

A New Empirical Formula for the Calculation of an Elementary Cell Parameter of Synthetic Oxides–Garnets

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An empirical formula is proposed which allows one to calculate the lattice constant of cubic synthetic oxides–garnets taking into account the chemical composition, the distribution of cation in the crystallographically nonequivalent positions, and well-known Shannon–Prewitt cation radii. The formula is developed assuming cation size effects on the elementary cell parameter for the cation radii r_{VIII} from 0.097 to 0.114 for the cations on dodecahedral, $0.054 < r_{\text{VI}} < 0.079$ for the cations on octahedral, and $0.028 < r_{\text{IV}} < 0.049$ for the cations on tetrahedral lattice sites. Selected crystal lattice parameters for 350 compositions, excluding garnets–silicates, have been used for derivation of the formula by means of the least-squares method for multimeasured functions (n -measured space with coordinates r_{VIII} , r_{VI} , r_{IV} , a). The average deviation of the calculated values a_{cal} from the experimental values is less than 0.001 nm. © 1997 Academic Press

At present, extensive use is made of synthetic garnets as matrices for solid-state lasers and substrates for the epitaxial growth of monocrystal ferro-garnet films which are the elements of magnetic optical devices.

Since the lattice constant a of the oxides–garnets $\{R_{3-\lambda_1}M_{\lambda_1}^I\}_{\text{VIII}} \cdot [M_{\lambda_4}^I M_{\lambda_3}^{\text{II}} M_{2-\lambda_3-\lambda_4}^{\text{III}}]_{\text{VI}} (M_{\lambda_2}^{\text{II}} M_{3-\lambda_2}^{\text{III}})_{\text{IV}} \text{O}_{12-\lambda_5-\delta} X_{\lambda_5}$ (space group $Ia3d$) is affected by the chemical composition “ C_i ”, by the valence m_i of $M_j^{m_i}$ cations, by their distribution λ in the crystallographically nonequivalent positions: dodecahedral {vIII}; octahedral [vI] and tetrahedral [Iv]; by their magnetic state (HS, LS), by their ordering (β), and, finally, by the completeness of three cation and anion sublattices, i.e., nonstoichiometry (δ) of garnets, it can be used as an indication or reference of these characteristics. However, the analytical expression of a interrelation with the above parameters C_i , m_i , λ , β , and δ is not known. The numerical determination of its relationship is not possible without a precise definition of these characteristics. In turn, the numerical evaluation of m_i , λ_i , β , and δ in each case is a complicated scientific task requiring precision-specific physical equipment and high skills from an investigator.

The three cation sites are accessible to magnetic and nonmagnetic ions of great variety, but conditions of elec-

tronic configuration and size determine the extent to which ions go into the different sites. This unlimited homeovalent and heterovalent isomorphism gives one the opportunity to make new synthetic garnet compositions with different physical, chemical, and mechanical properties. All variations of compositions and their properties are practically impossible to investigate. So, one of the important research tasks is that of prognostication of the properties of garnets to predict optimal predetermined characteristics (1, 2).

It should be noted that the parameters under discussion (m_i , λ_i , β , and δ) are the functions of not only the composition “ C_i ” but the temperature T as well. The last condition brings about additional restrictions and difficulties in the quantitative solution of the problem $a = f(c_i, m_i, \lambda_i, \beta, \delta)$ and points to the direct connection of these parameters with technological ones P , P_{O_2} , T , τ , and F (P , pressure; P_{O_2} , partial pressure of oxygen in gaseous media; τ , time of synthesis; F , conjugated phases) and, as a consequence, influences the solution of the reverse problem: the definition of the long-range order (λ_i), magnetic ordering (β), valence state, nonstoichiometry (δ), and the value of unknown ionic radii.

The thermodynamic functions $\Delta G(T)$, $\Delta H(T)$, and $\Delta S(T)$ are unknown for the majority of the garnets considered by us (except YIG). However, similar characteristics for simple oxides are compared with those of the garnets and can be used to estimate their thermodynamic stability. The diagrams $\Delta G(T) = -RT \ln P_{\text{O}_2}$ are given in the physical chemistry text books. It is readily seen from the latter which of the given oxides is the most unstable. For example, for the garnet $\{M_3^I\} [M_2^{\text{II}}] (M_3^{\text{III}}) \text{O}_{12}$ it is enough to find the tabular values (3) of the equilibrium constants of dissociation reactions $M_2^I \text{O}_3$, $M_2^{\text{II}} \text{O}_3$, $M_2^{\text{III}} \text{O}_3$, namely $K^I = P_{\text{O}_2}^I$, $K^{\text{II}} = P_{\text{O}_2}^{\text{II}}$, and $K^{\text{III}} = P_{\text{O}_2}^{\text{III}}$ and to compare them with P_{O_2} , the oxygen pressure, at the garnet synthesis temperature. Dissociation of the garnet is possible if $P_{\text{O}_2}^I > P_{\text{O}_2} > P_{\text{O}_2}^{\text{III}}$. Therefore, bivalence cations M^I and vacancies of oxygen will be the most probable sorts of defects. At $P_{\text{O}_2} > P_{\text{O}_2}^I > P_{\text{O}_2}^{\text{II}} > P_{\text{O}_2}^{\text{III}}$ the garnet is stable at the given external parameters P_{O_2} , T . The observable changes in it can be due to

the discrepancy of structures of gas and equilibrium phases. For example, partial (direct or dissociative) sublimation of one of the oxides occurs if $P_{M^i} \gg P_M$ (external). In this case it is obvious that the primary type of defects will be cation vacancies \square_{M^i} and anion defects according to the rule of the electroneutrality.

All this may be the reason why many proposals have been made to calculate of the garnet lattice constants. The main advantages and disadvantages of these analytical dependencies have been discussed (1,2) in detail. Stroka *et al.* (4) have obtained the relation for the calculation of the dimensions of a garnet elementary cell on the basis of the investigated garnets. They postulated that the lattice parameter is ascribed only to the sizes of cations and anions, cation distribution, and composition forming the garnet. It precisely describes the relation $a = f(r_V)$, where $r_V = r_{\text{VIII}}, r_{\text{VI}}, r_{\text{IV}}$ —the weighted means of the ion sizes in dodecahedral, octahedral, and tetrahedral positions.

$$a = b_1 + b_2 r_{\text{VIII}} + b_3 r_{\text{VI}} + b_4 r_{\text{IV}} + b_5 r_{\text{VIII}} r_{\text{VI}} + b_6 r_{\text{VIII}} r_{\text{IV}}, \quad [1]$$

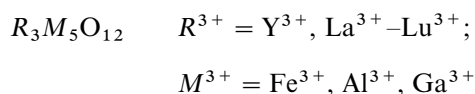
where

$$\begin{aligned} b_1 &= 7.02954 & b_2 &= 3.31277 \\ b_3 &= 2.49398 & b_4 &= 3.34124 \\ b_5 &= -0.87758 & b_6 &= -1.38777. \end{aligned}$$

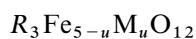
The average deviation 0.001 nm for the values a_{cal} calculated by the formula [1] and a_{exp} specify its preferable application.

The relationship [1] in spite of the successful application (5–11) in solving the inverse problem has the following disadvantages:

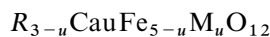
1. The problem of finding the analytical relation $a = f(r_V)$ is solved from the mathematical point of view incorrectly, because it was divided into two stages. In the first stage, algebraic relations $a = f(r_V)$ of the lattice crystal parameter from r_{VIII} were obtained for the following garnets:



and $a = f(u)$ from the compositional parameter u for solid solutions



$$M^{3+} = Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}$$



$$M^{4+} = Ge^{4+}, Si^{4+}, Zr^{4+}, Sn^{4+}, Ti^{4+}.$$

In the second stage the coefficients b_i ($i = 1 \dots 6$) derived by the least-squares method were calculated. Such a procedure leads to the increase of confidence intervals of b_i coefficients and, accordingly, to *increasing* error in the final formula.

2. The boundary conditions assumed in solving the problem were not exact. It was presumed that the limiting sizes (nm) of cations during the formation of cubic garnets were $0.097 < r_{\text{VIII}} < 0.114$, $0.054 < r_{\text{VI}} < 0.079$, $0.028 < r_{\text{IV}} < 0.049$. However, RE garnets have already been synthesized, in which the octahedral positions are occupied fully by lanthanoidal ions ($\{Ca_3\}[R_2](Ge_3)O_{12}$, $R^{3+} = Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}$). The sizes of the latter are much larger than the limits presumed.

3. Expression (1) is applicable for the limited group of garnets, as only the data of isomorphic solid solutions containing FeYG and FeGdG have been used for the derivation of the formula. So, during the calculation the deviations from a_{exp} for V-garnets ($\{Na_2R\}[Mg_2](V_3)O_{12}$, $R^{3+} = Sm^{3+} - Yb^{3+}$) are in the average 0.004 and 0.005 nm for rare-earth Ca-germanates ($\{Ca_3\}[R_2](Ge_3)O_{12}$, $R^{3+} = Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}$).

4. As follows from the analysis of formula [1] the preference has been given to the dodecahedral ions (see terms 5 and 6) which contributed much to a . At the same time this conclusion is not indisputable. For example, it has been recognized that $a-d$, $d-d$ and $a-a$ magnetic exchange interactions are the main ones for the Neel's model (12) of ferromagnetism for rare-earth ferrites-garnets. Besides, according to energetic crystal chemistry it is evident that couplings of "cation-anion" have the strongest chemical bonds in tetrahedrons and octahedrons. (Coulon's energy is inversely proportional to the square of the length of this bond). The conclusive proof of our assumption is presented in Table 1. The problem is undoubtedly very involved and conclusions drawn solely from the a_{exp} -cell lattice parameter measurements must be treated with reserve. It is more appropriate to resolve this problem together with thermodynamics of the simple oxides and crystallochemical simulation of the garnet cation ordering. So, as we see it, the sixth term of formula [1] must have the form $r_{\text{VI}} r_{\text{IV}}$ but not $r_{\text{VIII}} r_{\text{VI}}$,

$$a = b_1 + b_2 r_{\text{VIII}} + b_3 r_{\text{VI}} + b_4 r_{\text{IV}} + b_5 r_{\text{VIII}} r_{\text{IV}} + b_6 r_{\text{VIII}} r_{\text{IV}}, \quad [2]$$

The coefficients b_i of Eq. [2] have been derived, having eliminated these disadvantages in solving the Stroka's equation and using the least-squares method for multimeasured functions (n -measured) space with coordinates $r_{\text{VIII}}, r_{\text{VI}}, r_{\text{IV}}$,

TABLE 1
Values of Interaction Exchange Integrals J_{ij} (in Calvin's) for Ferrites–Garnets, Recommended (19)

Ferrite	J_{ad}	J_{dd}	J_{aa}	J_{dc}	J_{ac}	J_{cc}	Method of definition
$Gd_3Fe_5O_{12}$	-35.8	-15.0	-8.2	-3.7	-0.44	0	Molecular
				-4.8	-0.32	-0.22	Field
				-4.1	0	-0.04	NMR
				—	—	-0.13	NGR
$Y_3Fe_5O_{12}$	-34.8	-14.8	-8.3				Molecular
				-36.3	-14.8	-8.8	Field

a) and the experimental data presented (1,2,13) for 350 compositions, excluding garnets–silicates, and effective ionic radii of Shannon and Prewitt (14)

$$\begin{aligned} b_1 &= 10.092217 & b_2 &= 0.841118 \\ b_3 &= 0.734598 & b_4 &= -2.507813 \\ b_5 &= 3.133970 & b_6 &= 1.946901. \end{aligned}$$

The average deviations from the measured data are $\Delta a \cong 0.001$ nm for all compositions, which is much better than for those obtained by formula [1] (Fig. 1). However, the values a_{cal} obtained by the Stroka's formula are closer to a_{exp} for isomorphous solid solutions containing FeYG and FeGdG as

a base and having the coefficient of substitution $c_1, c_2 < 0.5$, due to the preferential application of a_{exp} for these compounds during its derivation.

Expression [2] can be applied to calculate the elementary cell sizes during the epitaxial growth of the garnet films on the substrate. With the chemical composition of monocrystals and epitaxial garnet film being equal, the difference in the values of the measured parameters of a crystal lattice (15, 16) does not exceed ± 0.00057 nm, which is less than the experimental error.

The wide range of the experimental values a_{exp} obtained by different authors (1,2,13) for the systems

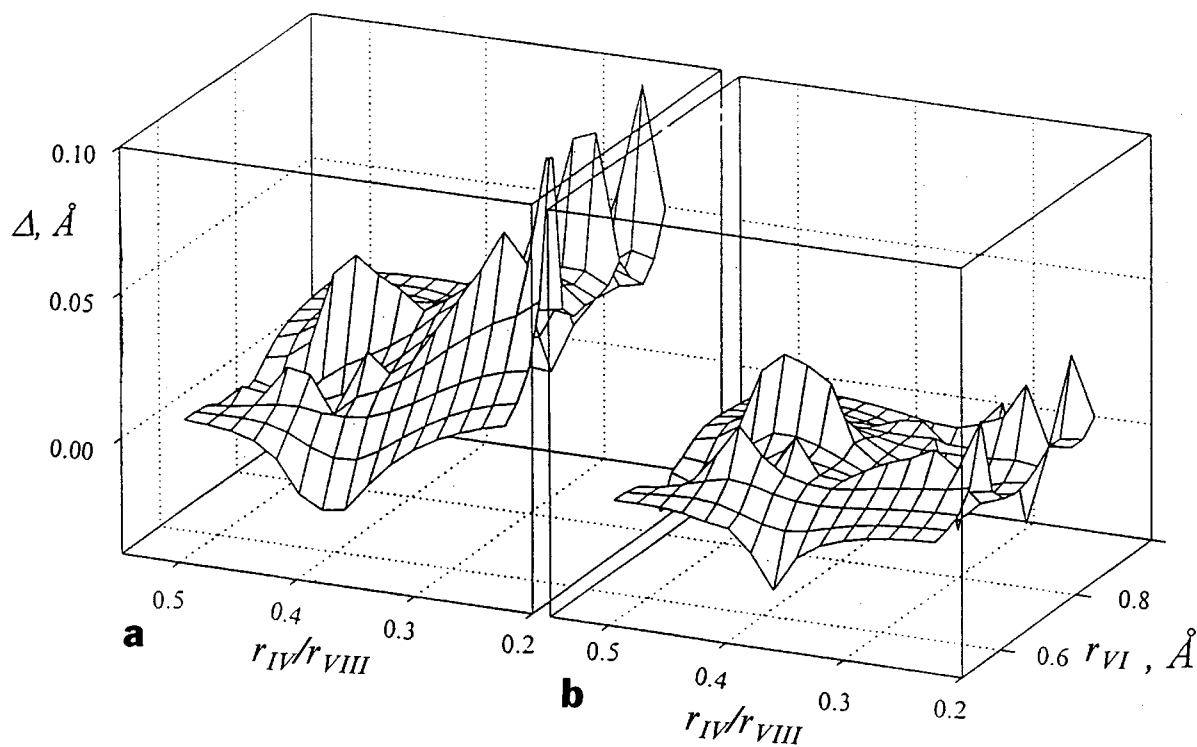
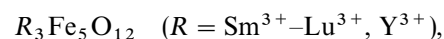
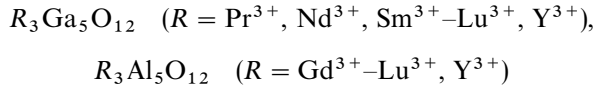


FIG. 1. Deviation of experimental data a_{exp} (1,2,13) of lattice constant calculated using (a) formula [1] and (b) formula [2].



can be explained by different heat and chemical treatment and, probably, it may be caused by different chemical purity of the initial materials. The calculated values a_{cal} are within the intervals of a_{exp} .

The calculation of nonstoichiometry δ for $\{R_3\} [Fe_{2-\lambda}^{3+} Fe_{\lambda}^{2+}] (Fe_3^{3+}) O_{12-\delta}$ ($R = Nd^{3+} - Lu^{3+}, Y^{3+}$), $\delta = \lambda/2$ gives the value δ not exceeding 0.2; for $\{R_3\} [Ga_{2-\lambda} \square_{\lambda}^{Ga}] (Ga_3) O_{12-\delta}$ ($R = Pr^{3+}, Nd^{3+}, Sm^{3+}-Lu^{3+}, Y^{3+}$), $\delta = 1.5\lambda$ not exceeding 0.35; for $\{R_3\} [Al_{2-\lambda}^{3+} Al_{\lambda}^{+}] (Al_3^{3+}) O_{12-\delta}$ ($R = Gd^{3+}-Lu^{3+}, Y^{3+}$), $\delta = \lambda$ not exceeding 0, 11 and for $\{Y_2R\} [Fe_{2-\lambda}^{3+} Fe_{\lambda}^{2+}] (Fe_3^{3+}) O_{12-\delta}$ ($R = Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}$), $\delta = \lambda/2$ not exceeding 0,1 (Table 2).

The linear relations $a = f(n)$, where n quantity of 4f-electrons R^{3+} described by straight lines [3, 5, 7, 9, 11, 13], calculated by Eq. [2], are verified in this way. The equations of straight lines [4, 6, 8, 10, 12, 14] are obtained by processing the discrete experimental values a_{exp} using the least-squares method,

for $R_3Fe_5O_{12}$

$$a_{cal} = 1.2719 - 0.0035n; 0 < n < 14 \quad [3]$$

$$a_{exp} = 1.2688 - 0.0030n; 3 < n < 14 \quad [4]$$

for $R_3Ga_5O_{12}$

$$a_{cal} = 1.2630 - 0.0036n; 0 < n < 14 \quad [5]$$

$$a_{exp} = 1.2609 - 0.0032n; 2 < n < 14 \quad [6]$$

for $R_3Al_5O_{12}$

$$a_{cal} = 1.2313 - 0.0030n; 0 < n < 14 \quad [7]$$

$$a_{exp} = 1.2341 - 0.0032n; 7 < n < 14 \quad [8]$$

for $\{Y_2R\}Fe_5O_{12}$

$$a_{cal} = 1.2489 - 0.0013n; 0 < n < 14 \quad [9]$$

$$a_{exp} = 1.24890 - 0.00126n; 2 < n < 5 \quad [10]$$

for $\{Na_2R\} [Mg_2] (V_3) O_{12}$

$$a_{cal} = 1.2497 - 0.0009n; 0 < n < 14 \quad [11]$$

$$a_{exp} = 1.25403 - 0.00142n; 3 < n < 14 \quad [12]$$

for $\{Sr_3\} [R_2] (Ge_3) O_{12}$

$$a_{cal} = 1.3522 - 0.0037n; 0 < n < 14 \quad [13]$$

$$a_{exp} = 1.3312 - 0.0022n; 10 < n < 14 \quad [14]$$

TABLE 2
Nonstoichiometry δ in Rare-Earth Oxides–Garnets

R	$R_3Fe_5O_{12}$	$R_3Ga_5O_{12}$	$R_3Al_5O_{12}$	$\{Y_2R\}Fe_5O_{12}$
Pr		0.04–0.32		0.08
Nd		0.15–0.27		0.08
Sm	0.02–0.06	0.23–0.33		0.07
Eu	0.04–0.08	0.02–0.12		0.1
Gd	0.04–0.06	0.15–0.35	0.06–0.10	
Tb	0.09–0.19	0.001	0.06–0.07	
Dy	0.03–0.11	0.08–0.26	0.04–0.11	
Ho	0.03–0.04	0.21	0.01	
Er	0.17–0.21	0.05	0.03–0.07	
Tm	0.12–0.18	0.02	0.05–0.06	
Yb	0.08–0.17	0.01	0.01	
Lu	0.16–0.18	0.01–0.02	0.01–0.02	
Y	0.05–0.06	0.11	0.01	

Note. $\{R_3\} [Fe_{2-\lambda}^{3+} Fe_{\lambda}^{2+}] (Fe_3^{3+}) O_{12-\delta}$, $\delta = \lambda/2$;
 $\{R_3\} [Ga_{2-\lambda} \square_{\lambda}^{Ga}] (Ga_3) O_{12-\delta}$, $\delta = 1.5\lambda$;
 $\{R_3\} [Al_{2-\lambda}^{3+} Al_{\lambda}^{+}] (Al_3^{3+}) O_{12-\delta}$, $\delta = \lambda$;
 $\{Y_2R\} [Fe_{2-\lambda}^{3+} Fe_{\lambda}^{2+}] (Fe_3^{3+}) O_{12-\delta}$, $\delta = \lambda/2$.

The Eqs. [3, 5, 7, 9, 11, 13] permit us to make the calculation of the lattice constant of not yet synthesized garnets $La_3Fe_5O_{12}$, $Pr_3Fe_5O_{12}$, $La_3Ga_5O_{12}$, $R_3Al_5O_{12}$ ($R = La-Eu$), etc.

Practically all metal cations take part in garnet formation. There are more than 80 metal elements in the periodic table, almost every one of them can have one, two, or several states of valence. That is why the purity of possible garnet forming cations exceeds 100 and the quantity of possible (theoretically) garnets (excluding thermodynamical inhibitions) equals

$$C_m^n + D_m + L_m^n = N,$$

where C_m^n is the number of combinations of garnet forming cations, D_m is the number of permutations of cations, L_m^n is the number of arrangements (with repetitions).

In accordance with (16) we consider that the limiting sizes of cations in the formation of cubic garnets are $0.0830 < r_{VII} < 0.1290$, $0.0530 < r_{VI} < 0.0958$, $0.0279 < r_{IV} < 0.0590$ nm.

The formation of solid solutions of substitution between oxides–garnets causes N to increase still further. Therefore, the determination of “ a -property” characteristics helps to find new compositions of garnets with predetermined (theoretically) physical properties. The crystals with a garnet structure have a cubic symmetry, hence, they have three independent components of the elasticity tensor: C_{11} , C_{12} , C_{44} . The modulus of compression B , modulus of shear G , and Young’s modulus E can be easily calculated if these constants are known

$$B = 1/3(C_{11} + 2C_{12}) \quad (\text{Pa}) \quad [15]$$

$$G = 1/5(3B - 3C_{12} + 3C_{44}) \quad (\text{Pa}) \quad [16]$$

$$E = (9BG)/(3B + G) \quad (\text{Pa}). \quad [17]$$

The algebraic expressions connecting the moduli of elasticity with the dimensions of the elementary cells $R_3M_5O_{12}$ ($R^{3+} = \text{Nd}^{3+} - \text{Lu}^{3+}, \text{Y}^{3+}$; $M^{3+} = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Ga}^{3+}$) have been obtained as an example to illustrate the existence of "property-crystal lattice parameter" relationships using the method of the regression analysis of the experimental data [18, 19] and concentration relations (c_i).

$$G = 7.2782 - 5.1501a \quad (10^{11} \text{ Pa}) \quad [18]$$

$$E = 17.0884 - 11.9461a \quad (10^{11} \text{ Pa}) \quad [19]$$

$$B = 6.4186 - 3.8099a \quad (10^{11} \text{ Pa}). \quad [20]$$

The calculated and experimental data are shown in Fig 2.

The maximum deviation of the values calculated by the formulas [15–17] and [18–20] is 0.06 (10^{11} Pa). It should be noted that values E , B , and G for ferrites disagree considerably. The reason for this is probably due to their complex magnetic structure.

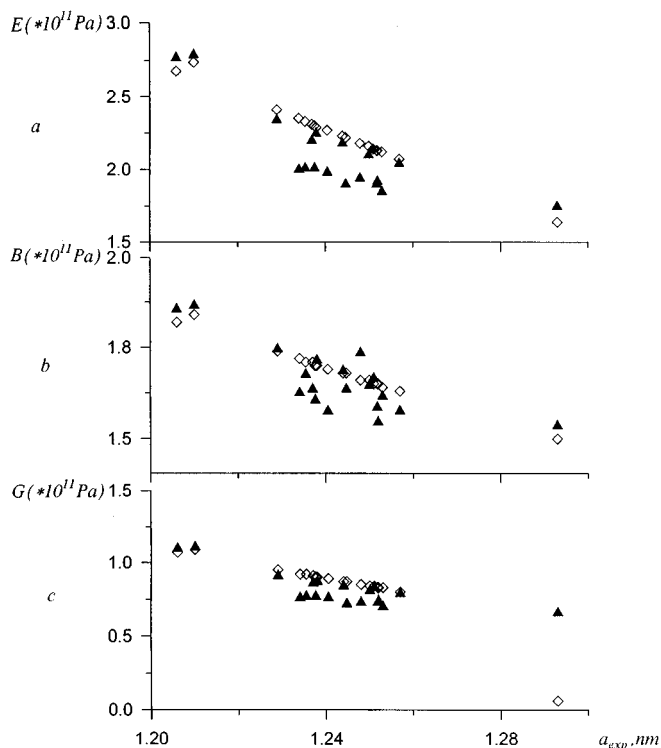


FIG. 2. Experimental data (▲) adduced (17, 18) and calculated values (◇) for formulas [18–20] of the modulus of (a) Young's modulus E , (b) compression B , and (c) modulus of shear G .

The deviations between a_{cal} and a_{exp} should not be explained only by the inaccuracy of the cation radii. It is evident that the sources of such deviations, first of all, are of the crystal defects, including the defects of the elementary cell (DEC): ions with different valences, vacancies, antistructural defects, etc., the revealing of which by the experimental methods is a difficult problem, therefore, the application of formula [2] instead of Stroka's formula, and thermodynamic analysis [5, 6] will help to make a quantitative evaluation. It will permit amending the technology of the garnet synthesis; i.e., it will be possible to make deliberate control and regulation of the quantity and variations of defects and, finally, of the garnet properties.

Evidently, existence of new analytical relations $a_{\text{cal}} = f(r_v)$ will change the numerical values (5–11), but the approach to the solution of the inverse problems will be the same.

CONCLUSION

A formula for the computation of the crystal lattice constant of the oxides-garnets with the exception of the silicates has been obtained on the basis of the regression analysis of the experimental data, adduced in (1, 2, 13) using the least-squares method. The average deviation of the calculated values a_{cal} from the experimental values is less than 0.001 nm. It will make possible, first, to use the formula to estimate the garnet crystal lattice parameters during the epitaxial growth of the garnet films on the substrate, second, to substitute the Stroka's formula for the quantitative evaluation of defects in the elementary cell of mono- and polycrystal garnets, as well as to appreciate the unknown meanings of ion dimensions (in HS and LS states).

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