u^2c^2]^{1/2}$	4.849		5.043	
				0.001		0.002
	3	$[\frac{4}{3}a^2 + (u - \frac{1}{2})^2c^2]^{1/2}$	4.847		5.040	

On the other hand the thermal disorder and thus the damping Debye–Waller term can be reduced by performing low-temperature measurements [21]. Figure 2 shows the imaginary part of the Fourier transform of $k\chi(k)$ for CdSe recorded at 77, 20 and 4.5 K. The contribution of the second and third shells are not separated. The figure clearly shows that the contributions of these shells are significantly increased for measurements at temperatures lower than 20 K. The analysis of the static structure of these atomic shells has indeed been possible for CdSe only for temperatures lower than 20 K.
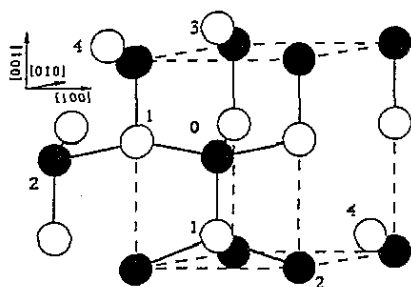
Figure 1. Ideal wurtzite structure. The central atom is labelled 0. The distances to the first four neighbours (labelled 1–4) are related to the lattice parameters a and c and to the parameter u.
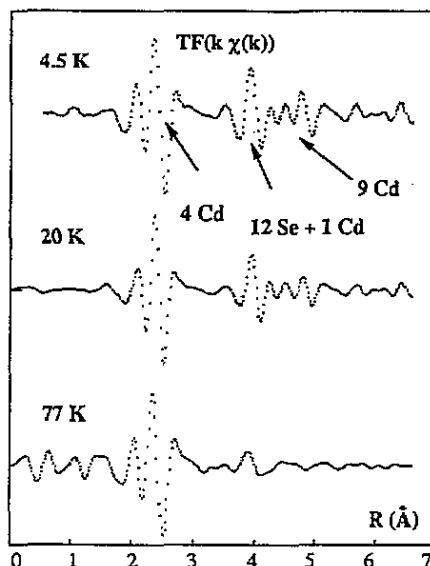
Figure 2. Imaginary part of the Fourier transform of $k\chi(k)$ for CdSe spectra recorded at the selenium K edge for different temperatures: 4.5, 20 and 77 K. The contribution of the second and third neighbours (12 chalcogen atoms and one cadmium) is very weak for $T = 77$ K.

Four compounds corresponding to $x = 0$, 0.2, 0.5 and 0.8 have been studied. Thin homogeneous powder samples are obtained from a water dispersion by powder deposition on millipore membranes. The thicknesses of the samples were about 40 μm, giving an absorption coefficient after the absorption edge of between 1 and 2 and an absorption jump at the edge greater than 0.2. X-ray diffraction measurements show that the powder is fully disoriented in the plane of the sample but not in the perpendicular plane. Because of the anisotropy of the structure, two limiting cases of preferential orientation of the powder grains can be considered: the [001] axis in the plane of the millipore or perpendicular to this plane. X-ray diffraction patterns agree with either one or the other of these two possibilities depending on the experimental conditions of preparation of the samples [33]. Owing to the polarized nature of the synchrotron beam, residual orientation may affect the amplitude of the EXAFS signal [25, 34]. In both cases the axis of minimal symmetry is perpendicular to the plane of the sample. Texture effects can then be cancelled by setting the plane of millipores at 35.3° with respect to the electric field vector of the beam [25]. In that geometry the EXAFS analysis can be performed as if the sample does not have any preferred orientation [35].

2.3. Measurements

The x-ray absorption measurements were performed at the selenium K edge (12 658 eV) using the synchrotron radiation provided by the DCI electron storage ring of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay, France). A two-silicon-crystal monochromator working with the reflection 311 was used, giving an overall energy resolution of about 4 eV. The spectra were recorded in the transmission mode. *The incident*

and transmitted x-ray beam intensities were measured using argon-filled ion chambers with a gas pressure of about 600 Torr in the chamber before the sample and 1000 Torr in the chamber after the sample.

The low-temperature (4.5 K) measurements were carried out with a liquid-helium 'circulation-type' cryostat [36]. The temperature was regulated by the helium flow and measured with a carbon probe to an accuracy of 0.2 K.

3. Results

The k-ranges for the analysis were the same (4.0–14.2 Å^{-1}) for all samples and for every atomic shell. The imaginary parts of the Fourier transform of $k\chi(k)$ are shown in figure 3 where the moluli of the Fourier transform are also reported. In the modulus of the Fourier transform, each peak corresponds to a contribution which can be studied separately from the others. The widths of the peaks range between 1.1 and 1.3 Å so that the maximum number of significant parameters is about eight for the refinement of each peak. The results of all refinements are given in table 3.

Table 3. Results of the EXAFS analysis for the four samples with $x = 0, 0.2, 0.5$ and 0.8, analysed in the same conditions: the natures, distances R and numbers N of neighbours, the Debye–Waller parameters σ, the parameters Γ characterizing the mean free path of the photoelectron and the energy shifts ΔE_0. s indicates that σ has been taken as having the same value as the previous subshell.

			R (Å)	N	σ (Å)	Γ (Å^{-2})	ΔE_0 (eV)
$x = 0$	First peak	Cd	2.634 ± 0.005	4.0	0.050 ± 0.003	1.80	−0.60
	2d peak	Se	4.294 ± 0.010	12.0	0.070 ± 0.005	1.55	1.51
		Cd	4.384 ± 0.010	3.0	0.070 ± 0.005	1.80	−0.50
	3d peak	Cd	5.051 ± 0.005	9.0	0.072 ± 0.005	1.80	−0.40
$x = 0.2$	First peak	Cd	2.630 ± 0.005	4.0 ± 0.50	0.054 ± 0.005	1.80	−0.60
	2d peak	Se	4.270 ± 0.015	9.6 ± 1.00	0.070 ± 0.005	1.55	1.50
		S	4.210 ± 0.015	2.4 ± 1.00	s	1.40	2.42
		Cd	4.350 ± 0.015	3.0	0.070 ± 0.005	1.80	−0.50
	3d peak	Cd	5.008 ± 0.010	9.0 ± 0.50	0.087 ± 0.005	1.80	−0.40
$x = 0.5$	First peak	Cd	2.623 ± 0.005	4.0 ± 0.50	0.054 ± 0.005	1.80	−0.60
	2d peak	Se	4.240 ± 0.015	5.7 ± 0.05	0.072 ± 0.005	1.55	1.50
		S	4.160 ± 0.015	6.3 ± 0.05	s	1.40	2.42
		Cd	4.330 ± 0.015	3.0	0.070 ± 0.005	1.80	−0.50
	3d peak	Cd	4.930 ± 0.015	9.0 ± 0.50	0.090 ± 0.005	1.80	−0.40
$x = 0.8$	First peak	Cd	2.617 ± 0.005	4.0 ± 0.50	0.054 ± 0.005	1.80	−0.60
	2d peak	Se	4.220 ± 0.015	3.0 ± 1.00	0.085 ± 0.005	1.55	1.50
		S	4.120 ± 0.015	9.0 ± 1.00	s	1.40	2.42
		Cd	4.290 ± 0.015	3.0	0.070 ± 0.005	1.80	−0.50
	3d peak	Cd	4.880 ± 0.020	9.0 ± 0.50	0.100 ± 0.005	1.80	−0.40
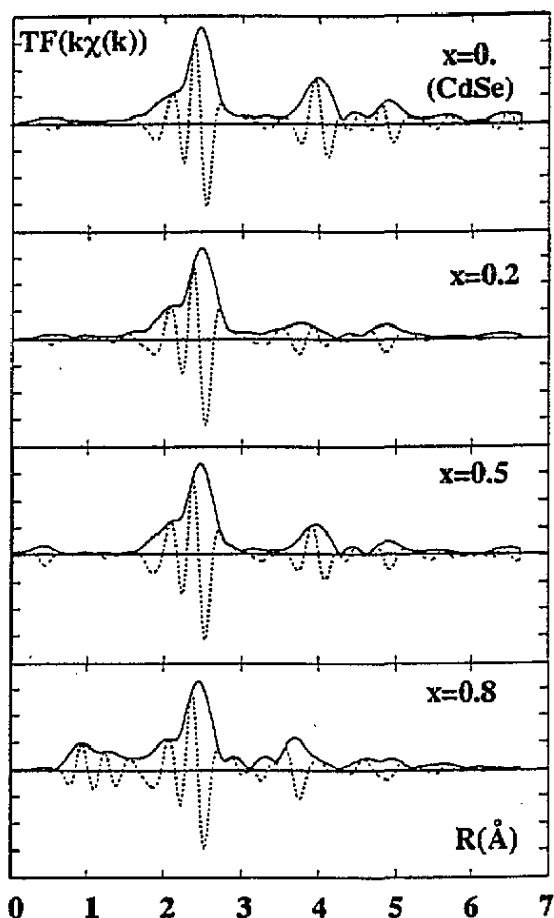
Figure 3. Modulus (——) and imaginary part ($\cdots$) of the Fourier transform of $k\chi(k)$ in the range 3.5 Å^{-1} $< k <$ 14.2 Å^{-1}, for the four samples. The first peaks due to the coordination shell have almost the same amplitudes and shapes in the four samples. Owing to interference effects between sulphur and selenium second neighbours the amplitude of the second peak is much lower in the ternary compounds than in the binary compound CdSe.

3.1. CdSe

3.1.1. Coordination shell. For the coordination shell the value of the constant Γ^1_{Se-Cd} was adjusted to give four nearest neighbours. This gives $\Gamma^1_{Se-Cd} = 1.80$ Å^{-2} with $\sigma = 0.05$ Å. The value of the distance R_{Cd-Se} is found to be in agreement with the structure ($R_{Se-Cd} = 2.634$ Å), with a ΔE_{01} value of -0.5 eV.

3.1.2. Fourth atomic shell. The analysis of this contribution gives a distance in agreement with the expected value ($R_{Se-Cd} = 5.02$ Å). The value Γ^4_{Se-Cd} which gives exactly nine atoms of cadmium is very close to that used to obtain four neighbours for the first shell ($\Gamma^4_{Se-Cd} = 1.68$ Å^{-2}). Using the value $\Gamma_{Se-Cd} = 1.8$ Å^{-2} the best fit gives 9.3 neighbours. The value $\Gamma_{Se-Cd} = 1.8$ Å^{-2} can then be considered as a good value for the analysis of all shells.

3.1.3. Second and third atomic shells. The contributions of the second and the third atomic shells are analysed together. Ten parameters (R, ΔE_0, N, Γ and σ for each subshell) should be determined *a priori*. However, Γ_{Se-Cd} is already fixed (1.8 Å^{-2}) and the number of selenium atoms as second neighbours is known to be 12, so that the number of free parameters can be restricted to eight. The distances obtained for the Se–Cd and Se–Se pairs ($d_2 = R_{Se-Cd} = 4.38$ Å and $d_3 = R_{Se-Se} = 4.29$ Å, respectively) are those expected for the wurtzite structure.

The analysis gives about three cadmium neighbours in the third shell although only one atom is expected according to the wurtzite structure. Because of the conditions used to record the data this cannot be the result of preferred orientations in the sample. This high value can be explained if we note that in the wurtzite structure the absorbing selenium atom, one of the cadmium first neighbours and the cadmium third neighbour are colinear along the [001] axis (figure 1). In this case the photoelectron outgoing from the third atomic shell is strongly scattered forwards by the collinear first neighbour, which results in a significant multiple-scattering contribution to the EXAFS signal. The amplitude enhancement yields an apparent number of neighbours greater than the real value in a single-scattering EXAFS analysis [21]. Comparisons between calculations of the cross sections of single scattering and double scattering for a three-shell cluster up to 70 eV after the edge confirms this explanation [37]. We have therefore considered that one atom of cadmium in this geometry yields an apparent number of neighbours of three in the usual single-scattering EXAFS analysis.

For this third shell the Debye–Waller factor has been found to be 0.07 Å.

3.2. Ternary compounds

The conditions of data reduction (normalization and Fourier transform) are the same as for CdSe. In order to compare the values of σ and Γ for corresponding shells in the ternary compounds and in CdSe, the k-range for the analysis is taken to have the same value. The results are given in table 3.

3.2.1. Coordination shell. The mean free path factor Γ_{Se-Cd} is set at the value 1.8 Å^{-2}. The analysis gives for the three samples four cadmium neighbours with a Debye–Waller factor of 0.054 Å. The distances Cd–Se in the three samples are 2.630 Å, 2.623 Å and 2.617 Å for $x = 0.2$, 0.5 and 0.8, respectively.

3.2.2. Fourth shell. With the same conditions of refinement as in CdSe, nine atoms of cadmium have been found at distances of 5.01 Å, 4.93 Å and 4.99 Å, respectively, for $x = 0.2$, 0.5 and 0.8. The quality of the refinement is good for $x = 0.2$ and gives a good accuracy (0.01 Å). The value of σ is 0.087. The quality of the refinement and the accuracy of the measurement decrease with decreasing selenium content. In CdS$_{0.8}$Se$_{0.2}$ the value of σ found when the analysis reaches the limiting value of 0.1 above which the results cannot be considered as meaningful.

3.2.3. Second and third shells. In the ternary compounds the chalcogen atoms in second-neighbour positions around the central selenium atom can be either sulphur or selenium atoms. A three-shell analysis with 15 parameters is then necessary. As concerns the cadmium and selenium subshells the values of Γ and ΔE_0 can be set to the values found for the corresponding shells in CdSe ($\Gamma_{Se-Cd} = 1.80$ Å^{-2} and $\Gamma_{Se-Se} = 1.50$ Å^{-2}; $\Delta E_{0Cd} = -0.5$ eV and $\Delta E_{0Se} = 1.5$ eV). The Debye–Waller parameter has been arbitrarily

imposed to be the same for the sulphur and the selenium subshells. For the cadmium subshell the values of N (3.2) and σ (0.07 Å^{-2}) have been set at the same values as in CdSe. The number of free parameters is then reduced to eight. Moreover the number of chalcogen atoms is adjusted by a scaling factor to give the total meaningful value of 12 atoms as second neighbours. The best refinements are given in figure 4 and the results are given in table 3.

In the three samples the numbers of sulphur and selenium in second-neighbour positions are approximately proportional to the respective molar ratios. For $x = 0.2$ and $x = 0.8$ there is no way to evaluate this ratio accurately because the contribution of one kind of neighbour (selenium and sulphur, respectively) is largely predominant. The uncertainty in the number of neighbours for $x = 0.2$ and $x = 0.8$ is about ±1.5. For $x = 0.5$ the two contributions of sulphur and selenium atoms are of the same order. Irrespective of the conditions imposed on the third cadmium shell, good refinements with a number of neighbours for each subshell varying between 5.7 and 6.3 are obtained. The accuracy in N is then about 0.5.

4. Discussion

The relaxation of the coordination shell has been studied in a previous paper [9]. As the present paper deals with an evaluation of the clustering parameter, we discuss only the respective numbers of sulphur and selenium atoms in second-neighbour positions in the three ternary compounds.

The numbers of neighbours are correlated with the Debye–Waller terms. Some comments about the experimental values of the Debye–Waller parameters for the first and fourth shells are needed first. At the temperature of the experiments the dynamic disorder can be considered very small compared with the static disorder. On the other hand the calculated Debye–Waller term resulting from the splitting of the shells in the wurtzite structure (table 2) is one order smaller than that obtained from the analysis. The approximation of an ideal wurtzite structure is then fully justified.

The Debye–Waller terms measured for the coordination shell are about the same in the three ternary compounds and are only increased by about 10% with respect to the binary compound. For the fourth atomic shell the increase in σ between CdSe and $CdS_{0.2}Se_{0.8}$ is about 20%. In the latter case the sulphur atoms can almost be considered as impurities in a CdSe lattice. The disorder due to the local lattice distortions around the sulphur atoms is limited to the very close neighbour shells. In the samples $CdS_{0.5}Se_{0.5}$ and $CdS_{0.8}Se_{0.2}$ the fourth-neighbour shell is not as well defined; the value of σ is higher and the refinements are not very satisfactory over the whole k-range. It is highly probable that such an effect is the result of a multimodal distribution of the cadmium atoms. Owing to the small amplitude of this contribution to the EXAFS signal, no meaningful analysis assuming two subshells has been possible.

The Debye–Waller terms found for the second subshell of selenium atoms in the ternary compounds are almost the same for $x = 0.2$ and $x = 0.5$ as that for CdSe. For $x = 0.8$, this term is found to be about 20% greater. As differences of the same order have been found for the Debye–Waller term in the coordination shell, these values are considered meaningful.

Information about clustering is obtained from the second-neighbour shell. In the limiting case of total clustering ($\beta = 1$) this shell would be made up of only selenium atoms. The necessity to take into account the contribution of sulphur atoms to analyse this shell excludes this hypothesis. To obtain further information an evaluation of the accuracy in the value of β is needed. In the case $\beta = 0$ (no clustering) we would have $N^0_{SeSe} = 12(1 - x)$. For

clustering $\beta \geqslant 0$, $N^{\beta}_{\text{SeSe}} = 12[(1 - x) + \beta x]$. As the accuracy in the determination of the number of neighbours in each subshell (sulphur and selenium) is ΔN, the accuracy in the determination of β is $\Delta\beta$, with $12\,\Delta\beta = \Delta N$. One obtains $\beta = 0.1\pm0.4$, $\beta = 0\pm0.05$ and $\beta = 0.1 \pm 0.2$ for $x = 0.2$, 0.5 and 0.8, respectively (figure 5). For each composition the accuracy $\Delta\beta$ then gives the maximum value of β compatible with the experiments. These limiting values are $\beta_{\text{max}} = 0.4$, $\beta_{\text{max}} = 0.05$ and $\beta_{\text{max}} = 0.2$ for $x = 0.2$, 0.5 and 0.8, respectively. The maximum accuracy is obtained for $x = 0.5$ and β is found to be smaller than 0.05 (figure 5). As the clustering is expected to be the largest for this composition, it can be concluded that β is smaller than 0.05 over the whole composition range. This value is much lower than that given by Verleur and Balkanski in 1967 [19] but not surprising with respect to the small lattice mismatch between CdS and CdSe.
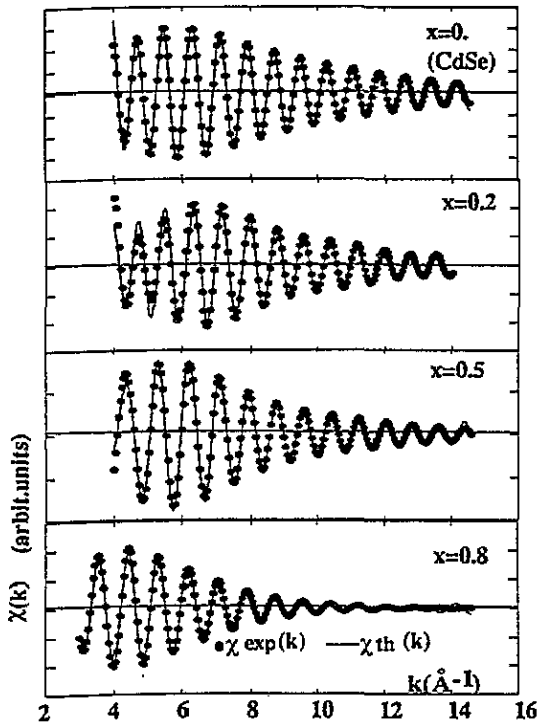

Figure 4. Best fit of the second peak in the Fourier transform of $\chi(k)$ for the four samples. The evolution of the shape of the envelope of $\chi(k)$ accounts from the evolution of the ratio of sulphur atoms to selenium atoms as second neighbours around the central selenium atom.

5. Concluding remarks

No clustering of the chalcogen atoms is observed in the ternary compounds CdS_xSe_{1-x}. However, because of the limited accuracy, only a maximal clustering parameter can be given. The accuracy is the best for $x = 0.5$ and in that case the maximum value compatible with experiment is $\beta = 0.05$. As clustering is expected to be the largest for this composition,
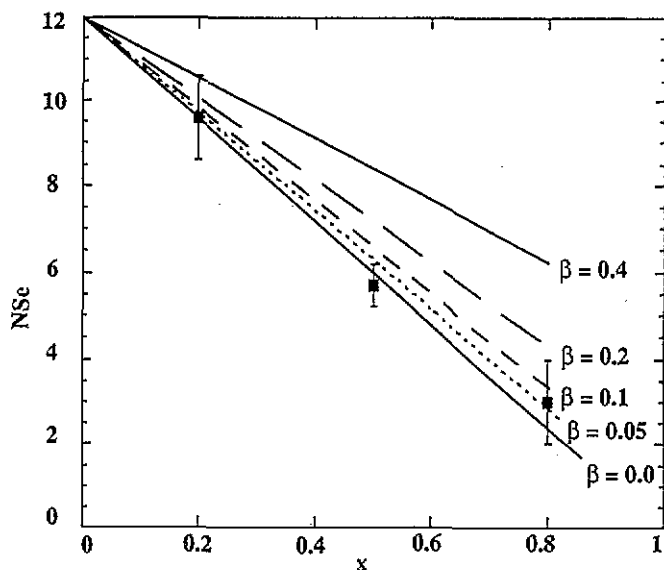
Figure 5. Plot of the number of selenium atom second neighbours around selenium against composition: ■, experimental data with the corresponding errors bars; the lines are the calculated data given for the cases $\beta = 0$, $\beta = 0.05$, $\beta = 0.1$, $\beta = 0.2$ and $\beta = 0.4$. For $x = 0.5$ the experimental results agree only for a clustering parameter smaller than 0.05.

it can be concluded that β is smaller than 0.05 over the whole composition range. This result is not surprising when one considers the small lattice mismatch between the lattice parameters of CdS and CdSe. Thermodynamic studies, already available for the zincblende structure, would probably be of a great interest to complete the full knowledge of the clustering in this wurtzite system.

Acknowledgments

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