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Effect of Substituting Cobalt for Nickel Ions on Electric Field Gradient in $Ni_{3-x}Co_xB_2O_6$

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Using the VASP software package, the principal components of the electric field gradient tensor for nickel and cobalt ions in $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ crystals were calculated. A comparison of the electric field gradient parameters on the Ni and Co ions in each crystal, obtained using experimental and theoretical structural data, suggests that in $Ni_2CoB_2O_6$, cobalt ions are substituted for nickel ions in the 2a crystallographic position, while in $Co_2NiB_2O_6$, cobalt ions are substituted for nickel ions in the 2a crystallographic position.

Keywords: kotoites, cationic ordering, ab initio calculations.

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1. Introduction

A substitutional solid solution is formed in the case when dimensions, valence and electronegativity of a substituted and a substituent atom are at certain ratios [1]. In the disordered solid solutions the substituted and substituent atoms are evenly distributed in the sample [2]. However, in the case when the compound includes several non-equivalent crystallographic positions, mixing of atoms in different crystallographic positions may be uneven. Thus, for example, in the collbranite structure there are four crystallographic positions occupied by metal ions, and depending on the composition, there may be both fully cation-ordered compound [3,4] and disordered one [5–8], besides, in some compositions every position contains two types of atoms, but with different probability, which considerably influences the properties [4].

$Ni_{3-x}Co_xB_2O_6$ compounds are perfect candidates to form substitutional solid solutions in the entire range of concentrations, since there are two extreme isostructural compounds: $Co_3B_2O_6$ and $Ni_3B_2O_6$; besides, nickel and cobalt atoms neighbor in the Mendeleev's Periodic Table, both ions in the composition are in bivalent state and have practically same ionic radius. However, in the kotoite structure, where $Ni_{3-x}Co_xB_2O_6$ compounds are implemented, metal ions occupy two crystallographic positions: 2a and 4f (Figure 1), and the question arises about the distribution of nickel and cobalt ions in crystallographic positions at different concentrations ($0 < x < 3$).

In many cases the X-ray diffraction method makes it possible to determine the extent of population of each position with different atoms, however, for the compounds, the composition of which includes atoms neighboring in the Mendeleev's Periodic Table, the neutron diffraction method becomes practically the only method, with the help of which it is possible to study the distribution of atoms in the positions and detect superstructural ordering [9]. However, the neutron diffraction method is not generally available and has some limitations (for example, for compounds containing isotope ^{10}B due to its high absorption).

Development of the methods to calculate the physical properties of compounds *ab initio* makes it possible to describe the physical properties of compounds, and in some cases even predict them [10]. As it was shown recently,

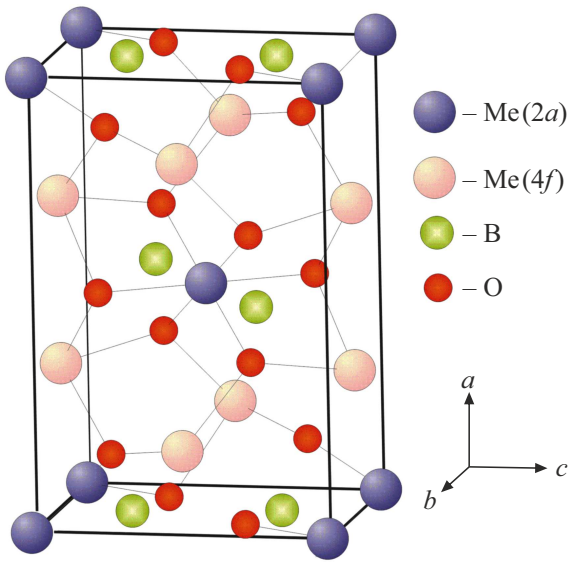

Figure 1. Kotoite structure. Dark purple and light pink circles indicate the positions of transition metal atoms 2a and 4f.

substitution of iron ions with Jahn–Teller ions Mn^{3+} in $HoFe_{1-x}Mn_xO_3$ crystals results in significant increase of temperature of the spin-flip transition [11]. Changes of angles and distances in oxygen octahedrons $(Fe,Mn)O_6$ play an important role causing change in the electric field gradient (EFG) and balance of exchange constants in a 3d-subsystem [11,12], which may indicate the impact of an oxygen octahedron on magnetic properties of orthoferrite. The electric field gradient is very sensitive to chemical and structural changes. Changes in the electric field gradient in cation substitution may allow simulating the preferable distribution of transition metal ions in crystallographic positions in solid solutions.

The study objects in the paper are $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds with kotoite structure, where metal ions occupy two non-equivalent positions. For $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds the question of metal ion distribution in the positions remains open. In paper [13] they studied the spectra of diffuse scattering of $Ni_3B_2O_6$ and $Co_2NiB_2O_6$ compounds, defined Racah parameters; comparision of Racah parameters for $Ni_3B_2O_6$ and $Co_2NiB_2O_6$ compounds demonstrated that nickel ions prefer to occupy the crystallographic position 4f [13]. However, this method is not a direct method to determine distribution of ions in crystalline positions. In paper [14] it was shown that distribution of metal ions in the positions had significant impact on the ground magnetic state in compounds $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$.

In this paper we study the impact of nickel ion substitution for cobalt ion in EFG in $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ crystals within the calculations *ab initio*.

2. Calculation method

The calculations were performed within the framework of density functional theory using Perdew–Burke–Ernzerhof exchange-correlation functionals with generalized gradient approximation (PBE-GGA) implemented in the VASP package [15,16]. The number of plane waves was limited by the energy of 400 eV. The Monkhorst–Pack grid [17] was chosen to be equal to $7 \times 5 \times 9$. The calculation used the GGA + U method in the Dudarev's approximation [18], in which parameter U for cobalt and nickel ions was selected as 4 eV. Configuration of valence electrons for ions of Co — $3d^84s^1$, Ni: $3d^94s^1$, B — $2s^22p^1$ and O ions— $2s^22p^4$. Electric field gradient tensor component values were calculated using the method described in papers [19] and implemented in the VASP package.

3. Results and discussion

This paper conducted theoretical calculations *ab initio* of EFG tensors for cobalt and nickel ions in $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds. The crystalline structure of the studied compounds is similar to

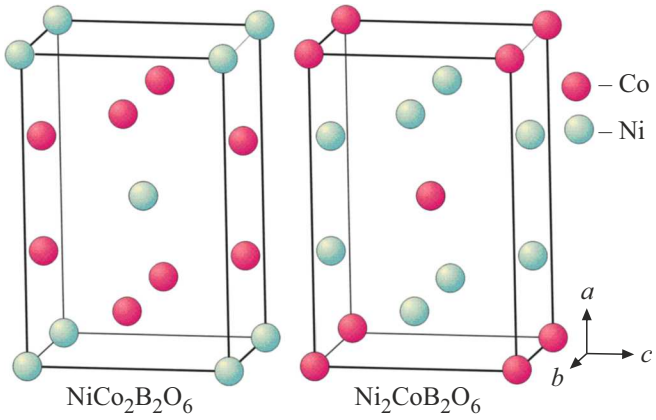

Figure 2. Distribution of cobalt ions (dark red circles) and nickel ions (light green circles) in non-equivalent crystallographic positions 2a and 4f in $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds.

the structure of the natural mineral kotoite and is described by the spatial group of symmetry Pnmn with rhombic crystal system; the lattice cell contains two formula units ($Z = 2$) (Figure 1). Cobalt and/or nickel ions occupy in the lattice cell two non-equivalent positions 2a and 4f (Wyckoff positions). It is assumed that in $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds the cobalt and nickel ions are distributed in non-equivalent positions as follows: four cobalt ions in position 4f and two nickel ions in position 2a for $Co_2NiB_2O_6$, four nickel ions in position 4f and two cobalt ions in position 2a for $Ni_2CoB_2O_6$ (Figure 2). However, you can also expect „admixture" of some ions with another ones in both positions, since nickel and cobalt ions have the same valence and close ionic radii.

Nickel and cobalt ions in isostructural compounds will have certain differences in the forms of the closest environment. And here, as it seems to us, it makes sense to compare EFG in these ions. Values of EFG tensor components and directions of their corresponding vectors are very sensitive to small distortions of the shape of the closest environment for the considered ion.

Previously we tested the method of EFG calculation in paper [20], which studied the impact of manganese impurity ion concentration on the structural and magnetic properties in the holmium orthoferrite crystal.

This paper used two sets of lattice parameters and atom coordinates for each studied compound. The first one — experimental, obtained using X-ray diffraction analysis conducted in papers [13,21]. The second one — theoretical, obtained in this paper by minimization of the full energy of the crystal in variation of structural parameters.

EFG calculations were carried out using experimental and theoretical structural data and were compared to each other for every compound. Therefore, we obtained information on the structural differences of experimental and theoretical data for a specific compound.

Within the method of electron density functionality, the full energy minimum was calculated for variable lattice pa-

Table 1. Lattice parameters and coordinates of atoms in studied compounds calculated in this paper and obtained experimentally in papers [13,21]

		$Co_3B_2O_6$		$Co_2NiB_2O_6$		$Ni_2CoB_2O_6$		$Ni_3B_2O_6$	
Lattice parameters									
		exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
a, Å		5.462	5.4011	5.4582	5.4026	5.4314	5.3677	5.396	5.3404
b, Å		8.436	8.3995	8.4269	8.4139	8.3789	8.2395	8.297	8.2561
c, Å		4.529	4.5347	4.5149	4.4742	4.4917	4.4924	4.459	4.4495
Atom	Position	Relative coordinates of atoms							
		exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
Co/Ni	2a	0; 0; 0	0; 0; 0	0; 0; 0	0; 0; 0	0; 0; 0	0; 0; 0	0; 0; 0	0; 0; 0
Co/Ni	4f	0.5 0.8136 0	0.5 0.8125 0	0.5 0.8144 0	0.5 0.8170 0	0.5 0.8152 0	0.5 0.8163 0	0.5 0.81572 0	0.5 0.81658 0
B	4g	0.2446 0.5 0.0417	0.2435 0.5 0.0442	0.2457 0.5 0.0439	0.2487 0.5 0.0445	0.2457 0.5 0.0432	0.2426 0.5 0.0412	0.2449 0.5 0.0439	0.2450 0.5 0.0441
O1	4g	0.1807 0.5 0.7480	0.1801 0.5 0.7504	0.1788 0.5 0.7483	0.1780 0.5 0.7490	0.1771 0.5 0.7475	0.1742 0.5 0.7449	0.1757 0.5 0.7489	0.1738 0.5 0.7466
O2	8h	0.2928 0.6385 0.1975	0.2925 0.6396 0.2010	0.2956 0.6390 0.1996	0.3004 0.6393 0.2023	0.2975 0.6396 0.2013	0.2944 0.6425 0.1977	0.2989 0.6399 0.2012	0.2994 0.6417 0.2034

rameters and free atom coordinates for $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds. The obtained equilibrium structural parameters are shown in Table 1.

For comparison, the experimental data is provided [13,21]. You can see a good agreement of estimated and experimental data. The deviation in the lattice parameters did not exceed 2%.

For the studied compounds, using theoretical and experimental structural data, the calculations were performed for the components of diagonalized tensors of electric field gradient V_{xx}, V_{yy}, V_{zz} ($|V_{zz}| > |V_{xx}| > |V_{yy}|$), field asymmetry parameter η ($\eta = |V_{xx} - V_{yy}|/|V_{zz}|$) and coordinates of eigen vectors $\mathbf{e}_{xx}, \mathbf{e}_{yy}, \mathbf{e}_{zz}$, which correspond to the main components of EFG tensor. The results are given in Table 2, the vectors are shown in Figure 3.

Table 2 demonstrates good agreement between the values of the main components of EFG tensor and asymmetry parameters obtained using theoretical and experimental structural data for $Co_3B_2O_6$. In Figure 3, $a-d$ you can see that the directions of eigen vectors corresponding to the main components of EFG tensor practically completely coincide. This means that the theoretical and experimental lattice parameters and atom coordinates agree well with each other (you can also see that in Table 1), and, what's most important, the shapes of the nearest-neighbor environment of cobalt ions are rather similar in the experimental and theoretical structures of this compound. A similar situation may be observed in Table 2 and in Figure 3, $m-p$ for $Ni_3B_2O_6$ compound. Therefore, you can conclude that the method of theoretical calculation used in this paper describes very well the structural properties of the studied compounds.

Besides, in Table 2 and in Figure 3 you can see that the values of EFG tensor components and directions of corresponding vectors, as well as the values of the asymmetry factor for cobalt ion in $Co_3B_2O_6$ differ significantly from such for nickel ion in $Ni_3B_2O_6$. This means that despite the same structural type of $Co_3B_2O_6$ and $Ni_3B_2O_6$ compounds, the cobalt and nickel ions form around each other the nearest-neighbor environment of the same symmetry, but of different shape.

From calculations obtained using the theoretical structural parameters, you can see the following. In $Ni_3B_2O_6$ and $Ni_2CoB_2O_6$ compounds for the nickel ion in crystallographic position 4f the EFG parameters (V_{xx}, V_{yy}, V_{zz}, $\mathbf{e}_{xx}$, $\mathbf{e}_{yy}$, $\mathbf{e}_{zz}$, η) have close values (Figure 3, l and p, Table 2). In $Co_3B_2O_6$ and $Ni_2CoB_2O_6$ for cobalt ion in crystallographic position 2a, the main components of EFG tensor and asymmetry factor have close values (Table 2). You can see the difference in the direction of eigen vectors corresponding to the main components of EFG tensor (Figure 3, b and j). However, we can obtain the location of vectors in space for cobalt ion in $Ni_2CoB_2O_6$, as for cobalt ion in position 2a in $Co_3B_2O_6$. For this purpose

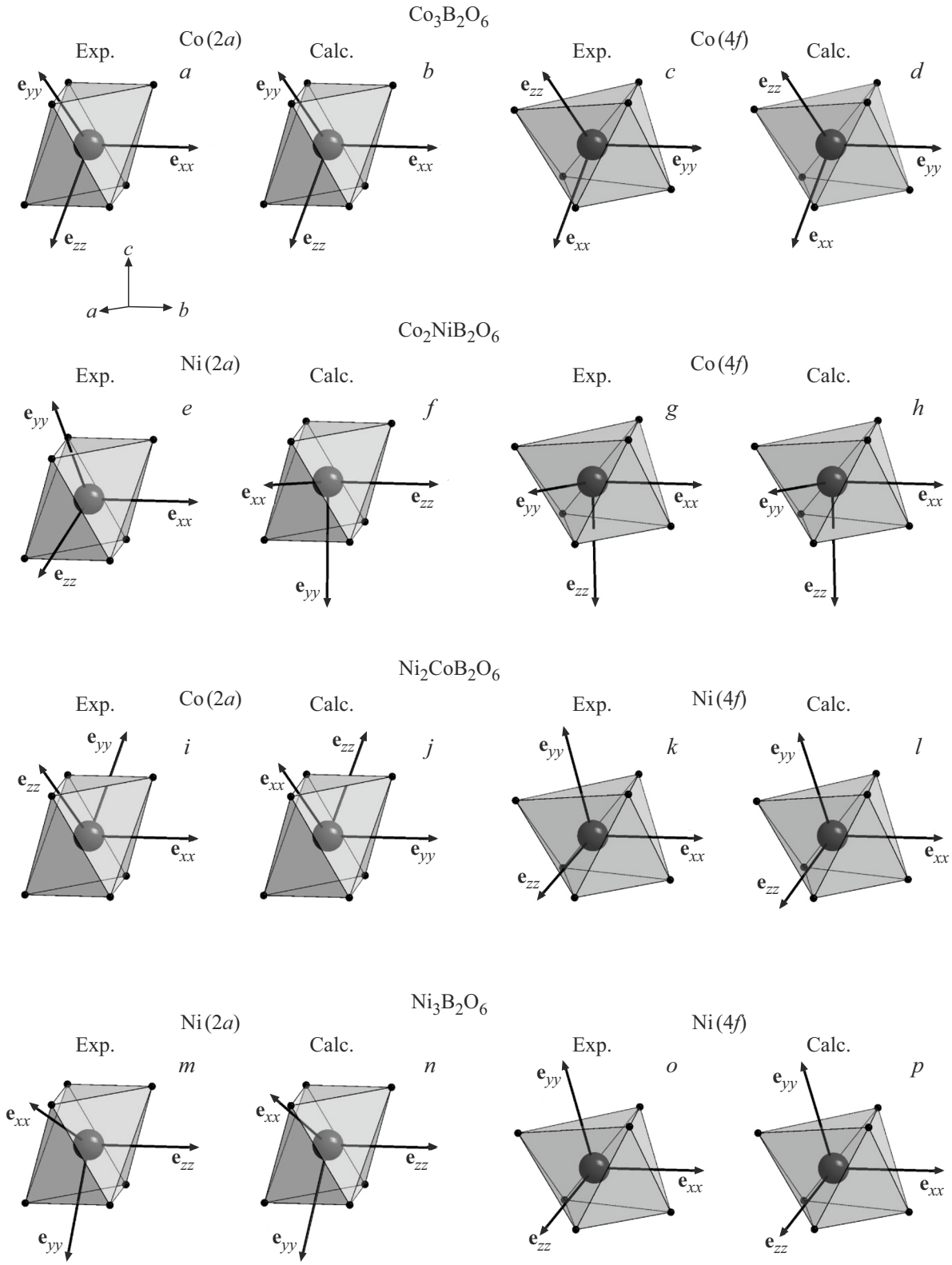

Figure 3. Eigen vectors $\mathbf{e}_{xx}$, $\mathbf{e}_{yy}$, $\mathbf{e}_{zz}$, corresponding to main components of EFG tensor for nickel and cobalt ions in the studied compounds.

Table 2. Main components of EFG tensor and asymmetry parameter obtained using the lattice parameters calculated in this paper (upper row in the cell) and found experimentally in papers [13,21] (lower row in the cell)

	V_{xx}, V/Å^2	V_{yy}, V/Å^2	V_{zz}, V/Å^2	η
$Co_3B_2O_6$				
Co (2a)	−59.823 −60.167	−56.524 −52.961	116.347 113.128	0.028 0.064
Co (4f)	−88.800 −91.666	−13.122 −8.466	101.922 100.132	0.743 0.831
$Co_2NiB_2O_6$				
Ni (2a)	−10.493 −10.315	−1.177 −3.560	11.670 13.875	0.798 0.487
Co (4f)	−70.854 −66.804	−40.807 −41.440	111.661 108.243	0.269 0.234
$CoNi_2B_2O_6$				
Co (2a)	−61.990 −175.366	−56.740 −91.015	118.730 266.381	0.044 0.317
Ni (4f)	−24.434 −21.661	−4.300 −4.066	28.733 25.727	0.701 0.684
$Ni_3B_2O_6$				
Ni (2a)	−12.619 −13.050	−0.080 −1.288	12.699 14.338	0.987 0.820
Ni (4f)	−23.436 −24.009	−4.012 −4.711	27.448 28.720	0.708 0.672

in $Ni_2CoB_2O_6$ compound for cobalt ion it is necessary to switch places of EFG tensor components V_{xx} and V_{yy} and their corresponding vectors $\mathbf{e}_{xx}$ and $\mathbf{e}_{yy}$, and to rename them: $V_{xx} \to V_{yy}$ and $V_{yy} \to V_{xx}$, $\mathbf{e}_{xx} \to \mathbf{e}_{yy}$ and $\mathbf{e}_{yy} \to \mathbf{e}_{xx}$. Such procedure may be performed, since the tensor components are to be named in the order of value increase as follows: $V_{zz} > V_{xx} > V_{yy}$, and in our case the values of V_{xx} and V_{yy} components are quite close to each other. For the triad of eigen vectors to be right, it is necessary to change the direction of ezz vector to the reverse one. In Figure 3 and Table 2 you can note substantial differences of EFG parameters for nickel ions in the crystallographic position 2a and cobalt ions in position 4f in $Co_2NiB_2O_6$ compound compared to EFG parameters of these ions in source $Ni_3B_2O_6$ and $Co_3B_2O_6$. Therefore, you can conclude that nickel and cobalt ions preserve the shape of the nearest-neighbor environment in one compound ($Ni_2CoB_2O_6$) the same as in the source compounds ($Ni_3B_2O_6$ and $Co_3B_2O_6$), only in crystallographic positions 4f and 2a, accordingly.

Let us compare the obtained results for the experimental and theoretical structure of $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds. In $Co_2NiB_2O_6$ for cobalt ion in position 4f there is a very good agreement of EFG parameters obtained using experimental and theoretical structural data (Figure 3, *g* and *h*, Table 2). A similar situation is observed for nickel ion in crystallographic position 4f in $Ni_2CoB_2O_6$ compound (Figure 3, *k* and *l*, Table 2). You can see the main differences in $Ni_2CoB_2O_6$ compound for cobalt ion in crystallographic position 2a. The values of the main components of EFG tensor V_{xx} and V_{zz} calculated using experimental structural data are more than double of V_{xx} and V_{zz} values calculated using theoretical structural parameters (Table 2). The asymmetry parameter values also differ substantially. In Figure 3, *i* and *j* you can see a discrepancy in the directions of eigen vectors $\mathbf{e}_{xx}$, $\mathbf{e}_{yy}$, $\mathbf{e}_{zz}$, obtained for the experimental and theoretical structures of $Ni_2CoB_2O_6$ compound. In $Co_2NiB_2O_6$ for nickel ion in position 2a the value of EFG tensor component V_{yy} obtained for the experimental structure is three-fold of that calculated for the theoretical structure (Table 2). This, in its turn, causes substantial difference in asymmetry factors. The discrepancy in the directions of vectors $\mathbf{e}_{xx}$, $\mathbf{e}_{yy}$, $\mathbf{e}_{zz}$ that comply with the main components of EFG tensor for nickel ion in position 2a obtained for the experimental and theoretical structures of $Co_2NiB_2O_6$ compound may be seen in Figure 3, *e* and *f*.

Taking into account the good agreement of EFG parameters calculated using the experimental and theoretical structural parameters, for cobalt and nickel ions in $Co_3B_2O_6$ and $Ni_3B_2O_6$, and also for cobalt and nickel ions in crystallographic position 4f in $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds accordingly, the following conclusion can be drawn. The differences of EFG parameters found in this paper and obtained using the experimental and theoretical structural parameters for cobalt and nickel ions in crystallographic position 2a in $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds mean that the filling of position 2a only with nickel ions in $Co_2NiB_2O_6$ and only with cobalt ions in $Ni_2CoB_2O_6$ does not correspond to the experimental crystal structure of the studied compounds. Apparently, in $Ni_2CoB_2O_6$ compound the cobalt ions are substituted with nickel ions in crystallographic position 2a. It is not possible to identify the nickel concentration in this position within this paper. The chemical formula of this sample may be recorded as $Ni_{2+\Delta}Co_{1-\Delta}B_2O_6$, where Δ is nickel concentration in position 2a. Similarly we can assume that in $Co_2NiB_2O_6$ compound the nickel ions are substituted with cobalt ions in crystallographic position 2a, and the chemical formula in this case may be recorded as $Co_{2+\Delta}Ni_{1-\Delta}B_2O_6$, where Δ is the cobalt concentration in crystallographic position 2a.

4. Conclusion

The calculations of the main components of electric field gradient tensor V_{xx}, V_{yy}, V_{zz}, coordinates of the corresponding eigen vectors $\mathbf{e}_{xx}$, $\mathbf{e}_{yy}$, $\mathbf{e}_{zz}$ and field asymmetry parameter η ($\eta = |V_{xx} - V_{yy}|/|V_{zz}|$) for nickel and cobalt ions in $Co_3B_2O_6$, $Ni_3B_2O_6$, $Co_2NiB_2O_6$ and $Ni_2CoB_2O_6$ compounds were done using lattice parameters and atom coordinates calculated in this paper and obtained exper-

imentally in papers [13,21]. Direct comparison of EFG parameters obtained using experimental and theoretical structural data in the corresponding ions in each crystal makes it possible to assume that in $Ni_2CoB_2O_6$ the cobalt ions are substituted in crystallographic position 2a with nickel ions. Similarly, in $Co_2NiB_2O_6$ the nickel ions are substituted in crystallographic position 2a with cobalt ions, which agrees with the experimental data [13].

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] W. Hume-Rothery. Elements of Structural Metallurgy. Institute of Metals, London (1961).
[2] V.S. Urusov. Teoriya izomorfnoj smesimosti. Nauka, M. (1977). 251 s. (in Russian).
[3] K. Bluhm, H. Müller-Buschbaum. Z. anorg. allg. Chemie 582, 1, 15 (1990).
[4] D.C. Freitas, M.A. Continentino, R.B. Guimarães, J.C. Fernandes, E.P. Oliveira, R.E. Santelli, J. Ellena, G.G. Eslava, L. Ghivelder. Phys. Rev. B **79**, *13*, 134437 (2009).
[5] J.A. Hriljac, R.D. Brown, A.K. Cheetham, L.C. Satek. J. Solid State Chem. **84**, *2*, 289 (1990).
[6] D.A. Perkins, J.P. Attfield. J. Chem. Soc., Chem. Commun. *4*, 229 (1991).
[7] R. Norrestam, M. Kritikos, K. Nielsen, I. Søtofte, N. Thorup. J. Solid State Chem. **111**, *2*, 217 (1994).
[8] S.N. Sofronova, A.V. Chernyshev, A.D. Vasil'ev, A.V. Shabanov. FTT **66**, *10*, 1736 (2024). (in Russian).
[9] M.S. Lucas, G.B. Wilks, L. Mauger, J.A. Muñoz, O.N. Senkov, E. Michel, J. Horwath, S.L. Semiatin, M.B. Stone, D.L. Abernathy, E. Karapetrova. Appl. Phys. Lett. **100**, *25*, 251907 (2012).
[10] P.A. Agzamova, S.V. Streltsov. Phys. Solid State **64**, *1*, 140, (2022).
[11] K.A. Shaykhutdinov, S.A. Skorobogatov, Yu.V. Knyazev, T.N. Kamkova, A.D. Vasiliev, S.V. Semenov, M.S. Pavlovsky, A.A. Krasikov. ZhETF **165**, *5*, 685 (2024). (in Russian).
[12] G. Kotnana, V.R. Reddy, S.N. Jammalamadaka. J. Magn. Magn. Mater. **429**, 353 (2017).
[13] S. Sofronova, E. Moshkina, A. Chernyshev, A. Vasiliev, N.G. Maximov, A. Aleksandrovsky, T. Andryushchenko, A. Shabanova. CrystEngComm **26**, *19*, 2536 (2024).
[14] S.N. Sofronova, D.A. Velikanov, E.M. Moshkina, A.V. Chernyshev. Bull. RAS: Phys. **88**, *Suppl. 1*, S47 (2024).
[15] G. Kresse, J. Furthmüller. Phys. Rev. B **54**, *16*, 11169 (1996).
[16] J.P. Perdew, K. Burke, M. Ernzerhof. Phys. Rev. Lett. **77**, *18*, 3865 (1996).
[17] H.J. Monkhorst, J.D. Pack. Phys. Rev. B **1**3, *12*, 5188 (1976).
[18] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C. Humphreys, A.P. Sutton. Phys. Rev. B **57**, *3*, 1505 (1998).
[19] H.M. Petrilli, P.E. Blöchl, P. Blaha, K. Schwarz. Phys. Rev. B **57**, *23*, 14690 (1998).
[20] Y.V. Knyazev, M.S. Pavlovskii, T.D. Balaev, S.V. Semenov, S.A. Skorobogatov, A.E. Sokolov, D.M. Gokhfeld, K.A. Shaykhutdinov. Crystals **14**, *12*, 1025 (2024).
[21] H. Effenberger, F. Pertlik. Z. Kristallogr. — Cryst. Mater, **166**, *1–4*, 129 (1984).

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