

Much empirical data indicate the existence of deviations from Vegard's law (from a linear dependence of the cell parameters or the interatomic distance on the composition of a solid solution). Usually these deviations are positive and are described by a simple parabolic function of the composition. The model we propose considers explicitly displacements about the impurity defect of both the nearest neighbors and the next-nearest neighbors, and in some cases the third-nearest neighbors. We show that displacements of nearest neighbors completely compensate each other, while second-order shifts (of next-nearest neighbors) lead to a positive deviation (parabolic in shape) of the cell parameters vs. composition. The magnitude of the deviations depends on the structure of the solid solution (the coordination number) and the difference between the cell parameters of the pure components. The calculation for solid solutions with structures of the NaCl, CsCl, and ZnS types is compared with available experimental data.

In the seventy years since the observation by Vegard [1] of a linear dependence of the cell parameters of a solid solution on composition

$$a = x_1 a_1 + x_2 a_2, \quad (1)$$

many confirmations of this rule have been found, as well as a large number of deviations from it. Generally with an increase in the accuracy of the experimental determinations, the number of observed deviations from Vegard's law increases.

Many attempts have been made to explain and predict deviations from Vegard's law [2-5]. Most of these attempts have been based on first-order and second-order elasticity theory [2-4] and have been used to explain deviations from Vegard's law in binary metallic alloys. As shown by analysis of these models in [6], the fraction of correct predictions is not great (about 40% on the average). However, in [7] a model based on elasticity theory was used successfully to explain the observed deviations from Vegard's law for the system rutile TiO_2 -cassiterite SnO_2 . Somewhat earlier [8], the reasons for the deviations from Vegard's law for essentially ionic solid solutions (halides, oxides, etc.) were separated into geometric and chemical factors.

If substitution of atoms occurs at several nonequivalent sites of the structure, then deviations from Vegard's law (including negative and variable-sign deviations) often can be explained by preferred filling of one or several sites [9]. The conditions for satisfaction of Vegard's law for multiple-sublattice solid solutions of the perovskite type [10, 11] or spinel type [12-14] were found using the quasielastic bond model.

Small positive deviations from Vegard's law can also be described using the volume additivity law (Retgers's law) [15], which in the case of a cubic crystal has the form:

$$a^3 = x_1 a_1^3 + x_2 a_2^3. \quad (2)$$

In most cases, the observed deviations from Vegard's law display a parabolic dependence on composition:

$$a = x_1 a_1 + x_2 a_2 + \Delta a = x_1 a_1 + x_2 a_2 + x_1 x_2 \delta. \quad (3)$$

The goal of this report is to analyze the possible geometric reasons for the deviations from Vegard's law for single-site substitutional solid solutions (insulators and semiconductors).

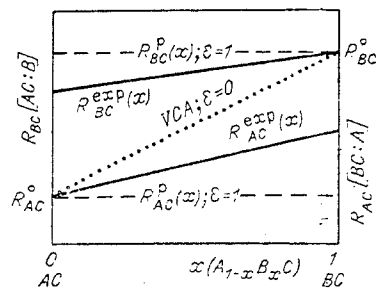


Fig. 1. Schematic variation of the bond lengths of components AC and BC as a function of composition: VCA) virtual crystal approximation, no relaxation, $\epsilon = 0$, Vegard's law is satisfied; RP) total relaxation, $\epsilon = 1$, individual bond lengths are equal to their values for the pure components; R^{exp}) possible real change in the individual bond lengths as a function of composition.

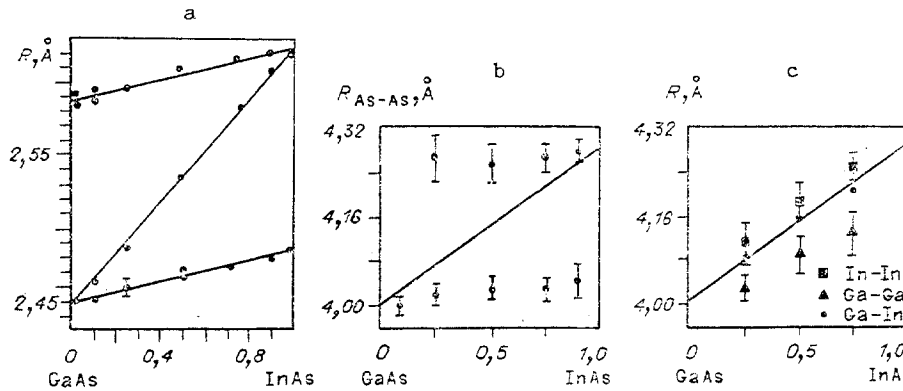


Fig. 2. Variation of the interatomic distances in the solid solution $(Ga_x-In_{1-x})As$ according to EXAFS data [19]: a) distances between nearest neighbors In-As and Ga-As. The average distance $R = x_1R_{In-As} + x_2R_{Ga-As}$ closely corresponds to Vegard's law; b) distances between next-nearest neighbors As-As; c) distances between next-nearest neighbors In-In, Ga-Ga, and Ga-In.

LOCAL DISPLACEMENTS OF ATOMS IN THE STRUCTURE OF A SOLID SOLUTION

If the solid solution follows Vegard's law (1), then the average bond lengths in its structure can be determined from the analogous additivity rule:

$$R(x) = \bar{R}_1(x) = \bar{R}_2(x) = x_1R_1 + x_2R_2 = R_2 - x_1\Delta R = R_1 + x_2\Delta R, \quad (4)$$

where R_1 and R_2 are the interatomic distances in the pure components; $\Delta R = R_2 - R_1$. The assumption that all the individual bond lengths in the mixed crystal are equal to their average values according to rule (4), i.e., relaxation is completely absent, corresponds to the idea of the so-called virtual crystal (Fig. 1).

For the other assumption, that all the atoms in the solid solution retain their own initial dimensions, i.e., for maximum relaxation of the structure, the individual bond lengths are equal to their lengths in the pure components (R_1 and R_2). This hypothesis leads to the "bond alternation" model in the solid solution.

Both extreme cases considered above agree equally well with Vegard's law, as shown schematically in Fig. 1. It is clear that the actual change in the different type of bond lengths should be found between the indicated limits. In other words, partial relaxation of the structure also does not contradict Vegard's law (see Fig. 1).

Determination of the degree of relaxation of the structure, i.e., the local displacements of the atoms, is an independent and rather complicated experimental and theoretical problem. It is especially difficult to obtain information about the local structure using traditional methods, which provide information about the average coordinates of the atoms in the crystal. Nevertheless, early x-ray studies of the solid solutions KCl-KBr and KCl-

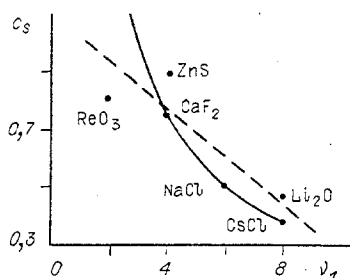


Fig. 3. Functional relationship between the compliance parameter c_s and the first coordination number ν_1 . The solid curve is the calculation using Eq. (15).

RbCl (1:1) carried out by Wasastjerna [16] observed a decrease in the intensity of reflections compared with the pure crystals, which cannot be explained only by thermal vibrations but rather require hypotheses of significant static displacements of the ions from their ideal positions. The local displacements of those atoms which are found in a mixed environment (K in the first case and Cl in the second case) proved to be especially greater, on the order of the difference between the interatomic distances of the pure components. The x-ray study of alloys in [17] also showed that when the spatial symmetry of the pure components is retained by the mixed crystal, weakening of the intensities of the reflections and appearance of regions of diffuse scattering near them are evidence for local deformation of the structure of the alloy at a distance of several bond lengths about the impurity atom. An attempt to analyze such effects in [18] led to the conclusion that local shifts are on the order of the difference in interatomic distances, but no rigorous correlation was observed.

It became possible only about 10 years ago to directly determine the different types of individual bond lengths in mixed crystals using EXAFS (extended x-ray spectroscopy of the absorption edge fine structure). Using this method, in 1979-1980 appreciable local displacements of atoms about an impurity were observed in metallic alloys, and then in mixed chalcogenides. In Fig. 2a, as an example we show the experimentally measured [19] dependences on composition of the nearest-neighbor distances Ga-As and In-As in the solid solution (Ga, In)As with the sphalerite structure (coordination number 4). We can see that the maximum change in the bond length in a dilute solution is only 20-25% of the difference between the bond lengths of the pure components $\Delta R = R_2 - R_1$ ($R_2 > R_1$). Thus the real interatomic distances are quite different from the virtual crystal model, although the weighted-mean of these distances is almost exactly described by Vegard's law.

Another observation made in this experiment [19] was that the width of the distributions of the Ga-As and In-As distances in the solid solution are virtually the same as in the pure crystals, in accordance with the fact that the immediate environment of both cations is homogeneous and consists only of As atoms. In contrast, about As we observe a bimodal distribution of distances, corresponding to a mixed cationic (Ga, In) environment for this atom.

The distances between the next-nearest neighbors (cation-cation and anion-anion) are quite different from one another in character. The EXAFS data clearly indicate the existence of two different As-As distances in the solid solutions: the shorter distances correspond to As-Ga-As configurations, and the longer distances correspond to As-In-As configurations (Fig. 2b). The weighted-mean of these two distances corresponds to Vegard's law, which is shown in Fig. 2b by the solid line. From these data it is clear that the anionic packing in the solid solution is strongly distorted compared with the regular cubic (closest) packing of the anions in the pure components.

The cation-cation distances of the next-nearest neighbors give a completely different pattern. As shown by Fig. 2c, all the interatomic distances Ga-Ga, In-In, In-Ga vary according to Vegard's law (within deviation limits on the order of 0.05 Å), as follows from the virtual crystal model. This means that in the mixed-composition (cationic) sublattice, in contrast to the unmixed (anionic) sublattice, the atoms occupy almost regular ties and the distortions of the ideal packing are relatively small.

Such results are mainly obtained by the EXAFS method for ionic solid solutions with the NaCl structure (coordination number six): (K, Rb)Br and Rb(Br, I) [20]. However, in these two cases, the maximum change in the distances is about twice that for essentially covalent crystals with the ZnS structure, and is about 40%. Relatively large changes in the distances of about 40% were also observed for Sr-substituted fluorite CaF₂ [21]. In

these solutions, the mixed sublattice can be represented as a slightly distorted packing, while the common atoms are shifted from the ideal positions. The local structure of the substitutional solid solution observed by the EXAFS method agrees well with numerous theoretical calculations of structure distortions about an impurity in an ionic crystal [22-26]. A typical result of such calculations is the fact that the shift of nearest neighbors about the impurity in an NaCl structure is about half the difference between the interatomic distances: $\delta R \approx (1/2)\Delta R$. The shifts of the next-nearest and more remote neighbors decrease approximately in proportion to the square of the interatomic distances, as follows from the elastic continuum model in [27].

A more detailed picture of the local displacements is given by modeling by the DLS [distance least squares] method, which involves least-squares optimization of the individual bond lengths, adjusting them to some standard distances (the latter for solid solutions are simply the distances in the pure components). Application of the DLS method for isovalent solid solutions with different structures allowed Dollase [28] to introduce the concept of "site compliance," by which is meant the real fraction of increase (or decrease) in the bond length in the infinite dilution limit (very small number of impurity atoms) relative to the difference between the bond lengths of the pure components. Analyzing his results [28], Dollase concluded that the compliance parameter c_s is inversely proportional to the coordination number of the nearest neighbors of the impurity, since it is specifically those neighbors which undergo the greatest displacement (Fig. 3). Thus large changes in the bond lengths characterize less closely packed structures (ZnS, ReO_3), while small changes characterize the more closely packed structures (NaCl, CsCl). It is important to note that DLS calculations agree well with experiment. Thus the predicted relaxation of the bond lengths in an NaCl structure is about 50%, while it is about 20% in a ZnS structure, corresponding closely to experimental data (40-50 and 20-25%, respectively).

FIRST-ORDER SHIFTS IN SIMPLE STRUCTURES

The experimental and theoretical data considered in the preceding section are evidence that the greatest displacements in the structure of a solid solution $(A_{x_1}B_{x_2})C$ are experienced by the C atoms in the sublattice in which mixing does not occur, while the A and B atoms form almost an undistorted packing. Further consequences of this situation are as follows.

If the environment of the common atom C is homogeneous, i.e., consists only of type A atoms or only of type B atoms, then all the A-C or B-C distances are identical and are equal to the average values of $R(x)$ (4). If the environment of the C atom is mixed, i.e., consists of some number of A atoms and some number of B atoms, then bond chains of the A-C-B type arise in the structure as well as a shift of the C atom from its ideal position in the middle between neighbors toward the smaller atom. For example, let the A atom be larger than the B atom. Then the C atom is shifted from the center of the A-C-B chain toward B, and the A-C distance becomes equal to $R + u$, where u is some shift of the C atom.

The change in the C-B distance in the A-C-B chain will depend on the bond angle $\angle A-C-B$, and to a first approximation may be represented as:

$$u_1 = u \cos \alpha, \quad (5)$$

where $\alpha = \angle A-C-B$.

In an NaCl structure (octahedral environment), the A-C-B chain is linear, $\alpha = 180^\circ$, and consequently $u_1 = -u_0$.

In a ZnS structure (tetrahedral coordination), $\alpha = 109^\circ 28'$ and therefore $u_1 = -1/3u$.

In a CsCl structure with a cubic environment of the central atom, three systems of bond chains appear with angles 180° , $109^\circ 28'$, and $70^\circ 32'$. From Eq. (5) it follows that in this case

$$\begin{aligned} u_1 &= -u, \\ u_1' &= \pm \frac{1}{3} u. \end{aligned}$$

Thus in the first approximation considered here, mutual compensation of bond lengths about the impurity for an NaCl structure occurs owing to the change in the lengths of the two bonds by $+u$ and $-u$, respectively; in a ZnS structure, the shift of the common atom along

one of the bond lines by u is compensated by the change in the lengths of the other three bonds in the tetrahedron by $-1/3u$ each. In a CsCl structure, the shift of the atom from the center of the cube simultaneously increases the length of one of the bonds by u and decreases the other by $-u$, but in addition the increase in the bond length by u is accompanied by shortening of the other three bonds by $-1/3u$, and a corresponding decrease in the bond length by $-u$ is accompanied by lengthening of the other three bonds by $1/3u$.

In other words, first-order shifts completely compensate each other and cannot explain the observed deviations from Vegard's law.

RADIAL FORCE MODEL IN A STATISTICAL SOLID SOLUTION

Let us now attempt to estimate the magnitude of the first-order shifts using a simple radial force model. Let us designate as $\varepsilon(R)$ the energy of some pair of atoms bonded with each other, separated by the distance R . The number of A-C bonds in A-C-A chains will be proportional to the probability of encountering these pairs of bonds in the solid solution, i.e., x_1^2 ; the number of A-C bonds in A-C-B chains will be proportional to x_1x_2 . Similarly, the number of B-C bonds in B-C-B chains will be proportional to x_2^2 , and in B-C-A bonds it will be proportional to x_2x_1 .

Then the change in energy upon formation of the solid solution can be represented as:

$$\Delta E = Nv [x_1^2 [\varepsilon_1(R) - \varepsilon_1(R_1)] + x_2^2 [\varepsilon_2(R) - \varepsilon_2(R_2)] + x_1x_2 [\varepsilon_1(\bar{R}_1) - \varepsilon_1(R_1)] + x_2x_1 [\varepsilon_2(\bar{R}_2) - \varepsilon_2(R_2)]]. \quad (6)$$

Here N is Avogadro's number; v is the coordination number; $\varepsilon_1(R_1)$ and $\varepsilon_2(R_2)$ are the energies of pair interactions in the pure components; $\varepsilon_1(R)$ and $\varepsilon_2(R)$ are the energies of the two types of bonds (A-C and B-C) at the average distance R in symmetric chains of bonds; $\varepsilon_1(\bar{R}_1)$ and $\varepsilon_2(\bar{R}_2)$ are the energies of the same bonds in asymmetric chains of bonds.

The distances \bar{R}_1 and \bar{R}_2 depend on the shifts of the C atoms in accordance with the magnitude of the bond angle, as shown in the preceding section. For example, for an NaCl structure:

$$\begin{aligned} \bar{R}_2 &= R + u \\ \bar{R}_1 &= R - u. \end{aligned}$$

Let us expand the energy ΔE in a Taylor series, limiting ourselves to second-order terms and considering that in the equilibrium state $\varepsilon'(R) = 0$ (at $T = 0$ K):

$$\varepsilon(R) - \varepsilon(R_0) = \frac{1}{2} \varepsilon''(R_0) (R - R_0)^2.$$

If we also assume that the properties of the components are similar, i.e., $\varepsilon_1''(R_1) = \varepsilon_2''(R_2) = \varepsilon''(R)$, then from (6) we obtain:

$$\Delta E = \frac{1}{2} Nve''(R) [x_1^2 (R - R_1)^2 + x_2^2 (R - R_2)^2 + x_1x_2 (R - R_1 - u)^2 + x_1x_2 (R - R_2 + u)^2]. \quad (7)$$

Using Vegard's law (4), let us rewrite (7) in the following form:

$$\Delta E = \frac{x_1x_2}{2} Nve''(R) [2x_1x_2 (\Delta R)^2 + (x_2\Delta R - u)^2 + (-x_1\Delta R + u)^2]. \quad (8)$$

Minimizing the change in energy ΔE relative to the shift u , we obtain the condition:

$$\frac{d\Delta E}{du} = \frac{x_1x_2}{2} Nve''(R) [-2x_2\Delta R + 2u - 2x_1\Delta R + 2u] = 0,$$

From this $4u = 2\Delta R(x_1 + x_2)$.

Since $x_1 + x_2 = 1$, we finally have

$$u = \frac{1}{2} \Delta R. \quad (9)$$

This result means that for an NaCl structure, the shift of the common atom is half the difference between the interatomic distances in the pure components. This estimate agrees

closely with the experimental data in [20] and the compliance parameter of the DLS method in [28].

In solid solutions with the ZnS structure, the shift of the common atom when it has an asymmetric environment [i.e., in the A-C-(B) chain] by u is coupled with a simultaneous change in the lengths of the other three B-C bonds by $-1/3u$. Consequently, the individual bond lengths are equal to:

$$\begin{aligned}\bar{R}_2 &= R + u = R_2 - x_1\Delta R + u, \\ (3 \times) \bar{R}_1 &= R - \frac{1}{3}u = R_1 + x_2\Delta R - \frac{1}{3}u.\end{aligned}\quad (10)$$

The radial force model was already used earlier in [29] for a mixed-composition tetrahedral environment of the central atom, and the following value of the primary shift was found:

$$u = \frac{3}{4} \Delta R. \quad (11)$$

The value obtained for the primary shift is consistent with the displacements of the atoms observed by the EXAFS method (by 20-25% of the bond length in the pure component) and with those predicted by the DLS method [28] (compliance parameter $c_s = 0.84$).

As shown in the preceding section, in solid solutions with a CsCl structure, each primary shift by $\pm u$ is accompanied by three shifts by $\mp 1/3u$. Hence the total change in energy in the radial force approximation can be expressed as:

$$\Delta E = \frac{x_1 x_2}{2} N v \varepsilon''(R) \left[2x_1 x_2 (\Delta R)^2 + (x_1 \Delta R - u)^2 + (-x_2 \Delta R + u)^2 + 6 \left(\frac{u}{3} \right)^2 \right]. \quad (12)$$

Minimization of (12) relative to u gives:

$$\frac{d\Delta E}{du} = \frac{x_1 x_2}{2} N v \varepsilon''(R) \left(-2x_1 \Delta R + 2u - 2x_2 \Delta R + 2u + \frac{4}{3}u \right) = 0, \quad (13)$$

from this we have $u = (3/8)\Delta R$.

This result again agrees well with the estimate of the site compliance in a CsCl structure: $c_s = 0.38$ [28] (compare with $3/8 = 0.375$).

Generalizing the estimates obtained above for the primary shifts of the central atom of the coordination polyhedron when it has an asymmetric environment, we can write the expression:

$$u = \frac{3}{v_1} \Delta R, \quad (14)$$

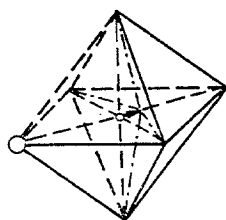
where v_1 is the first coordination number. This corresponds to the conclusion by Dollase [28] that the site compliance is inversely proportional to the number of ligands. In other words, we obtain the following simple connection between c_s and v :

$$c_s = 3/v_1, \quad (15)$$

which is compared in Fig. 3 with the results of the DLS method.

SECONDARY SHIFTS AND DEVIATIONS FROM VEGARD'S LAW

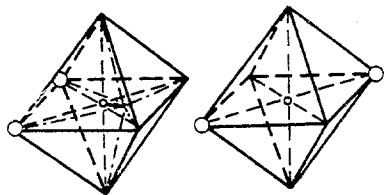
The primary shifts of neighbors of the central atoms of a mixed-composition coordination polyhedron, which can be estimated using formula (1), involve second-order and higher-order displacements. In fact, let us consider an octahedral environment with one substituted atom at the vertex of a regular octahedron, while starting from the assumption of regular undistorted packing of the mixed-composition sublattice (Fig. 4). We can see that the shift of the C atom from the center of the octahedron along the bond direction causes not only changes in the two bond lengths by $+u$ and $-u$ respectively, but also in the remaining four bonds. It is easy to determine that the change in the lengths of symmetric bonds will be $\delta_1 = \sqrt{R^2 + u^2} - R \approx u^2/(2R)$ (to accuracy up to second-order terms). In the case of two substituted atoms at the vertices of the octahedron (Fig. 5), all the bonds undergo additional secondary shifts by $\delta_2 = u^2/R$, and in the case of three substituted atoms (Fig. 6) by $\delta_3 = 3u^2/2R$.



$$\delta R = 2 \frac{u^2}{2R}$$

$$P = 6(x_1 x_2^5 + x_2 x_1^5)$$

Fig. 4

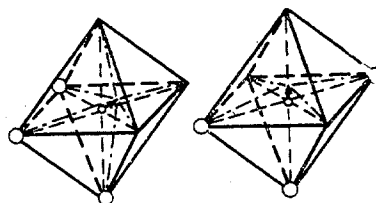


$$\delta R = 2 \frac{u^2}{R}$$

$$\delta R = 0$$

$$P = 12(x_1^2 x_2^4 + x_1^4 x_2^2) \quad P = 3(x_1^2 x_2^4 + x_1^4 x_2^2)$$

Fig. 5



$$\delta R = 2 \frac{3u^2}{2R}$$

$$\delta R = 2 \frac{u^2}{2R}$$

$$P = 8 x_1^3 x_2^3$$

$$P = 12 x_1^3 x_2^3$$

Fig. 6

Fig. 4. Octahedral environment of the central atom with one substituted vertex (δR is the change in the distances to the next-nearest neighbors; P is the probability of the configuration).

Fig. 5. Octahedral environments with two substituted vertices, the changes in the bond lengths δR corresponding to them and the probabilities P .

Fig. 6. Octahedral environments with three substituted vertices, the changes in the bond lengths δR corresponding to them and the probabilities P .

The general expression for the secondary shifts are the following: $\delta_i = (i/2)(u^2/R)$ ($i = 1, 2, 3$). The doubled and tripled values of the shifts for $i = 2$ and $i = 3$ are connected with the fact that all the ligands become next-nearest neighbors of the two ($i = 2$) or three ($i = 3$) substituting atoms.

The fractions of different types of configurations for the different compositions can be easily calculated using Newton's binomial formula

$$P = (x_1 + x_2)^v. \quad (16)$$

The probabilities of the individual configurations are determined by the expression

$$P_i = m_i x_1^{v-\omega} x_2^\omega, \quad (17)$$

where ω is the number of different types of atoms at the vertices of the polyhedron; m_i is the multiplicity of the given configuration (corresponding to the coefficient in Newton's binomial). The multiplicity m_i can be easily determined from the obvious relationship

$$m_i = \frac{n_i}{n}, \quad (18)$$

where n is the symmetry number of the regular coordination polyhedron; n_i is the symmetry number of the i -th configuration (the "substituted" polyhedron). For example, the multiplicity of the first type of configuration in Fig. 4 is

$$m_1 = \frac{48}{8} = 6,$$

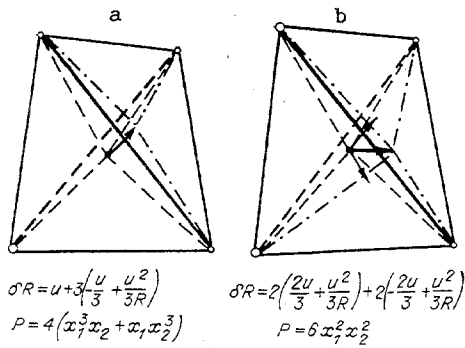


Fig. 7

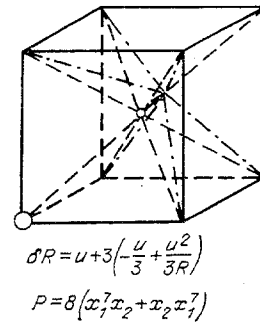


Fig. 8

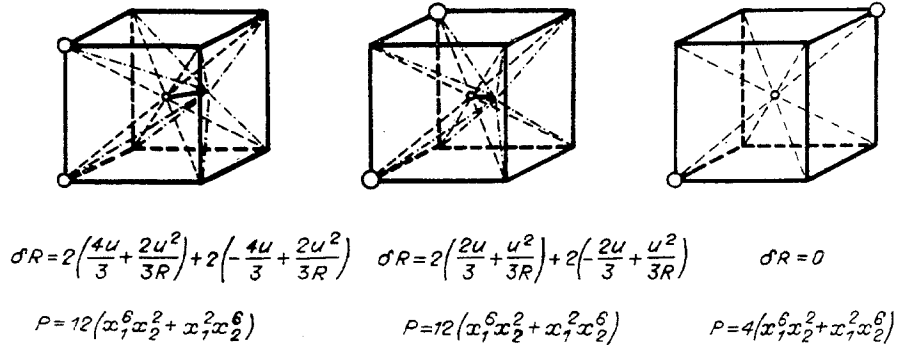


Fig. 9

Fig. 7. Tetrahedral environments with one (a) and two (b) substituted vertices, the changes in the bond lengths δR corresponding to them, and the probabilities of the configurations P .

Fig. 8. Cubic environment with one substituted vertex, the changes in the bond lengths δR , and the probability P .

Fig. 9. Cubic environments with two substituted vertices, the corresponding changes in the bond lengths δR , and the probabilities P .

since 48 is the symmetry number of the (m3m) regular octahedron, 8 is the symmetry number of the (4mm) "singly-substituted" octahedron.

We should also consider that the secondary shifts pertain to distances between the central atom and the next-nearest neighbors of the substitution defect, while (16) and (17) compute the relative probabilities of the primary shifts. The number of secondary shifts are related to the number of primary shifts as $\varrho = \nu_2/\nu_1$, where ν_1 and ν_2 are the first and second coordination numbers, respectively. From this we can calculate the probabilities of the shifts from the formula

$$P'_i = m_i x_1^{\nu_1 - \varrho} x_2^{\varrho} \quad (19)$$

Then we can obtain the final equation:

$$\delta R = \sum_i P'_i \delta_i \quad (20)$$

Considering that for the NaCl (B1) structure $\varrho = (12/6) = 2$ and using the previously obtained values $\delta_i = iu^2/2R$ ($i = 1, 2, 3$), after a series of transformations of the sum in (20) we obtain

$$\delta R_{B1} = 6x_1 x_2 \left(\frac{u^2}{R}\right) \quad (21)$$

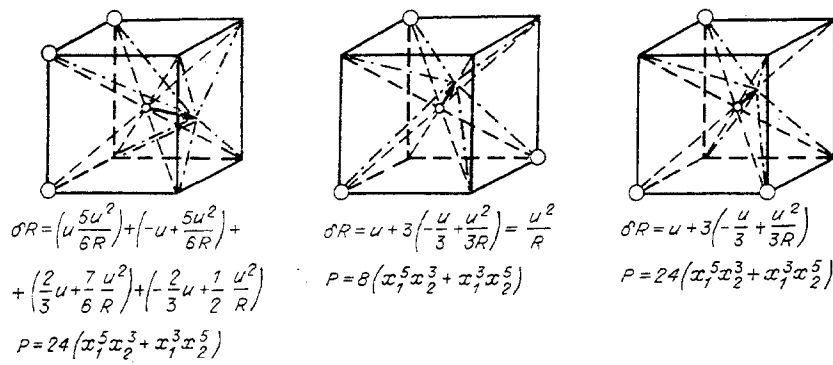


Fig. 10. Cubic environments with three substituted vertices, the corresponding changes in the bond lengths δR , and the probabilities P .

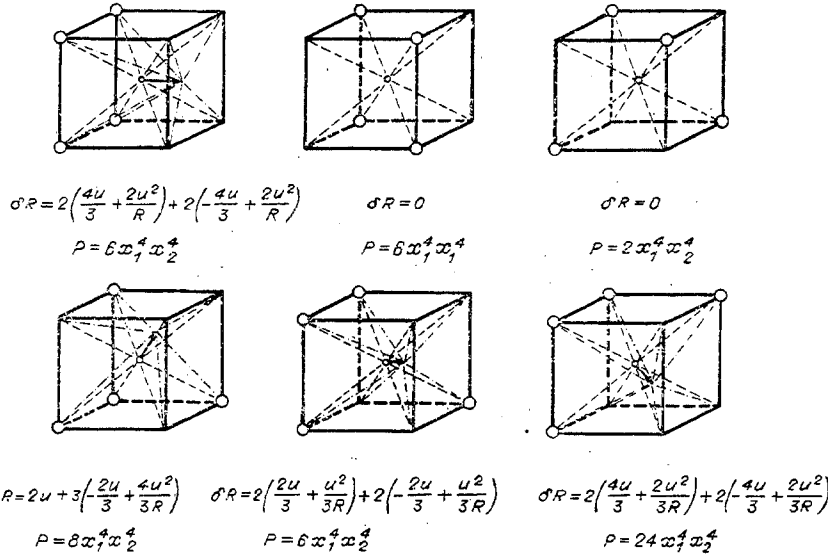


Fig. 11. Cubic environments with four substituted vertices, the corresponding changes in the bond lengths δR , and the probabilities P .

As was found in the preceding section, for the NaCl structure $u = \Delta R/2$. Therefore,

$$\delta R_{B1} = \frac{3}{2} x_1 x_2 \frac{(\Delta R)^2}{R}. \quad (22)$$

In the case of a tetrahedral environment, two configurations arise, with one and two substituting atoms (Fig. 7). The corresponding primary and secondary shifts and their probabilities are indicated in Fig. 7. The ratio of the number of secondary and primary shifts is $\lambda = 3$, in accordance with the ratio $\nu_2/\nu_1 = 12/4 = 3$.

Summing (20) in this case gives the expression

$$\delta R_{B3} = 4x_1 x_2 \left(\frac{u^2}{R}\right) \quad (23)$$

and considering that for the ZnS (B3) structure $u = (3/4)\Delta R$, we obtain

$$\delta R_{B3} = \frac{9}{4} x_1 x_2 \frac{(\Delta R)^2}{R}. \quad (24)$$

The cubic environment in the CsCl (B2) structure allows for 13 different configurations with substitutions of one, two, three, and four vertices of the cube. The corresponding primary and secondary shifts and their probabilities are presented in Figs. 8-11. For the B2 structure, the ratio of the number of secondary shifts to the number of primary shifts is $\lambda = 3.25$, in accordance with the fact that next-nearest neighbors ($\nu_2 = 6$), third-nearest neighbors ($\nu_3 = 12$), and fourth-nearest neighbors ($\nu_4 = 8$) of the impurity defects participate in them. Summing (20) in this case gives

TABLE 1. Measured and Calculated Deviations from Vegard's Law (Å)

x_1	NaCl-KCl		NaCl-NaBr		KCl-KBr		RbI-RbBr	
	expt. [34]	calcu-lation	expt. [35]	calcu-lation	expt. [36]	calcu-lation	expt. [37]	calcu-lation
0.1	0,0045	0,0048	0,0020	0,0013	0,0010	0,0010	—	0,0020
0.3	0,0111	0,0110	0,0035	0,0031	0,0016	0,0023	0,0050	0,0050
0.5	0,0127	0,0133	0,0040	0,0037	0,0023	0,0027	0,0080	0,0060
0.7	0,0105	0,0110	0,0027	0,0031	—	0,0023	0,0040	0,0050
0.9	0,0053	0,0048	0,0012	0,0013	0,0008	0,0010	—	0,0020

$$\delta R_{B2} = 8x_1x_2 \left(\frac{u^2}{R} \right). \quad (25)$$

Recalling that for the B2 structure $u = (3/8)\Delta R$, we have

$$\delta R_{B2} = \frac{9}{8} x_1x_2 \frac{(\Delta R)^2}{R}. \quad (26)$$

Equations (21), (23), and (25) can be rewritten in the general form

$$\delta R = v_1 x_1x_2 \left(\frac{u^2}{R} \right), \quad (27)$$

while Eqs. (22), (24), and (26) can be rewritten in the form

$$\delta R = \frac{9}{v_1} x_1x_2 \frac{(\Delta R)^2}{R}. \quad (28)$$

COMPARISON OF THE GEOMETRIC MODEL WITH EXPERIMENT

For solid solutions with the CsCl structure, only a very few measurements are available on the lattice parameter as a function of composition. Thus for the CsCl-CsBr system, the measured deviations from Vegard's law are no more than +0.002 Å for all compositions [30, 31]. The calculation using formula (26) leads to the following result: the maximum deviation for the composition $x_1 = x_2 = 0.5$ is +0.0017 Å, which does not contradict experiment. For TlCl-TlBr and TlBr-TlI, the measured [32] deviations for $x_2 = 0.3$ and 0.5 are 0.003 and 0.007 Å (the calculation gives 0.006 and 0.003 Å).

In [33], the cell parameters were studied as a function of composition for low-temperature (B2 structure) and high-temperature (B1 structure) solid solutions $\text{NH}_4\text{Cl-NH}_4\text{Br}$. The positive deviation of the interatomic distances from Vegard's law for intermediate compositions ($x = 0.5$) of the low-temperature series is about 0.004 ± 0.002 Å (high-angle measurements). From formula (26), we obtain 0.002 Å, which also does not contradict experiment.

There are significantly more measurements available for solid solutions with the NaCl structure. In Table 1, we compare the calculated [according to Eq. (22)] and the measured deviations from Vegard's law for four systems. We can see that the agreement between the theoretical estimates and the experiment is very good.

In addition, less exact measurements have been made for the systems KCl-RbCl [38] and KBr-KI [39]. The positive deviations of the interatomic distances from additivity for the first of these systems are within the range 0.001-0.008 Å, while the theoretical values are within the narrower range 0.001-0.003 Å. For the second system, the scatter in the experimental deviations is greater, ranging from -0.001 to 0.017 Å. The deviations calculated from Eq. (22) are no more than 0.006 Å.

Very many measurements have been made on the cell parameters as a function of composition for solid solutions with the sphalerite (B3) and wurtzite (B4) structure. The results of these measurements, done with different degrees of accuracy, sometimes contradict one another. Thus, for the system wurtzite ZnS-greenockite CdS (B4), both positive and negative deviations from Vegard's law have been observed, although most of the measurements agree with Vegard's law within experimental error limits ($\pm 10^{-3}$ Å) [40, 41]. Calculations using the geometric model [Eq. (22)] show that the maximum positive deviation of the parameters a

and c from linearity for intermediate compositions should not be greater than 0.012-0.015 Å.

Multiple measurements of the composition dependence of the cubic cell (B3) parameters of the solid solutions sphalerite ZnS-metacinnabarite HgS show agreement with Vegard's law within limits which in any case are no greater than ± 0.02 Å [41]. Calculations using Eq. (24) predict a maximum positive deviation of 0.016 Å for intermediate compositions.

However, for the parameter a in the series of solid solutions ZnS- γ -MnS (structure B4), an appreciable positive deviation from additivity was observed in [41], reaching 0.03 Å for intermediate compositions. The geometric model predicts much smaller positive deviations. This shows that the chemical factors for the deviations of intermediate interatomic distances from additivity should be subjected to additional analysis.

We also cannot exclude the possibility that the accuracy of the predictions of the geometric model drops with a decrease in the density of packing of the atoms in the crystal. In fact, this model is based on the assumption that the mixed-composition sublattice forms a regular packing, i.e., the coordination polyhedra about the central atom (in the unmixed sublattice) are undistorted. In fact, this is not quite true, as shown experimentally by the EXAFS method for the system InAs-GaAs [19]. As we see from Fig. 2c, the In-In distances are systematically 0.08 Å greater than the Ga-Ga distances for all the compositions of the solid solution, while the Ga-In and In-Ga distances have intermediate values and are close to additive according to Vegard's law. Hence relaxation of the solid solution encompasses (although to different degrees) both sublattices, and therefore the changes in the bond lengths (both first- and second-order) relative to the original lengths should be less than in the model considered above.

In conclusion, we should emphasize that the deviation from additivity (i.e., from ideal behavior) of the geometric characteristics of solid solutions is closely connected with the nonideality of other properties: in particular, the enthalpy of mixing of solid solutions is a function of the square of the size parameter $\Delta R/R$

$$\Delta H_{\text{mix}} = x_1 x_2 c (\Delta R/R)^2, \quad (29)$$

where c is some parameter which is constant for individual groups of crystals [42]. From this follows the linear correlation between these properties

$$\delta R / \Delta H_{\text{mix}} = R / \lambda, \quad (30)$$

where λ is some energy parameter.

I am pleased to express my sincere appreciation to I. P. Deineko for helping considerably in all stages of this work.

LITERATURE CITED

1. L. Vegard, Z. Phys., 5, 17 (1921).
2. B. J. Pines, J. Phys. USSR, 3, 309 (1940).
3. J. Friedel, Phil. Mag., 46, 514 (1955).
4. K. A. Gschneider and G. H. Vineyard, J. Appl. Phys., 33, No. 12, 3444 (1962).
5. P. G. Fournet, J. Phys. Rad., 14, 374 (1953).
6. W. B. Pearson, The Crystal Chemistry and Physics of Metals and Alloys [Russian translation], Mir, Moscow (1977).
7. M. Park, T. E. Mitchel, and A. H. Heaer, J. Am. Ceram. Soc., 58, No. 1-2, 43-47 (1975).
8. H. E. Steinwehr, Z. Krist., 125, 360 (1967).
9. R. C. Newton and B. J. Wood, Am. Miner., 65, 733 (1980).
10. N. V. Dergunova, V. P. Sakhnenko, and E. G. Fesenko, Kristallografiya, 23, No. 1, 94 (1978).
11. V. P. Sakhnenko, E. G. Fesenko, and N. V. Dergunova, Z. Kristallogr., 185, No. 1-4, 530 (1988).
12. V. M. Talanov, Izv. Akad. Nauk SSSR, Neorg. Mater., 16, 8 (1980).
13. V. M. Talanov, Phys. Status Solidi (b), 106, No. 1, 99 (1981).
14. V. M. Talanov, J. Solid State Chem., 48, 86 (1983).
15. E-an Zen, Am. Miner., 41, 523 (1956).
16. J. A. Wasastjerna, Soc. Sci. Fenn.-Comm. Phys.-Math., XIII, No. 5, 1-24 (1946).
17. K. Huang, Proc. R. Soc. London, A190, 102 (1947).

18. V. I. Iveronova, Tr. Inst. Kristallogr. Akad. Nauk SSSR, 10, 339-347 (1954).
19. J. C. Mikkelsen and J. B. Boyce, Phys. Rev., B28, No. 12, 7139-7140 (1983).
20. J. B. Boyce and J. C. Mikkelsen, Phys. Rev., B31, No. 10, 6903-6905 (1985).
21. S. P. Vernon and M. B. Stearns, Phys. Rev., B29, 6968 (1984).
22. G. S. Durham and J. A. Hawkins, J. Chem. Phys., 19, 2 (1951).
23. J. Hietala, Ann. Acad. Sci. Fenn., AVI, No. 121 (1963).
24. B. G. Dick and T. P. Das, Phys. Rev., 127, No. 4, 1053 (1962).
25. T. B. Douglas, J. Chem. Phys., 45, No. 12, 4571 (1966).
26. J. R. Hardy, J. Phys. Chem. Solids, 23, 116-123 (1962).
27. J. D. Eshelby, Solid State Phys., 3, 79-114 (1956).
28. W. A. Dollase, Phys. Chem. Minerals, 6, 295-304 (1980).
29. C. K. Shih et al., Phys. Rev., B31, No. 2, 1139-1144 (1985).
30. V. Hovi, Ann. Univ. Turkuensis, A1, 26 (1957).
31. H. L. Link and L. J. Wood, J. Am. Chem. Soc., 62, 766 (1940).
32. A. Haav and T. Muirsepp, Izv. Akad. Nauk Est. SSR, Ser. Fiz.-Mat., 20, 300-308 (1971).
33. S. J. E. Callahan and N. O. Smith, Adv. X-Ray Anal., 9, 156-169 (1966).
34. W. T. Barrett and W. E. Wallace, J. Am. Chem. Soc., 76, 2 (1954).
35. I. E. Nickels, M. A. Fineman, and W. E. Wallace, J. Phys. Colloid. Chem., 53, No. 1, 625 (1949).
36. O. D. Slagle and H. A. McKinstry, Acta Cryst., 21, 1013 (1966).
37. M. Ahtee, Ann. Acad. Sci. Fenn., AVI, No. 313, 11 (1969).
38. A. Hovi, Suomen Kemi, B23, No. 11-12, 80-86 (1950).
39. T. Teatum and N. O. Smith, J. Phys. Chem., 61, 697-698 (1957).
40. A. V. Chichagov and L. V. Sipavina, Lattice Parameters of Solid Solutions [in Russian], Nauka, Moscow (1982).
41. V. L. Tauson and L. V. Chernyshev, Experimental Study of Crystal Chemistry and Geochemistry of Zinc Sulfide [in Russian], Nauka, Novosibirsk (1981).
42. V. S. Urusov, Theory of Isomorphic Miscibility [in Russian], Nauka, Moscow (1977), p. 245.