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Lattice Parameters and Stability of the Spinel Compounds in Relation to the Ionic Radii and Electronegativities of Constituting Chemical Elements

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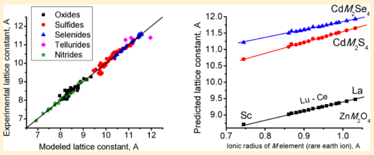

ABSTRACT: A thorough consideration of the relation between the lattice parameters of 185 binary and ternary spinel compounds, on one side, and ionic radii and electronegativities of the constituting ions, on the other side, allowed for establishing a simple empirical model and finding its linear equation, which links together the above-mentioned quantities. The derived equation gives good agreement between the experimental and modeled values of the lattice parameters in the considered group of spinels, with an average relative error of about 1% only. The proposed model was improved further by separate consideration of several groups of spinels, depending on the nature of the anion (oxygen, sulfur, selenium/tellurium, nitrogen). The developed approach can be efficiently used for prediction of lattice constants for new isostructural materials. In particular, the lattice constants of new hypothetic spinels $ZnRE_2O_4$, $CdRE_2S4$, $CdRE_2Se_4$ (RE = rare earth elements) are predicted in the present Article. In addition, the upper and lower limits for the variation of the ionic radii, electronegativities, and their certain combinations were established, which can be considered as stability criteria for the spinel compounds. The findings of the present Article offer a systematic overview of the structural properties of spinels and can serve as helpful guides for synthesis of new spinel compounds.

1. INTRODUCTION

The crystal structure of any crystalline material can be described in a unique way by giving the values of the unit cell parameters (lattice constants, LCs, along each of the crystallographic axes and angles between these axes), atomic positions expressed in units of the LCs, and site occupancies by specific atoms entering chemical formula of a considered compound. If the symmetry properties for each atomic position are known, the whole crystal lattice can be built up by repeating the unit cell in three directions with a proper application of the corresponding symmetry operations.

There are well-known methodics of experimental determination of the crystal structure from a thorough analysis of the X-ray and neutron diffraction patterns. From the theoretical point of view, it is also possible nowadays to get the structural properties of any crystal using the widely spread reliable *ab initio* methods of calculations. The rapid development and improvement of both experimental facilities and computational techniques allowed for getting trustworthy information on crystal structure of a large number of materials, which has been collected into various commercial and freely available databases. Comparing the accuracy of the experimental and theoretical methods of determination of crystal structure, it is worthwhile to note that the structural discrepancy between the theoretically calculated and experimentally deduced parameters for the same crystal typically does not exceed a few percent on average and very often is even less than 1%.

At the same time, the two above-mentioned methodics of determination of the crystal lattice structure (no matter how precise they can be in every particular case) give no opportunity to make a quick and reliable estimation and/or prediction of the structural parameters for even isostructural compounds, since all measurements and/or calculations are essentially *ad hoc* and should be repeated again for any new crystal. It is also noteworthy that both methods require sophisticated equipment and/or computational skills; in addition to that, they are expensive and time-consuming.

In this connection, a simple empirical model, which encompasses a large group of isostructural materials and links together the lattice structure parameters with various characteristics of their constituting elements (e.g., ionic radii, oxidation state, electronegativity, etc.) can be useful for researchers working in the experimental materials science and chemistry. The usefulness of such models originates from their simplicity and ability to make quickly reliable predictions and/or estimations of the LCs for those materials, which have not been experimentally found yet. One of the possible applications of such models can be related to a choice of proper substrates (with suitable structural properties) for the thin films' growth.

It is a long-established fact that the ionic radii are one of the most important parameters, responsible for the interionic

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separations and, as a consequence, LCs of crystals. Two other key parameters are the electronegativity and oxidation state,[1] which can greatly affect the chemical bond properties and, finally, the interionic separation. It should be kept in mind that these parameters are the empirical quantities, which may be defined in different ways, and depending on definitions and/or degree of experimental precision, they can be given somewhat different values.

Speaking about electronegativity, we mention here that there exist several different electronegativity scales, e.g., Martynov—Batsanov scale,[2] Phillips scale,[3] Jaffe scale,[4] Allen scale,[5] etc. Throughout this Article, the use is made of the Pauling electronegativity scale[6] and the Shannon's ionic radii[7] for all considered ions.

A thorough statistical analysis of a large number of crystals of a given structure can help in finding a functional relation between these or any other parameters and LC values. The cubic crystals with their single crystal lattice parameter *a* are a special group of materials, whose LCs can be analyzed in terms of the properties of the constituting chemical elements. Recently, several papers[8−12] dealing with the empirical modeling of the LCs for the cubic perovskite crystals were published. The linear relations between the value of *a* and several other variables (ionic radii, number of valence electrons, and electronegativity) in various combinations were proposed and successfully tested. In a similar way, the LCs of a group of the A_2XY_6 cubic crystals (A = K, Cs, Rb, Tl; X = tetravalent cation, Y = F, Cl, Br, I)[13] and cubic pyrochlores[14] were modeled and achieved good agreement between the predicted and experimental LC values. A recent analysis of the pyrochlore structural data[15] allowed the introduction of a new empirical tolerance factor for the representatives of this group of compounds. So, modeling of the crystal lattice constants and structures has never stopped and still appears to be an interesting and attractive problem of fundamental and applied importance.

In the present work we consider a group of crystals with the spinel structure. This is a very large family of compounds. They are not only widely spread in nature occurring as pure (or mixed) minerals all over the globe: the spinels are also significant in many branches of technology and science. Many spinels are typical semiconductors with a rather narrow band gap (this is true especially for spinels containing the halogen atoms as anions), whereas the oxygen-based spinels have considerably wider band gaps and thus are typical dielectrics, which can be easily doped with rare earth and transition metal ions. For example, $MgAl_2O_4$ and $ZnGa_2O_4$ doped with Co^{2+} ions were shown to be promising materials for solid state lasers;[16] Ni^{2+}-doped $MgAl_2O_4$ was named as an active medium for the tunable infrared solid state laser.[17] The spinel-based transparent ceramics for high-energy laser systems were designed recently.[18] There are also numerous examples of doping spinel compounds with rare earth ions, e.g., $ZnAl_2O_4$:Ce^{3+}, Tb^{3+},[19] $MgGa_2O_4$:Pr^{3+},[20] $MgAl_2O_4$:Nd^{3+},[21] Dy^{3+}, Sm^{3+}, Er^{3+}, Eu^{3+}, and Tm^{3+} doped $MgIn_2O_4$,[22] etc. Many spinels exhibit magnetic properties, which are a subject of many research works[23−25] with practical applications in view.

The spinel-type compounds have been known for a long time already, and much effort was applied to clarify and understand their structural properties.[26−31] The "classical" spinels are the ternary compounds that are described by the AM_2X_4 chemical formula, where A and M are the metals occupying the tetra- and octahedrally coordinated positions, respectively, and X stands for the anion, which can be any of the following elements: oxygen, sulfur, selenium, tellurium, nitrogen. There exists a certain "internal degree of freedom" in distributions of the cations through the tetra- and octahedral positions; one can distinguish between the so-called "normal" $A(M_2)X_4$ and "inverse" $M(AM)X_4$ distributions, where the ions in the parentheses are located at the octahedral sites.[32] Intermediate distributions can also occur, covering the whole range between the normal and inverse spinels; they can be generally described as $A_{1-\lambda}M_\lambda(A_\lambda M_{2-\lambda})X_4$ with λ representing the degree of inversion ($\lambda = 0$ for the normal spinels and $\lambda = 1$ for the inverse ones). The anion fractional coordinate *u* in the spinel structure was shown to depend strongly on the cation inversion parameter.[33]

It has been demonstrated that the octahedral and tetrahedral bond lengths (i.e., the interionic distances in the A—X and M—X pairs, respectively) in the spinel structure can be used to predict the lattice constant *a* and the anion positional coordinate *u*.[27] Several works also have been published that stress out existing correlations between various physical properties of spinels and ionic radii of the constituting ions. Thus, a relation between the magnetic and ionic properties of spinels with the ionic radii of cations and anions was discussed earlier.[34] Systematics of some spinel compounds based on the ionic radii of the constituting ions and geometrical factors of the spinel's crystal lattice structure were suggested in refs 27, 35, 36. In particular, a comprehensive database of the spinel-type compounds was collected in ref 36.

In the present work we propose a new semiempirical approach, which allowed us to model and describe the lattice parameters of ternary and binary spinels. The model treats the ionic radii and electronegativities of the constituting ions forming the spinel crystal lattice as the main factors to determine the value of the lattice parameter. Inclusion of electronegativities into our model extends and refines previous attempts of modeling spinel crystal lattices,[26−31,35,36] which were based on the geometrical factors only, such as ionic radii and interionic separations.

The reason for addition of electronegativity is due to the fact that the purely geometric consideration based on the ionic radii alone cannot explain why some compounds, although built up from the ions with equal ionic radii, have, nevertheless, different LCs. One example of this kind is the pair of the Cs_2GeF_6 and Cs_2MnF_6 crystals: although the ionic radii of Ge^{4+} and Mn^{4+} (the only different ions in these compounds) are equal, their LCs are slightly different.[13] Inclusion of the electronegativity as one of those parameters, which determine the bonding properties, can help in handling this issue and refine further those models, based entirely on the geometrical considerations and ionic radii, when the ions in a crystal lattice are treated as incompressible hard spheres.

The model developed and described in the present Article was tested by considering a group consisting of 185 binary and ternary stoichiometric AM_2X_4 spinel compounds, which can be divided into four subgroups depending on the anion X. These subgroups are conditionally referred to in the present Article as the oxides (X = O, 83 compounds), sulfides (X = S, 56 compounds), selenides/tellurides (25 selenides and 3 tellurides, X = Se, Te, 28 compounds in total), and nitrides (X = N, 18 compounds). All the nitride spinels included into the present model were reported only theoretically, using the *ab initio* calculation techniques for optimizing their crystal structure, and as such, they stand apart from other considered compounds.

The main aim of the performed analysis was to find simple empirical rules for a proper description of lattice parameters of the experimentally found spinels and predict the LCs of those new materials, experimentally not found yet, which can be, in principle, synthesized. Among the experimental spinel-type compounds are those synthesized at high pressure (metastable), simple, inverse, and binary spinels; putting them together gives only a general view of the structural properties of spinels.

The linear relation between the LCs, ionic radii, and electronegativities of the constituting ions allowed us to calculate the LCs of already existing spinels with an average deviation between the experimental data and our model estimations of less than 1%, the fact which serves as a firm justification of the validity, applicability, and potential predictive abilities of the derived equation. A closer look at certain relations, which link together the ionic radii and electronegativity of existing stable spinels, helped us to reveal certain limits (or typical ranges) for variations of these parameters, which may set up the boundaries of stability of spinel compounds. This should be of paramount importance in a search for new not-synthesized yet materials, since such conditions, once established, effectively reduce the number of possible combinations of chemical elements to be considered potentially suitable.

2. RESULTS AND DISCUSSION

All chosen compounds crystallize in the $Fd\bar{3}m$ space group (No. 227), with eight formula units in one unit cell. The unit cell of $MgAl_2O_4$, a classical representative of the spinel group, is shown in Figure 1.

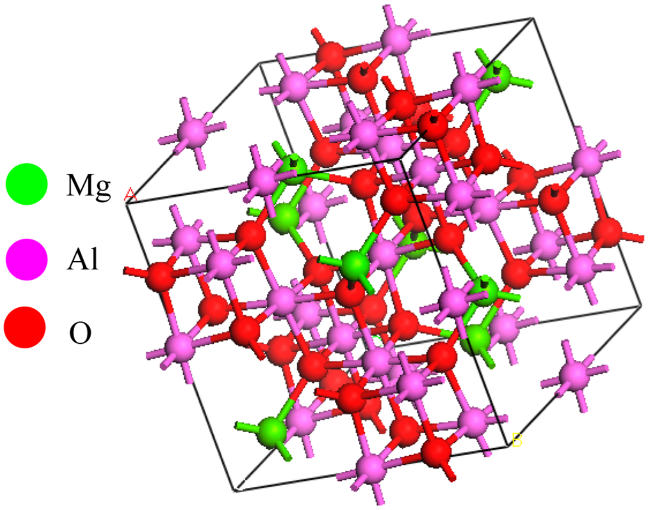

Figure 1. One unit cell of $MgAl_2O_4$ as an example of the spinel's structure.

In this material the oxygen ions form a cubic close packing; the Mg ions occupy $^1/_8$ of the available 4-fold coordinated tetrahedral positions, whereas the Al ions occupy $^1/_2$ of the available 6-fold coordinated octahedral sites.[37]

Table 1 collects the LCs values found in the literature. The vast majority of the data included in Table 1 correspond to the experimental structural studies of the synthesized spinel compounds. Some structural data were taken from the theoretical works on *ab initio* studies of the spinel compounds (followed by an asterisk in Table 1), and no corresponding experimental data were found. The set of the data collected in Table 1 is considerably extended if compared to that one from ref 36; more recent literature data were used when compiling Table 1.

The ionic radii of all ions were taken from ref 7, and the Pauling electronegativities were those listed in ref 38. The LCs were taken mainly from the Inorganic Crystal Structure Database (ICSD)[39] and from some additional publications, explicitly cited in the table. All compounds in Table 1 are sorted as follows: oxides, sulfides, selenides, tellurides, nitrides. In each of these groups the alphabetical ordering was used to list all entries.

As can be found from this table, the oxide spinels have the LCs in the range between 8.044 Å ($SiNi_2O_4$) and 9.26 Å ($MoAg_2O_4$), those of the sulfide spinels vary from 9.4055 Å (Co_3S_4) to 11.26 Å ($CdDy_2S_4$), and those of the selenide spinels are in the interval from 10.20 Å (Co_3Se_4) to 11.647 Å ($CdDy_2Se_4$). Three telluride spinels, whose structural data were found in the ICSD, are $AgCr_2Te_4$, $CdDy_2Te_4$, and $CuCr_2Te_4$ with the LCs of 11.371, 11.38, and 11.26 Å, correspondingly. A group of the nitride spinels has LCs in the range from 7.2867 Å (c-SiC_2N_4) to 9.1217 Å (c-Zr_3N_4). So, the *total* range for the LC values presented in the table covers a wide interval from 7.2867 to 11.647 Å, more than 4.3 Å. We also emphasize again that most of the nitride spinels listed in Table 1 were obtained theoretically only, using the *ab initio* calculations. The binary spinels, such as Co_3O_4 and Fe_3O_4, are listed as $CoCo_2O_4$ and $FeFe_2O_4$, to distinguish between the doubly and triply positively charged ions at the tetra- and octahedral sites, respectively.

In a vast majority of the selected spinels (except for nitrides), the oxidation state of the ion located at the tetrahedral site is "+2", the oxidation state of the octahedrally coordinated ion is "+3", and the oxidation state of the anion is "−2". These oxidation states appear as a consequence of the partial occupancy of the tetra- and octahedral sites and are characteristic of normal spinels. The exceptions are as follows: (i) A = Ge, Si, Sn (oxidation state +4, oxidation state of the M cation +2); (ii) A = Li (oxidation state +1, oxidation state of the M cation +3.5, obtained as a one-to-one mixture of the cations in the oxidation states +3 and +4); (iii) A = Mo, W (oxidation state +4 or +6, then the M cation has the oxidation state +2 or +1, respectively).

At first, all the LCs from Table 1 were fitted to the linear function of the following variables: two sums of ionic radii ($R_A + R_X$), ($R_M + R_X$) and two differences of electronegativities ($\chi_X - \chi_M$), ($\chi_X - \chi_A$). The choice of these variables seems to be quite natural, since both A and M ions are surrounded by the X ions. The sum of ionic radii of two neighboring ions can be taken as an interionic separation. This is, of course, an approximation only, since it is based on a model representing both atoms as rigid incompressible spheres. The difference of electronegativities of two neighboring ions is a characteristic of degree of ionicity (covalency) of the chemical bond: the greater the difference, the more ionic the bond. For pure covalent bonds, like in the diatomic molecules of hydrogen or oxygen, the difference of electronegativities of the atoms forming the chemical bond is obviously zero; in the case of heteropolar bonds such difference is not zero, which indicates certain ionicity of such bonds.

The performed least-squares fit resulted in the following linear function, describing the LCs of the chosen crystals:

Table 1. Experimental and Predicted (This Work) Lattice Constants of Various Spinel Compounds AM_2X_4[a]

				eq 1			eqs 2−5		
no.	ICSD no. or ref	composition	LC expt, Å	LC calcd, Å	abs error (expt − calcd), Å	relative error, %	LC calcd, Å	abs error (expt − calcd), Å	relative error, %
1	40	$CdAl_2O_4$	8.355	8.402 65	−0.047 65	0.570 27	8.381 45	−0.026 45	0.316 58
2	37 428	$CdCr_2O_4$	8.567	8.611 01	−0.044 01	0.513 66	8.577 02	−0.010 02	0.116 96
3	66 133	$CdFe_2O_4$	8.7089	8.671 64	0.037 26	0.4279	8.6373	0.0716	0.822 15
4	43 743	$CdGa_2O_4$	8.59	8.607 03	−0.017 03	0.198 24	8.576 56	0.013 44	0.156 46
5	4118	$CdIn_2O_4$	9.166	9.092 33	0.073 67	0.803 74	9.028 91	0.137 09	1.495 64
6	28 954	$CdRh_2O_4$	8.73	8.673 09	0.056 91	0.651 88	8.648 39	0.081 61	0.934 82
7	28 961	CdV_2O_4	8.695	8.6814	0.0136	0.156 45	8.642 08	0.052 92	0.608 63
8	77 743	$CoAl_2O_4$	8.0968	8.140 57	−0.043 77	0.540 57	8.117 51	−0.020 71	0.255 78
9	36	$CoCo_2O_4$	8.0835	8.310 08	−0.226 58	2.803 03	8.281 59	−0.198 09	2.450 55
10	69 503	$CoCr_2O_4$	8.333	8.348 93	−0.015 93	0.191 14	8.313 09	0.019 91	0.238 93
11	36	$CoFe_2O_4$	8.35	8.409 56	−0.059 56	0.713 27	8.373 36	−0.023 36	0.279 76
12	77 744	$CoGa_2O_4$	8.3229	8.344 95	−0.022 05	0.264 96	8.312 62	0.010 28	0.123 51
13	109 301	$CoRh_2O_4$	8.495	8.411 01	0.083 99	0.988 65	8.384 45	0.110 55	1.301 35
14	36	CoV_2O_4	8.4070	8.419 32	−0.012 32	0.146 56	8.378 15	0.028 85	0.343 17
15	172 130	$CuAl_2O_4$	8.0778	8.126 33	−0.048 53	0.600 75	8.103 78	−0.025 98	0.321 62
16	36	$CuCo_2O_4$	8.054	8.295 84	−0.241 84	3.002 74	8.267 85	−0.213 85	2.6552
17	36	$CuCr_2O_4$	8.2700	8.334 69	−0.064 69	0.782 18	8.299 35	−0.029 35	0.3549
18	36	$CuFe_2O_4$	8.369	8.395 32	−0.026 32	0.314 45	8.359 62	0.009 38	0.112 08
19	61 028	$CuGa_2O_4$	8.298	8.330 71	−0.032 71	0.394 19	8.298 89	-8.9×10^{-4}	0.010 73
20	27 922	$CuMn_2O_4$	8.33	8.427 72	−0.097 72	1.173 13	8.383 82	−0.053 82	0.6461
21	36	$CuRh_2O_4$	8.29	8.396 77	−0.106 77	1.287 96	8.370 72	−0.080 72	0.9737
22	36	$FeAl_2O_4$	8.149	8.206 36	−0.057 36	0.703 88	8.183 63	−0.034 63	0.424 96
23	98 551	$FeCo_2O_4$	8.242	8.375 87	−0.133 87	1.624 28	8.3477	−0.1057	1.282 46
24	43 269	$FeCr_2O_4$	8.378	8.414 72	−0.036 72	0.438 27	8.3792	−0.0012	0.014 32
25	36	$FeFe_2O_4$	8.394	8.475 35	−0.081 35	0.969 12	8.439 47	−0.045 47	0.5417
26	28 285	$FeGa_2O_4$	8.363	8.410 74	−0.047 74	0.570 87	8.378 73	−0.015 73	0.188 09
27	36	$FeTi_2O_4$	8.500	8.575 83	−0.075 83	0.892 14	8.526 99	−0.026 99	0.317 53
28	28 666	$FeMn_2O_4$	8.51	8.507 75	0.002 25	0.026 39	8.463 66	0.046 34	0.544 54
29	109 150	$FeNi_2O_4$	8.288	8.345 63	−0.057 63	0.695 38	8.320 12	−0.032 12	0.387 55
30	28 962	FeV_2O_4	8.543	8.485 11	0.057 89	0.677 62	8.444 26	0.098 74	1.1558
31	69 497	$GeCo_2O_4$	8.318	8.427 96	−0.109 96	1.321 89	8.370 77	−0.052 77	0.634 41
32	36	$GeFe_2O_4$	8.411	8.527 43	−0.116 43	1.384 27	8.462 54	−0.051 54	0.612 77
33	1086	$GeMg_2O_4$	8.2496	8.427	−0.1774	2.150 44	8.357 55	−0.107 95	1.308 55
34	36	$GeNi_2O_4$	8.2210	8.277 26	−0.056 26	0.684 32	8.230 75	−0.009 75	0.1186
35	41	$HgCr_2O_4$	8.658	8.794 73	−0.136 73	1.579 26	8.789 84	−0.131 84	1.522 75
36	36	$LiMn_2O_4$	8.2460	8.396 35	−0.150 34	1.823 25	8.311 61	−0.065 61	0.795 66
37	36	LiV_2O_4	8.22	8.448 65	−0.228 65	2.781 67	8.362 17	−0.142 17	1.729 56
38	36	$MgAl_2O_4$	8.0832	8.190 28	−0.107 08	1.324 78	8.134 11	−0.050 91	0.629 82
39	36	$MgCo_2O_4$	8.1070	8.3598	−0.2528	3.118 28	8.298 18	−0.191 18	2.358 21
40	171 106	$MgCr_2O_4$	8.3329	8.398 64	−0.065 74	0.788 97	8.329 68	0.003 22	0.038 64
41	172 279	$MgFe_2O_4$	8.36	8.459 27	−0.099 27	1.187 49	8.389 96	−0.029 96	0.358 37
42	37 359	$MgGa_2O_4$	8.280	8.394 67	−0.114 67	1.384 88	8.329 22	−0.049 22	0.594 44
43	24 231	$MgIn_2O_4$	8.81	8.879 97	−0.069 97	0.794 19	8.781 57	0.028 43	0.3227
44	109 299	$MgRh_2O_4$	8.53	8.460 73	0.069 27	0.812 08	8.401 05	0.128 95	1.511 72
45	28 324	$MgTi_2O_4$	8.474	8.559 76	−0.085 76	1.012 01	8.477 48	−0.003 48	0.041 07
46	60 412	MgV_2O_4	8.42	8.469 04	−0.049 04	0.582 39	8.394 74	0.025 26	0.3
47	157 282	$MnAl_2O_4$	8.2104	8.272 93	−0.062 53	0.761 64	8.236 15	−0.025 75	0.313 63
48	31 161	$MnCr_2O_4$	8.437	8.481 29	−0.044 29	0.524 99	8.431 72	0.005 28	0.062 58
49	28 517	$MnFe_2O_4$	8.511	8.541 92	−0.030 92	0.363 33	8.491 99	0.019 01	0.223 36
50	17 067	$MnGa_2O_4$	8.4577	8.477 32	−0.019 62	0.231 94	8.431 25	0.026 45	0.312 73
51	24 999	$MnIn_2O4$	9.007	8.962 62	0.044 38	0.492 76	8.883 61	0.123 39	1.369 93
52	109 300	$MnRh_2O_4$	8.613	8.543 38	0.069 62	0.808 32	8.503 09	0.109 91	1.276 09
53	22 383	$MnTi_2O_4$	8.6	8.642 41	−0.042 41	0.4931	8.579 52	0.020 48	0.238 14
54	109 148	MnV_2O_4	8.52	8.551 69	−0.031 69	0.3719	8.496 78	0.023 22	0.272 54
55	36 187	$MoAg_2O_4$	9.26	9.443 57	−0.183 57	1.982 41	9.343 41	−0.083 41	0.900 76
56	21 114	$MoFe_2O_4$	8.509	8.423 57	0.085 43	1.003 98	8.410 44	0.098 56	1.1583
57	44 523	$MoNa_2O_4$	9.108	9.281 92	−0.173 92	1.909 49	9.157 68	−0.049 68	0.545 45
58	21 117	$NiAl_2O_4$	8.045	8.1011	−0.0561	0.697 27	8.077 85	−0.032 85	0.408 33
59	24 211	$NiCo_2O_4$	8.114	8.270 61	−0.156 61	1.930 11	8.241 92	−0.127 92	1.576 53

Table 1. continued

				eq 1			eqs 2−5		
no.	ICSD no. or ref	composition	LC expt, Å	LC calcd, Å	abs error (expt − calcd), Å	relative error, %	LC calcd, Å	abs error (expt − calcd), Å	relative error, %
60	84 376	$NiCr_2O_4$	8.3155	8.309 45	0.006 05	0.072 71	8.273 42	0.042 08	0.506 04
61	36	$NiFe_2O_4$	8.3250	8.370 08	−0.045 08	0.541 55	8.333 69	−0.008 69	0.104 38
62	27 903	$NiGa_2O_4$	8.258	8.305 48	−0.047 48	0.574 93	8.272 95	−0.014 95	0.181 04
63	9403	$NiMn_2O_4$	8.4	8.402 49	−0.002 49	0.029 64	8.357 88	0.042 12	0.501 43
64	36	$NiRh_2O_4$	8.36	8.371 54	−0.011 54	0.138 04	8.344 79	0.015 21	0.181 94
65	30 076	$PdZn_2O_4$	8.509	8.3175	0.1915	2.250 52	8.3045	0.2045	2.403 34
66	23 498	$RuCo_2O_4$	8.241	8.243 39	−0.002 39	0.028 94	8.241 01	-1×10^{-5}	0.000 12
67	845	$SiCo_2O_4$	8.14	8.282 92	−0.142 92	1.755 75	8.211 21	−0.071 21	0.874 82
68	36	$SiFe_2O_4$	8.2340	8.021 02	0.212 98	2.586 57	7.965 66	0.268 34	3.258 93
69	86 504	$SiMg_2O_4$*	8.069	8.281 97	−0.212 97	2.639 31	8.197 99	−0.128 99	1.598 59
70	8134	$SiNi_2O_4$	8.044	8.132 22	−0.088 22	1.096 72	8.071 19	−0.027 19	0.338 02
71	167 193	$SiZn_2O_4$*	8.0755	8.296 15	−0.220 65	2.732 36	8.218 59	−0.143 09	1.7719
72	167 815	$SnMg_2O_4$*	8.525	8.275 46	0.249 54	2.927 14	8.194 91	0.330 09	3.872 02
73	18 186	$TiFe_2O_4$	8.521	8.784 49	−0.263 49	3.092 21	8.746 67	−0.225 67	2.6484
74	36	$TiMg_2O_4$	8.4450	8.336 02	0.108 98	1.290 47	8.280 14	0.164 86	1.952 16
75	75 377	$TiMn_2O_4$	8.6806	8.509 01	0.171 59	1.976 75	8.4468	0.2338	2.693 36
76	36	$TiZn_2O_4$	8.4870	8.376 97	0.110 03	1.296 39	8.325 72	0.161 28	1.900 32
77	2133	WNa_2O_4	9.133	9.272 31	−0.139 31	1.525 34	9.160 11	−0.027 11	0.296 84
78	75 629	$ZnAl_2O_4$	8.0867	8.189 65	−0.102 95	1.273 08	8.154 75	−0.068 05	0.841 51
79	171 889	$ZnCr_2O_4$	8.3291	8.398 01	−0.068 91	0.827 33	8.350 33	−0.021 23	0.254 89
80	66 128	$ZnFe_2O_4$	8.4465	8.458 64	−0.012 14	0.143 72	8.4106	0.0359	0.425 03
81	81 105	$ZnGa_2O_4$	8.3342	8.394 03	−0.059 83	0.717 92	8.349 86	−0.015 66	0.1879
82	109 298	$ZnRh_2O_4$	8.54	8.4601	0.0799	0.935 66	8.4217	0.1183	1.385 25
83	36	ZnV_2O_4	8.409	8.4684	−0.0594	0.706 41	8.415 39	−0.006 39	0.075 99
84	43 025	$CdAl_2S_4$	10.24	9.996 63	0.243 37	2.376 67	10.026 76	0.213 24	2.082 42
85	39 415	$CdCr_2S_4$	10.24	10.204 99	0.035 01	0.341 91	10.242 39	−0.002 39	0.023 34
86	52 798	$CdDy_2S_4$	11.26	11.050 93	0.209 07	1.856 78	11.256 99	0.003 01	0.026 73
87	100 518	$CdEr_2S_4$	11.1	10.989 72	0.110 28	0.993 49	11.186 14	−0.086 14	0.776 04
88	37 405	$CdHo_2S_4$	11.24	11.020 33	0.219 68	1.9544	11.221 57	0.018 43	0.163 97
89	108 215	$CdIn_2S_4$	10.797	10.686 31	0.110 69	1.025 17	10.739 55	0.057 45	0.532 09
90	37 410	$CdLu_2S_4$	10.945	10.908 62	0.036 38	0.332 36	11.091 51	−0.146 51	1.3386
91	94 994	$CdSc_2S_4$	10.726	10.5877	0.1383	1.289 44	10.723 24	0.002 76	0.025 73
92	41 111	$CdTm_2S_4$	11.085	10.9618	0.1232	1.111 44	11.153 63	−0.068 63	0.619 12
93	61 697	CdY_2S_4	11.216	11.018 81	0.197 19	1.758 15	11.222 08	−0.006 08	0.054 21
94	41 112	$CdYb_2S_4$	11.055	10.947 04	0.107 97	0.976 62	11.170 04	−0.115 04	1.040 62
95	24 212	$CoCo_2S_4$	9.4055	9.904 07	−0.498 57	5.300 79	9.771 69	−0.366 19	3.893 36
96	52 942	$CoCr_2S_4$	9.923	9.942 91	−0.019 91	0.200 67	9.861 51	0.061 49	0.619 67
97	36	$CoIn_2S_4$	10.559	10.424 24	0.134 76	1.2763	10.358 66	0.200 34	1.897 34
98	42	$CoNi_2S_4$	9.424	9.873 83	−0.449 83	4.7732	9.732 33	−0.308 33	3.271 75
99	174 043	$CoRh_2S_4$	9.805	10.005	−0.2	2.039 76	9.794 84	0.010 16	0.103 62
100	43 527	$CrAl_2S_4$	9.914	9.8313	0.0827	0.834 19	9.859 84	0.054 16	0.5463
101	43 528	$CrIn_2S_4$	10.59	10.393 25	0.196 75	1.857 93	10.364 71	0.225 29	2.127 38
102	52 942	$CuCo_2S_4$	9.923	9.889 82	0.033 18	0.334 33	9.748 38	0.174 62	1.759 75
103	625 675	$CuCr_2S_4$	9.813	9.928 67	−0.115 67	1.178 44	9.8382	−0.0252	0.256 80
104	75 531	$CuIr_2S_4$	9.8474	10.040 17	−0.192 77	1.957 54	9.842 54	0.004 86	0.049 35
105	41 900	$CuRh_2S_4$	9.788	9.990 76	−0.202 75	2.071 47	9.771 53	0.016 47	0.168 27
106	170 227	$CuTi_2S_4$	10.0059	10.089 78	−0.083 78	0.837 33	10.039 27	−0.033 27	0.3325
107	10 035	CuV_2S_4	9.8	9.999 06	−0.199 06	2.031 24	9.9212	−0.1212	1.236 73
108	27 027	$CuZr_2S_4$	10.378	10.247 93	0.130 07	1.253 34	10.256 58	0.121 42	1.169 97
109	95 399	$FeCr_2S_4$	9.9756	10.0087	−0.0331	0.331 83	9.957 74	0.017 86	0.179 04
110	42 535	$FeFe_2S_4$	9.876	10.069 33	−0.193 33	1.957 59	9.986 85	−0.110 85	1.122 42
111	68 411	$FeIn_2S_4$	10.618	10.490 03	0.127 97	1.205 26	10.4549	0.1631	1.536 07
112	71 678	$FeLu_2S_4$	10.786	10.712 34	0.073 66	0.682 96	10.806 86	−0.020 86	0.1934
113	42 590	$FeNi_2S_4$	9.465	9.939 62	−0.474 62	5.014 43	9.828 56	−0.363 56	3.8411
114	174 045	$FeRh_2S_4$	9.902	10.070 79	−0.168 79	1.704 58	9.891 07	0.010 93	0.110 38
115	37 425	$FeSc_2S_4$	10.525	10.391 41	0.133 59	1.269 27	10.438 59	0.086 41	0.821
116	37 419	$FeYb_2S_4$	10.838	10.750 75	0.087 25	0.805 05	10.885 39	−0.047 39	0.437 26
117	608 160	$HgAl_2S_4$	10.28	10.180 36	0.099 64	0.9693	10.1744	0.1056	1.027 24
118	53 129	$HgCr_2S_4$	10.235	10.388 71	−0.153 72	1.501 86	10.390 03	−0.155 03	1.5147

Table 1. continued

				eq 1			eqs 2−5		
no.	ICSD no. or ref	composition	LC expt, Å	LC calcd, Å	abs error (expt − calcd), Å	relative error, %	LC calcd, Å	abs error (expt − calcd), Å	relative error, %
119	56 081	$HgIn_2S_4$	10.812	10.870 04	−0.058 04	0.5368	10.887 19	−0.075 19	0.695 43
120	53 096	$MgIn_2S_4$	10.687	10.473 95	0.213 05	1.993 52	10.574 74	0.112 26	1.050 44
121	37 420	$MgLu_2S_4$	10.949	10.696 26	0.252 74	2.308 32	10.9267	0.0223	0.203 67
122	37 423	$MgSc_2S_4$	10.627	10.375 34	0.251 67	2.368 17	10.558 43	0.068 57	0.645 24
123	37 417	$MgYb_2S_4$	10.957	10.734 67	0.222 33	2.029 07	11.005 23	−0.048 23	0.440 18
124	53 133	$MnCr_2S_4$	10.110	10.075 28	0.034 72	0.343 45	10.116 92	−0.006 92	0.068 45
125	65 986	$MnIn_2S_4$	10.72	10.5566	0.1634	1.524 24	10.614 07	0.105 93	0.988 15
126	37 421	$MnLu_2S_4$	10.921	10.778 91	0.142 09	1.301 06	10.966 03	−0.045 03	0.412 32
127	37 424	$MnSc_2S_4$	10.623	10.457 98	0.165 02	1.553 38	10.597 77	0.025 23	0.2375
128	37 418	$MnYb_2S_4$	10.949	10.817 32	0.131 68	1.202 63	11.044 56	−0.095 56	0.872 77
129	23 773	$NiCo_2S_4$	9.424	9.864 59	−0.440 59	4.675 21	9.713 95	−0.289 95	3.076 72
130	53 103	$NiIn_2S_4$	10.505	10.384 76	0.120 24	1.144 59	10.300 92	0.204 08	1.942 69
131	36 271	$NiNi_2S_4$	9.457	9.834 35	−0.377 35	3.990 19	9.674 59	−0.217 59	2.300 84
132	105 326	$NiRh_2S_4$	9.6	9.965 52	−0.365 52	3.807 53	9.737 09	−0.137 09	1.428 02
133	53 065	$RhCo_2S_4$	9.67	9.804 55	−0.134 55	1.3914	9.5525	0.1175	1.2151
134	53 524	$RhFe_2S_4$	9.87	9.944 18	−0.074 18	0.751 53	9.715 07	0.154 93	1.569 71
135	105 326	$RhNi_2S_4$	9.6	9.720 77	−0.120 77	1.258 03	9.454 95	0.145 05	1.510 94
136	35 380	$ZnAl_2S_4$	10.009	9.783 63	0.225 37	2.251 64	9.769 57	0.239 43	2.392 15
137	42 019	$ZnCr_2S_4$	9.982	9.991 99	−0.009 99	0.1001	9.9852	−0.0032	0.032 06
138	81 811	$ZnIn_2S_4$	10.622	10.473 32	0.148 68	1.399 77	10.482 36	0.139 64	1.314 63
139	36	$ZnSc_2S_4$	10.478	10.3747	0.1033	0.985 88	10.466 05	0.011 95	0.114 05
140	51 423	$CdAl_2Se_4$*	10.73	10.5337	0.1963	1.829 49	10.6894	0.0406	0.378 38
141	78 554	$CdCr_2Se_4$	10.7346	10.742 06	−0.007 06	0.065 72	10.832 34	−0.097 34	0.906 75
142	246 499	$CdDy_2Se_4$	11.647	11.587 99	0.059 01	0.506 62	11.586 74	0.060 26	0.517 39
143	37 406	$CdEr_2Se_4$	11.603	11.526 79	0.076 21	0.656 81	11.535 36	0.067 64	0.582 95
144	40 583	$CdHo_2Se_4$	11.631	11.557 39	0.073 61	0.632 86	11.561 05	0.069 95	0.601 41
145	52 811	$CdIn_2Se_4$	11.345	11.223 38	0.121 62	1.072 02	11.161 31	0.183 69	1.619 13
146	620 129	$CdLu_2Se_4$	11.515	11.445 69	0.069 31	0.601 91	11.466 34	0.048 66	0.422 58
147	620 411	$CdSc_2Se_4$	11.208	11.124 76	0.083 24	0.742 67	11.200 96	0.007 04	0.062 81
148	40 582	$CdTm_2Se_4$	11.56	11.498 86	0.061 14	0.528 86	11.511 68	0.048 32	0.417 99
149	620 457	CdY_2Se_4	11.66	11.555 87	0.104 13	0.893 04	11.562 62	0.097 38	0.835 16
150	37 408	$CdYb_2Se_4$	11.528	11.4841	0.0439	0.380 79	11.541 21	−0.013 21	0.114 59
151	42 538	$CoCo_2Se_4$	10.2	10.441 13	−0.241 13	2.364 05	10.423 03	−0.223 03	2.186 57
152	87 477	$CuCr_2Se_4$	10.3364	10.465 74	−0.129 74	1.255 19	10.491 01	−0.155 01	1.499 71
153	41 903	$CuRh_2Se_4$	10.264	10.527 82	−0.263 82	2.570 36	10.369 78	−0.105 78	1.030 59
154	608 163	$HgAl_2Se_4$	10.78	10.717 42	0.062 58	0.580 49	10.761 51	0.018 49	0.171 52
155	402 408	$HgCr_2Se_4$	10.7418	10.925 78	−0.183 78	1.710 87	10.904 45	−0.162 45	1.512 29
156	630 754	$MgEr_2Se_4$	11.475	11.314 43	0.160 57	1.399 31	11.459 49	0.015 51	0.135 16
157	44 912	$MgLu_2Se_4$	11.43	11.233 33	0.196 67	1.720 66	11.390 46	0.039 54	0.345 93
158	76 051	$MgTm_2Se_4$	11.469	11.2865	0.1825	1.591 22	11.435 81	0.033 19	0.289 39
159	76 052	MgY_2Se_4	11.57	11.343 51	0.226 49	1.957 55	11.486 74	0.083 26	0.719 62
160	76 053	$MgYb_2Se_4$	11.444	11.271 74	0.172 26	1.505 23	11.465 33	−0.021 33	0.186 39
161	74 407	$MnSc_2Se_4$	11.106	10.995 05	0.110 95	0.999	11.1229	−0.0169	0.152 17
162	76 225	$MnYb_2Se_4$	11.42	11.354 39	0.065 61	0.574 51	11.463 14	−0.043 14	0.377 76
163	609 325	$ZnAl_2Se_4$	10.61	10.3207	0.2893	2.726 67	10.495 82	0.114 18	1.076 15
164	150 966	$ZnCr_2Se_4$	10.46	10.529 06	−0.069 06	0.660 22	10.638 75	−0.178 75	1.708 89
165	71 695	$AgCr_2Te_4$	11.371	11.520 62	−0.149 62	1.315 81	11.105 41	0.265 59	2.335 68
166	619 806	$CdDy_2Te_4$	11.38	12.3805	−1.0005	8.791 77	11.956 04	−0.576 04	5.061 86
167	43 041	$CuCr_2Te_4$	11.26	11.258 25	0.001 75	0.015 59	10.860 31	0.399 69	3.549 64
168	43	c-Si_3N_4*	7.8367	7.578 18	0.258 52	3.298 81	7.7635	0.0732	0.934 07
169	43	c-Ti_3N_4*	8.4459	8.4008	0.0451	0.533 94	8.5555	−0.1096	1.297 67
170	[44]	c-C_3N_4*	6.8952	6.657 24	0.237 96	3.451 08	6.9308	−0.0356	0.5163
171	44	c-Ge_3N_4*	8.2110	8.058 48	0.152 52	1.857 56	8.2578	−0.0468	0.569 97
172	44	c-Sn_3N_4*	8.9658	8.691 16	0.274 64	3.063 22	8.8975	0.0683	0.761 78
173	44	c-Zr_3N_4*	9.1217	8.960 96	0.160 74	1.762 12	9.1393	−0.0176	0.192 95
174	44	c-CSi_2N_4*	7.5209	7.374 91	0.145 99	1.941 18	7.4617	0.0592	0.787 14
175	44	c-SiC_2N_4*	7.2867	6.860 52	0.426 18	5.848 77	7.2326	0.0541	0.742 45
176	44	c-CGe_2N_4*	7.7407	7.710 16	0.030 54	0.394 51	7.7514	−0.0107	0.138 23
177	44	c-GeC_2N_4*	7.4284	7.005 56	0.422 84	5.692 28	7.4373	−0.0089	0.119 81

Table 1. continued

no.	ICSD no. or ref	composition	LC expt, Å	eq 1 LC calcd, Å	eq 1 abs error (expt − calcd), Å	eq 1 relative error, %	eqs 2−5 LC calcd, Å	eqs 2−5 abs error (expt − calcd), Å	eqs 2−5 relative error, %
178	44	c-$SiGe_2N_4$*	8.0871	7.913 44	0.173 66	2.1474	8.0531	0.034	0.420 42
179	44	c-$GeSi_2N_4$*	8.0011	7.723 22	0.277 88	3.473 02	7.9682	0.0329	0.411 19
180	44	c-CTi_2N_4*	7.8351	7.965 32	−0.130 22	1.661 98	7.9161	−0.081	1.033 81
181	44	c-TiC_2N_4*	7.5400	7.092 73	0.447 27	5.932	7.5703	−0.0303	0.401 86
182	44	c-$SiTi_2N_4$*	8.2168	8.168 59	0.0482	0.586 66	8.2179	−0.0011	0.013 39
183	44	c-$GeTi_2N_4$*	8.4002	8.313 63	0.086 57	1.030 55	8.4226	−0.0224	0.266 66
184	44	c-$TiGe_2N_4$*	8.3158	8.145 65	0.170 15	2.046 14	8.3908	−0.075	0.9019
185	44	c-$TiZr_2N_4$*	8.9276	8.732 94	0.194 66	2.1804	8.8103	0.1173	1.3139

[a] Compounds whose lattice constants were *ab initio* calculated earlier are marked with an asterisk.

$$a_{\text{calc}} = 1.207\,40(R_A + R_X) + 2.676\,82(R_M + R_X) + 0.115\,73(\chi_X - \chi_M) + 0.108\,40(\chi_X - \chi_A) + 0.267\,05 \quad (1)$$

In this equation the ionic radii R_A, R_M, R_X and the calculated LC a_{calc} are expressed in Å; the electronegativities χ_A, χ_M, χ_X are dimensionless. Therefore, the fitting coefficients before the ionic radii sums $(R_A + R_X)$ and $(R_M + R_X)$ are dimensionless, whereas the coefficients before the electronegativities differences $(\chi_X - \chi_M)$, $(\chi_X - \chi_A)$ have the dimension of Å.

The correlation between the LCs taken from the literature and calculated by eq 1 is shown in Figure 2. In addition, the numerical results obtained from eq 1 are also given in Table 1, along with the absolute (in Å) and relative (in %) errors in comparison with the experimental data. The straight line in Figure 2 has a slope equal to unity and corresponds to the perfect one-to-one match between the experimental and predicted LCs. Since the nitride-based spinels were predicted theoretically using the *ab initio* calculations, they all are shown by empty symbols, to separate them clearly from the experimentally reported spinels.

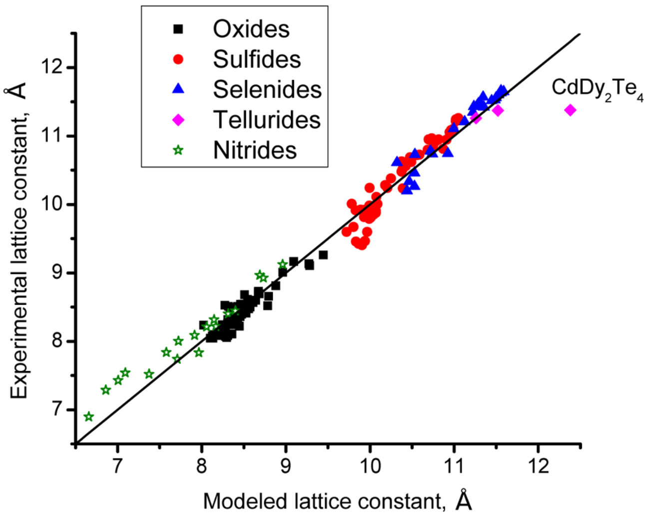

Figure 2. Correlation between the calculated and experimental LCs in the group of 185 considered spinels as obtained by using eq 1.

Despite the simplicity of eq 1, it already gives a reasonable estimate of the lattice parameter for most of the considered spinels. The average error is 1.45%; the root-mean-square deviation between the calculated and experimental LCs is 0.182 Å. The greatest error between the experimental and predicted LCs is 8.79% for $CdDy_2Te_4$, which also may give some hint of the necessity to reconsider the corresponding experimental LC of this compound.

Among those 185 spinels, considered in the presented model, for 84 compounds the relative error does not exceed 1.0%, for 62 crystals the relative error is in the range from 1.0% to 2.0%, for 22 crystals the relative difference between the calculated and experimental values is from 2.0% to 3.0%, for 9 of them the relative error varies from 3.0% to 4.0%, for 2 of them the relative error is from 4% to 5%, for 5 of them the relative error is from 5% to 6%, and for 1 crystal it is equal to 8.79%.

However, the fact that there was such a big error (8.79%) found between our model and literature data for the $CdDy_2Te_4$ spinel induced us to refine the model and treat separately various groups of spinels, depending on the anion, like oxides, sulfides, selenides together with tellurides, and nitrides, because in eq 1 we do not distinguish between these groups of spinels with different anions.

Then new linear fits of the LCs for oxides, sulfides, selenides/tellurides, and nitrides were obtained as follows:

$$a = 1.270\,84(R_A + R_X) + 2.498\,67(R_M + R_X) + 0.086\,40(\chi_X - \chi_M) + 0.051\,41(\chi_X - \chi_A) + 0.603\,40 \quad \text{(oxides)} \quad (2)$$

$$a = 1.518\,99(R_A + R_X) + 2.909\,26(R_M + R_X) + 0.342\,15(\chi_X - \chi_M) + 0.405\,73(\chi_X - \chi_A) - 1.555\,48 \quad \text{(sulfides)} \quad (3)$$

$$a = 1.175\,46(R_A + R_X) + 2.010\,22(R_M + R_X) + 0.357\,65(\chi_X - \chi_M) + 0.449\,93(\chi_X - \chi_A) + 1.666\,29 \quad \text{(selenides/tellurides)} \quad (4)$$

$$a = 1.721\,12(R_A + R_X) + 2.224\,17(R_M + R_X) - 0.004\,47(\chi_X - \chi_M) + 0.173\,00(\chi_X - \chi_A) + 0.474\,11 \quad \text{(nitrides)} \quad (5)$$

Figure 3 shows the results of applications of eqs 2−5 to the considered groups of spinels. With these new equations, agreement between the predicted and experimental/*ab initio* (the latter is related to the nitride spinels) data on the LCs has been improved considerably (compare with Figure 2). The averaged deviation between the calculated and literature LCs is

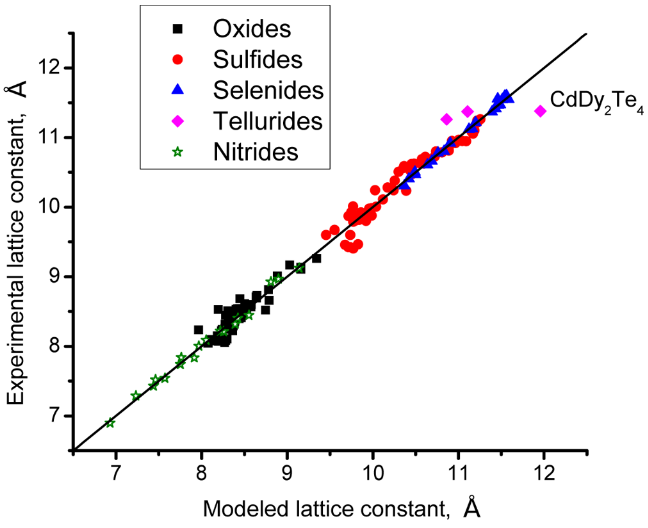

Figure 3. Correlation between the calculated and experimental LCs in the group of 185 considered spinels as obtained by using eqs 2−5.

now 0.90%. With those individual fittings for each group of spinels, LCs of 122 compounds are described by the absolute error less than 1%, for 43 the absolute error is between 1% and 2%, for 12 it is between 2% and 3%, for 7 it is between 3% and 4%, and for 1 it is 5.06% (the same CdDy$_2$Te$_4$). The root-mean-square deviation between the calculated and experimental LCs is now 0.10 Å for oxide spinels, 0.145 Å for sulfide spinels, 0.187 Å for selenide/telluride spinels, and 0.069 Å for nitride spinels.

It can be noticed immediately that the nitride spinels represent a somewhat special class of compounds, since for them the coefficient at $(R_A + R_X)$ is considerably greater and the coefficient at $(R_M + R_X)$ is considerably smaller than for the remaining spinel groups. It is also easy to see that the role played by the electronegativities difference is not the same in these groups: the coefficients at $(\chi_X - \chi_M)$ and $(\chi_X - \chi_A)$ are very small for oxide spinels, whereas their values are much greater in the cases of the sulfide and selenide/telluride spinels.

One of the possible factors, which is extremely hard, if possible at all, to model, is that many spinels are described as the structures, which are intermediate between the normal and inverse spinels, with quite different occupations numbers of the tetra- and octahedral positions. As a rule, the majority of the tetrahedral sites are occupied by the A ions, and the majority of the octahedral sites are occupied by the M ions. For example, in CuAl$_2$O$_4$ the tetrahedral sites are occupied as follows: 64% by the Cu^{2+} ions and 36% by the Al^{3+} ions, whereas 82% of the octahedral sites are taken by the Al^{3+}, and 18% by the Cu^{2+} ions. In ZnAl$_2$O$_4$ 98.4% of the tetrahedral sites are occupied by the Zn^{2+} ions and the remaining 1.6% by the Al^{3+} ions. At the same time, in this spinel 99.2% of the octahedral sites are taken by the Al^{3+}, and only 0.8% by the Zn^{2+} ions. An almost opposite example is CuCo$_2$O$_4$: the tetrahedral sites are occupied by both Cu^{2+} and Co^{3+} ions with the 1:1 ratio, whereas the 25% of the octahedral sites are occupied by the Cu^{2+} ions and 75% by the Co^{3+} ions.

These examples show a rather random character of variation of the tetra-/octahedral sites' occupation ratio. Therefore, in our model we assumed that the A ions are always at the tetrahedral sites (except for the RhM$_2$S$_4$ compounds), whereas the M ions are always at the octahedral ones (the normal spinel structure). However, even with this assumption the developed model gives an adequate description of the distribution of the LCs values in the spinels' group.

One additional reason, which without any doubts contributes to the discrepancy between the estimated LCs from our model and those from the literature, is associated with the different experimental conditions at which the data are taken. Quite often, for the same compound a search can reveal several experimental LC values, which may differ by several percent. Obviously, the experimental conditions (temperature, pressure) and crystal growth procedure (which may or may not lead to contamination of the samples by some unwanted impurities) are those factors, which, on one hand, to a large extent

Table 2. Predicted Lattice Parameters (in Å) for the Hypothetical AM$_2$X$_4$ (A = Zn, Cd, M = Sc, Y, Ln⋯Lu, X = O, S, Se) Spinels

	A = Zn, X = O, oxides		A = Cd, X = S, sulfides		A = Cd, X = Se, selenides	
	expt	predicted	expt	predicted	expt	predicted
ASc$_2$X$_4$		8.709 55		10.701 24		11.2119
AY$_2$X$_4$		9.1218		11.213 39		11.598 03
ALa$_2$X$_4$		9.472 94		11.649 809		11.927 07
ACe$_2$X$_4$		9.414 41		11.577 072		11.872 23
APr$_2$X$_4$		9.361 82		11.513 863		11.824 48
ANd$_2$X$_4$		9.342 93		11.489 424		11.8061
APm$_2$X$_4$		9.309 96		11.454 218		11.779 32
ASm$_2$X$_4$	9.228[45,a]	9.275 89		11.404 176		11.7419
AEu$_2$X$_4$	9.214[45,a]	9.245 15		11.360 680		11.709 33
AGd$_2$X$_4$		9.221 81		11.333 839		11.689
ATb$_2$X$_4$		9.1903		11.324 744		11.680 91
ADy$_2$X$_4$		9.152 92	11.26	11.249 173	11.647	11.625 13
AHo$_2$X$_4$		9.123 66	11.24	11.212 804	11.631	11.597 71
AEr$_2$X$_4$		9.0944	11.1	11.176 436	11.603	11.570 29
ATm$_2$X$_4$		9.067 73	11.085	11.143 050	11.56	11.545 13
AYb$_2$X$_4$		9.047 68	11.055	11.160 720	11.528	11.556 71
ALu$_2$X$_4$		9.016 98	10.945	11.079 259	11.515	11.497 06

[a] These experimental data were not included into the main fit (eqs 1−2), since the conditions of the samples preparations could not be verified and checked.

determine the degree of precision of the reported experimental LCs, but, on the other hand, are extremely difficult to evaluate in order to choose the most reliable experimental result. Having realized this, we tried to select the experimental structural data obtained at ambient pressure and at room (or low, where available) temperature.

Successful modeling of the lattice parameters of the existing compounds allows us to check the predictive power of the model. Table 2 below collects the structural data for three groups of spinels: ZnM_2O_4, CdM_2S_4, and CdM_2Se_4, with M = Sc, Y, La–Lu. Only very few experimental data on some members of the chosen group do exist and have been reported so far; however, the greatest portion of these compounds has not been synthesized yet. The predicted lattice constants for these potentially new spinels are given in the table; they were obtained by using eqs 3–5. We note here that for the selenide spinels we have used a slightly modified equation, which was obtained by excluding the tellurides compounds (since there are only three of them) from the fit:

$$a = 1.715\,60(R_A + R_X) + 2.258\,28(R_M + R_X) + 0.257\,86(\chi_X - \chi_M) + 0.804\,66(\chi_X - \chi_A) - 0.675\,82$$

The calculated LC values from Table 2 can be checked if the spinels mentioned there would be synthesized experimentally.

Figure 4 allows for visualizing a linear trend, which exists between the predicted LCs in Table 2 and ionic radii of the M ions (M = Sc, Y, La–Lu). The "lanthanide contraction" (a decrease of the trivalent lanthanide ionic radii when going from La to Lu) is accompanied by a decrease of the LCs. The lines shown in Figure 4 are the guides to the eye only; we refrained from performing a linear fit of these data points (which might be done, of course), since it would eliminate an influence of anions (O, S, Se) and electronegativities on the calculated result.

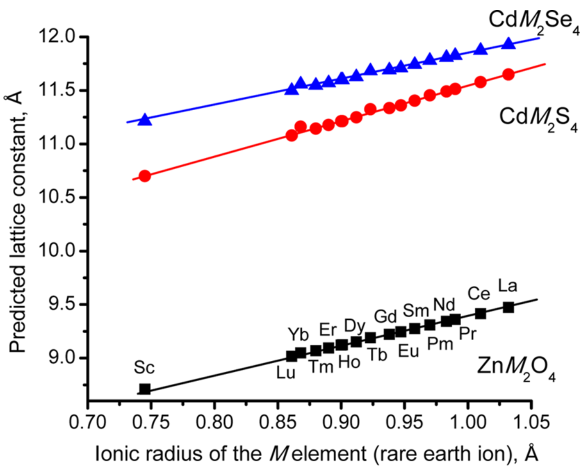

Figure 4. Variation of the predicted lattice constants of the ZnM_2O_4, CdM_2S_4, and CdM_2Se_4 (M = Sc, Y, La–Lu) from Table 2 against the ionic radii of the rare earth ions. The straight lines are guides to the eye only. The order of the data points in the two upper groups is the same as in the lowest one, where all M ions are indicated.

Nevertheless, a linear variation of the LCs in each of the considered groups, which agrees with Vegard's law, can serve as an additional argument favoring the estimations of LCs for those rare-earth-based spinels that are not reported yet.

3. STABILITY RANGES OF TERNARY SPINELS

Careful consideration of the properties of the constituting ions in ternary spinels can help in establishing limits for the stable/unstable compounds, thus effectively narrowing down the search space for the new materials. Although various combinations of the characteristics of crystal lattice ions can be constructed, one of those, which eventually turned out to be most useful, is the bond stretching force constant[35]

$$K_{AM} = \frac{\chi_A \chi_M}{(R_A + R_X)^2 + (R_M + R_X)^2 + 1.155(R_A + R_X)(R_M + R_X)} \qquad (6)$$

where all quantities have been defined above. This quantity, as emphasized by Kugimiya and Steinfink,[35] was extremely efficient for indicating the stability ranges for various AM_2O_4 structures, including the spinel and olivine phases. Figure 5 shows dependence of the experimental lattice constant of all spinels from Table 1 on the K_{AM} value. It can be immediately seen from the figure that the group of spinels differing by the anions occupy different regions in that diagram. The oxides, for example, are well-separated from other compounds. The nitride spinels are scattered over a wide area, but this can be explained by instability of the nitride spinels and by the facts that many of those nitride compounds were reported theoretically only.

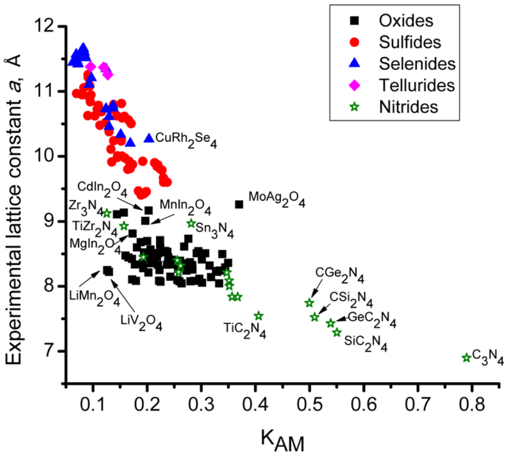

Figure 5. Correlation between the experimental LCs and K_{AM} value (eq 6) in the group of 185 considered spinels.

Figure 6 shows the scattered plot of the experimental lattice parameter versus a nondimensional ratio of the sums of ionic radii $(R_A + R_X)/(R_M + R_X)$. This diagram imposes certain limits for this ratio: thus, if the upper limit is about 1.2 for all compounds, the lower limit of $(R_A + R_X)/(R_M + R_X)$ is about 0.88 for sulfides/selenides/tellurides, and about 0.5 for oxides. So, the generalization of this diagram can be put forward as follows: if the atomic radii in the AM_2X_4 ternary spinels are concerned, the $(R_A + R_X)/(R_M + R_X)$ ratio is expected to be between 0.5 and 1.2, and existence of stable ternary spinels with ionic radii not satisfying these conditions seems to be unlikely, at least, at the ambient conditions.

As an intrinsic check for the reliability of our predicted lattice constants of the rare-earth-based oxide, sulfide, and selenide

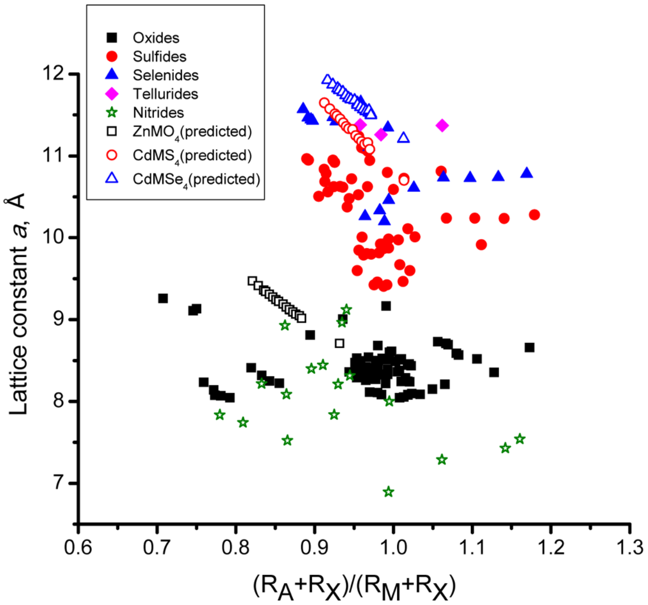

Figure 6. Correlation between the experimental LCs and nondimensional ratio of the sum of ionic radii $(R_A + R_X)/(R_M + R_X)$ in the group of 185 considered spinels. The predicted lattice constants of the $ZnMO_4$, $CdMS_4$, and $CdMSe_4$ (M = Sc, Y, La–Lu) from Table 2 are shown by the open squares, circles, and triangles, respectively.

spinels from Table 2, we included the corresponding data points (shown by the empty symbols to make them easily distinguishable from the rest of the figure) in Figure 6. These predicted compounds are all in the above-suggested stability range, since the above-introduced $(R_A + R_X)/(R_M + R_X)$ ratio for all of them is between 0.8–0.95 (oxides) and 0.9–1.0 (sulfides, selenides).

We also present in Figure 7 another scatter plot, which suggests a certain correlation between the sum of electronegativities $\chi_A + \chi_M + \chi_X$ and the sum of ionic radii $R_A + R_M + R_X$ in the group of 185 considered spinels. An important observation to be made is that the value of $R_A + R_M + R_X$ about 3 Å is a border between the oxide spinels with $R_A + R_M + R_X <$ 3 Å and sulfides, selenides, tellurides with $R_A + R_M + R_X >$3 Å. One oxide spinel $MoAg_2O_4$ and one telluride spinel $CdDy_2Te_4$ clearly fall out from the corresponding groups, and this can be a hint to certain experimental inaccuracies in determination of their LCs or certain questions regarding their stability. Another possible reason for that can be related to a large difference between electrical charges of Mo and Ag ions (+6 and +1, respectively), whereas in other considered spinels the cations' charges are +2 and +3. As far as $CdDy_2Te_4$ is concerned, it should be mentioned that the experimental data on this compound are very scarce, and can hardly be verified. The region of the stable oxide spinels is characterized by the sum of electronegativities in the range from 6 to 7.7 and an averaged sum of three ionic radii $R_A + R_M + R_X$ about 2.6 Å. The sulfide and selenide spinels cannot be clearly separated in this diagram; their representative data points occupy the area with the electronegativity sum between 5 and 6.8 and the ionic radii sum between 3 and 3.7 Å, with the averaged value of about 3.3 Å. The possibility to group the representing data points of different spinels in Figure 7 into various regions of stability can help in choosing suitable chemical elements for new spinels.

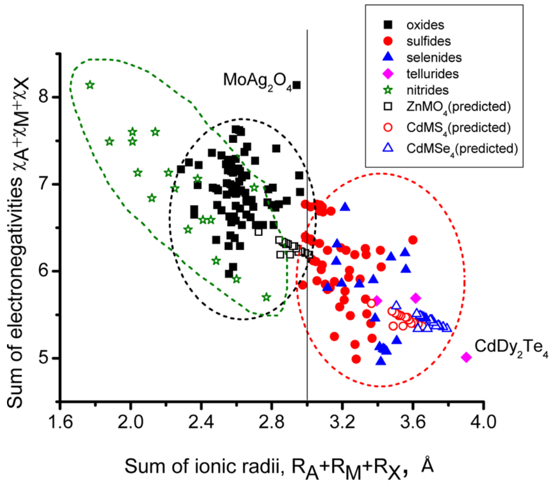

Figure 7. Correlation between the sums of electronegativities and sum of ionic radii in the group of 185 considered spinels. The positions of the predicted spinels $ZnMO_4$, $CdMS_4$, and $CdMSe_4$ (M = Sc, Y, La–Lu) from Table 2 are shown by the open squares, circles, and triangles, respectively.

Finally, Figure 8 presents a well-determined correlation between the unit cell volumes of the considered spinel compounds and the sums of volumes of individual ions (the latter are considered as the hard spheres with the Shannon ionic radii). The relation between these quantities is a linear one, as shown by the linear fits with explicitly given equations of those fits. As follows from Figure 8, there are certain lower and upper limits, within which the spinels of certain types (oxides, sulfides, selenides, tellurides, nitrides) can exist.

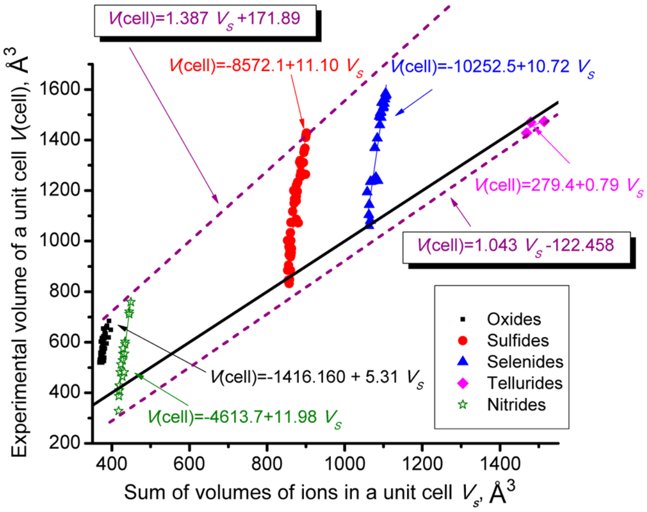

Figure 8. Correlation between the experimental volume of the unit cell V(cell) and sum of volumes of ions V_S in a unit cell in the group of 185 considered spinels. The black solid line corresponds to the condition V(cell) = V_S. See text for more details.

For example, the experimental volume of the unit cell of the oxide spinels varies between 500 and 800 Å^3 with a sum of volumes of individual ions in a unit cell less or about 400 Å^3. The experimental volume of the unit cell of the sulfur spinels is in the range ~800 and 1500 Å^3 due to a greater ionic radius of sulfur if compared with that of oxygen; a sum of volumes of individual ions in a unit cell of sulfide spinels is less or about 900 Å^3. The sum of individual volume of ions in one unit cell of the selenide spinels is about 1100 Å^3, whereas the experimental volumes of one unit cell are confined within the 1000−1600 Å^3 range.

An observation can be made that the ratio of the experimental volume of one unit cell to the sum of volumes of ions in such a cell is decreasing when going from oxide spinels to sulfides and further to selenides. In other words, in more covalent spinels, such as sulfides and selenides, the ions are packed more closely, and the fraction of the empty space between the ions is decreasing. The nitride spinels in this sense are more ionic and share more resemblance with the oxygen-based spinels. However, the circumstance that many of the nitrides mentioned in the present Article were obtained only theoretically prevents us from making any further conclusions regarding their stability.

The group of the telluride spinels, which consists only of three members, is also included in Figure 8 for the sake of completeness of the undertaken study. Tellurium is the largest anion among all considered in the present Article, and the sum of the individual ions volumes in a unit cell of the tellurium-based spinels is practically equal to the experimental volume of a unit cell.

The dashed lines in Figure 8 are the lower and upper boundaries, within which all the studied compounds are located; these limiting lines determine the filling factors (ratio of the sum of volumes of the constituting ions to that of the unit cell). For the oxide spinels such filling factor varies from 0.52 to 0.72 with the average value of 0.64. For the group of the sulfide and selenide compounds this range is shifted toward greater values: 0.63−1.03 with the average value of 0.80 and 0.69−1.00 with the average value of 0.79 for the sulfide and selenide spinels, respectively. The filling factor is about 1 for three tellurium-based spinels. As a guide to the eyes, we also plotted in Figure 8 a straight line with a slope equal to 1, which would mean that the experimental volume of a unit cell is equal to the sum of volumes of individual ions; such a condition is practically never met.

As for the filling factor, in the system of equally sized spheres the dense packing corresponds to filling of 0.81. In the system of spheres of two or more different sizes, dense packing may mean a filling factor closer to 0.9. The value of about 1 (seen in Figure 8) means just that the bond lengths in the crystal are shorter than those resulting from a simple hard spheres model. If we would assume that the shortening results in volume reduction of 10%, this means that the bonds are shorter by about 3% for the spinel compounds located in Figure 8 at the line corresponding to the filing factor 1.

It can be anticipated that the spinel compounds (including those which are not synthesized yet), whose representing points would appear in Figure 8 outside of the region bordered by the two dashed straight lines, would be unstable or would require special conditions for synthesis (high pressure, for example).

4. CONCLUSIONS

We propose in the present Article a simple model, which allows for establishing a simple correlation between the lattice constant, ionic radii, and electronegativities of the constituting ions in the case of the ternary spinel compounds AM_2X_4, where A and M are the metals occupying the tetra- and octahedrally coordinated positions, respectively, and X stands for the anion. A linear equation was obtained that links together the lattice constant with sums of the pairs of ionic radii $(R_A + R_X)$, $(R_M + R_X)$ and differences of pairs of electronegativities $(\chi_X - \chi_M)$, $(\chi_X - \chi_A)$. The developed model has been tested in a group of 185 spinels, whose structural data were found in the literature. The fitting was performed separately for the spinels with different anions (oxygen, sulfur, selenium/tellurium, nitrogen). The model's equation yields good agreement between the experimental and predicted lattice constants, with an average error of 0.90% only; for 122 spinels out of 185 considered compounds the relative error between the experimental and calculated lattice constants is less than 1%. The model proposed in the present Article is an empirical one, and the choice of its main parameters, ionic radii and electronegativities, looks to be a natural choice, since these factors to a large extent and in the first approximation determine the interionic separations, size of the interstitial positions in the crystal lattice, and, finally, the lattice constants themselves. It should be also emphasized that the coefficients in eqs 1−5, obtained from the linear fit to the experimental data, depend on the scale of electronegativities and ionic radii, as has been mentioned clearly in the Introduction. Our results held true for the Pauling electronegativities and Shannon radii.

A close look at the experimental and modeled lattice constants collected in the present work reveals that the chemical and physical properties of the constituting chemical elements can also significantly contribute to the deviation between the model and experiment. Thus, the spinels with transition metal ions, such as Mn, Fe, Co, Ni, which exhibit magnetic properties due to the presence of the unfilled 3d electron shell and its active participation in chemical bonding, are those compounds whose modeled lattice constants in many cases deviate more significantly from the experimental results. This circumstance may be a hint for a further development of the present model, which can be a future perspective.

Careful consideration of the interplay between the experimental lattice constants and/or ionic radii, bond stretching force constant, sum of volumes of the constituting ions, and their ionic radii and electronegativities allows us to identify the certain regions of stability, within which the stable spinel compounds can be expected to exist. The obtained trends were represented by the two-dimensional plots; their meaning was discussed in the text. The main application of those plots, as it is deemed now, would be to narrow down the search for new spinels by choosing those potential compounds whose representative points would fall down within the domains of existing stable compounds.

We believe that the obtained empirical dependence of the lattice constant on the ionic radii and electronegativity difference, expressed by eqs 1−5 from this Article, will be helpful for the chemists and materials scientists, since it gives an opportunity to estimate in a very simple and efficient way the lattice constants for new ternary compounds with the spinel structure. It is essential that the model developed here not only takes into account the ionic radii as the main geometrical factors to determine the lattice constant, but also accounts, at least partially, for a difference in chemical properties of the constituting ions by considering explicitly the difference of electronegativities of nearest neighbors making chemical bonds. We also hope that the results obtained in the present Article can be useful for meaningful guided choice of chemical elements for a synthesis of new spinel compounds.

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Notes

The authors declare no competing financial interest.

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