

Article **Lattice Dynamics of Ni3-xCoxB2O⁶ Solid Solutions**

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> **Abstract:** On the one hand, $Ni_{3-x}CoxB_2O_6$ solid solutions are promising anode materials for lithium batteries, and on the other hand, they have antiferromagnetic properties. This study examines the lattice dynamics of $Ni_{3-x}Co_xB_2O_6$ solid solutions for $x = 0, 1, 2, 3$ by means of quantum chemistry and Raman spectroscopy. The vibrational spectra of the compound $NiCo₂B₂O₆$ have been studied using the polarized Raman spectroscopy method. Good agreement was found between the theoretical and experimental results. As expected, the largest change in frequencies was observed in the modes where the vibrations of the metal ion had a large amplitude. The substitution of cobalt by nickel does not lead to the appearance of soft modes. This fact indicates that the structures of the solid solutions are stable.

Keywords: kotoite; lattice dynamic; ab initio calculation

1. Introduction

Oxyborates Ni₃B₂O₆ and Co₃B₂O₆ and solid solutions of Ni_{3-x}Co_xB₂O₆ were obtained in the 1990s [\[1–](#page-9-0)[5\]](#page-9-1). These compounds are interesting both from the fundamental point of view and as promising anode materials for lithium-ion and sodium-ion batteries [\[6\]](#page-9-2). The compounds $Ni₃B₂O₆$ and $Co₃B₂O₆$ are antiferromagnets, but their easy axis of magnetization is different [\[7](#page-9-3)[,8\]](#page-9-4). Mixing magnetic ions with incompatible single-ion anisotropies gives rise to what can be thought of as an atomic-level composite. This random site-dependent anisotropy in combination with the inter-species exchange interaction creates frustration in the system and may result in what is known as an oblique antiferromagnetic phase [\[9](#page-9-5)[–15\]](#page-10-0). Thus, the solid solutions of $Ni_{3-x}Co_xB_2O_6$ are interesting in terms of magnetic properties, but it is not only their magnetic properties that should attract the attention of researchers. The investigation of the lattice dynamics of $Ni₃B₂O₆$ shows several new phonon modes to appear at the antiferromagnetic ordering temperature [\[16\]](#page-10-1). In $\text{Co}_3\text{B}_2\text{O}_6$, such effects are not observed [\[17\]](#page-10-2). To understand the mechanisms of the appearance of new modes during the antiferromagnetic phase transition, it is necessary to study the lattice dynamics of the $Ni_{3-x}Co_xB_2O_6$ solid solutions. For the practical application of new materials, in particular solid solutions, it is fundamentally important that the structures stay stable when the temperature decreases [\[18–](#page-10-3)[20\]](#page-10-4). One of the implicit advantages of the density functional theory is that the modeling performs at temperatures close to zero. If unstable modes are detected as a result of the calculation, then the structure is unstable and can undergo a phase transition when the temperature decreases. In this paper, we present a theoretical study of the lattice dynamics of the $\rm Ni_2CoB_2O_6$ and $\rm Co_2NiB_2O_6$ solid solutions and an experimental study of the Raman spectra of $Co₂NiB₂O₆$.

2. The Crystal Structure

The crystal structure of $Ni_{3-x}Co_xB_2O_6$ is classified as the kotoite structure and belongs to the space symmetry group *Pnnm* (58) (Figure [1\)](#page-1-0). The unit cell of kotoite contains six transition

Citation: Sofronova, S.N.; Pavlovskii, M.S.; Krylova, S.N.; Vtyurin, A.N.; Krylov, A.S. Lattice Dynamics of Ni3-xCoxB2O⁶ Solid Solutions. *Crystals* **2024**, *14*, 994. [https://doi.org/](https://doi.org/10.3390/cryst14110994) [10.3390/cryst14110994](https://doi.org/10.3390/cryst14110994)

Received: 23 October 2024 Revised: 8 November 2024 Accepted: 14 November 2024 Published: 17 November 2024

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metal atoms occupying two crystallographic positions 2a and 4f. The transition metal atoms are located in oxygen octahedra, which are strongly distorted. Boron and oxygen ions form the BO₃ group. In the solid solutions $\rm Ni_2CoB_2O_6$ and $\rm NiCo_2B_2O_6$, nickel and cobalt ions can randomly occupy both positions (2a and 4f). Lattice dynamics have been calculated for the cation ordered state. In $\rm Ni_2CoB_2O_6$, the cobalt ions occupy the 2a crystallographic position, while the nickel ions occupy the 4f position. In $NiCo₂B₂O₆$, the cobalt ions occupy the 4f crystallographic position, while the nickel ions occupy the 2a position. position.

to the space symmetry group *Pnnm* (58) (Figure 1). The unit cell of kotoite contains six

Figure 1. The crystal structure of kotoite. The 2a and 4f crystallographic positions of the transition **Figure 1.** The crystal structure of kotoite. The 2a and 4f crystallographic positions of the transition metal ions are shown by different colors. metal ions are shown by different colors.

The first-principles calculations were carried out using the projector-augmented The first-principles calculations were carried out using the projector-augmented wave (PAW) [meth](#page-10-5)od $[21]$ within the density functional theory (DFT) , as implemented in the VASP code [22,23]. We used the generalized gradient approximation (GGA) functional with Perdew– Burke–Ernzerhof (PBE) [para](#page-10-8)metrization [24]. Electronic configurations were chosen as follows: Burke–Ernzerhof (PBE) parametrization [24]. Electronic configurations were chosen as follows:
Ni, 3d⁹4s¹; Co, 3d⁸4s¹; B, 2s²2p¹; and O, 2s²2p⁴. The plane-wave cutoff was set at 400 eV. The size of the k-point mesh for the Brillouin zone, based on the Monkhorst–Pack scheme [\[25\]](#page-10-9), was $7 \times 5 \times 9$. The GGA+U calculations within the Dudarev's approach were performed by applying a Hubbard-like potential for d states of Fe [\[26\]](#page-10-10). $\,$

The lattice parameters and ion coordinates were optimized until the residual forces The lattice parameters and ion coordinates were optimized until the residual forces acting on the ions became less than 0.02 eV/A . In this case, the lattice parameters are determined with an accuracy of 10⁻⁵ and the coordinates of atoms up to 10^{-6} . The optimized lattice parameters for $\text{Ni}_{3-x}\text{Co}_{x}\text{B}_{2}\text{O}_{6}$ (x = 0, 1, 2, 3) are presented in [Tab](#page-1-1)le 1. Here, good agreement ment with the experimental data is observed with the difference being less than 2 percent. with the experimental data is observed with the difference being less than 2 percent.

Table 1. The calculated lattice parameters in comparison with the experimental data. **Table 1.** The calculated lattice parameters in comparison with the experimental data.

3. The Lattice Dynamics Calculations

The phonons were calculated by constructing a supercell (2 \times 2 \times 2) and calculating the force constants using the small displacement method implemented in PHONOPY [\[24\]](#page-10-8). The decomposition of the complete vibrational representation into irreducible representations at the center of the Brillouin zone has the following form [\[16\]](#page-10-1):

 $\Gamma = 8A_g + 8B_{1g} + 7B_{2g} + 7B_{3g} + 7A_u + 7B_{1u} + 11B_{2u} + 11B_{3u}$, including acoustic modes $B_{1u} + B_{2u} + B_{3u}$.

The calculated phonon frequencies for $Ni_{3-x}Co_xB_2O_6$ (x = 0, 1, 2, 3) are presented in Tables [2](#page-2-0) and [3.](#page-3-0) The experimental phonon frequencies of $Ni₃B₂O₆$ and $Co₃B₂O₆$ from [\[16,](#page-10-1)[17\]](#page-10-2) are also given in the tables for comparison.

Table 2. The calculated phonon frequencies (g-symmetry) for $\text{Ni}_{3\times}\text{Co}_{\text{x}}\text{B}_{2}\text{O}_{6}$ (x = 0, 1, 2, 3). The experimentally measured frequencies are presented for comparison.

Mode		$Co3B2O6$	$Co2NiB2O6$	$Ni2CoB2O6$		$Ni3B2O6$
	calc.	exp. [17]	calc.	calc.	calc.	exp. [16]
$\rm A_g$	218.823	205.6	220.277	233.985	234.541	238
	246.300	248.4	257.783	258.942	271.995	278
	314.787	304.8	329.223	337.229	351.245	351
	378.206	382.4	422.192	397.743	401.149	403
	647.449	661.7	630.713	655.072	662.172	681
	715.109	766	690.641	719.200	717.404	766
	897.375	912.1	890.618	898.151	896.602	912
	1233.794	1233.6	1243.923	1224.707	1235.202	1238
$\rm B_{1g}$	266.622		271.890	276.774	279.385	283
	276.010	275.2	285.502	295.481	305.040	310
	349.905	291.5	360.570	361.562	372.938	372
	396.303	335.2	403.110	410.896	412.032	415
	654.899		663.616	661.465	667.399	690
	717.897	669.3	720.375	721.263	719.727	777
	898.160	777	894.392	899.595	898.444	915
	1249.602		1248.000	1244.990	1255.120	1256
$\rm B_{2g}$	132.321		131.920	139.540	145.820	158
	172.158	160.9	173.819	191.752	192.945	205
	193.600		213.262	219.947	236.276	287
	291.116		297.232	317.036	325.069	337
	396.421	384.0	408.239	417.038	423.669	400
	560.903	569.7	557.106	568.877	566.685	553
	1126.315	1147.0	1123.931	1138.100	1127.122	1142
B_{3g}	143.602	136.4	142.851	157.678	159.502	151
	176.230	187.6	175.470	200.386	202.162	189
	259.677		278.456	273.387	291.196	231
	319.456		320.319	333.151	337.236	311
	357.962	346.3	379.684	394.317	399.470	421
	531.206		526.714	537.991	538.014	584
	1144.021	1164.8	1139.638	1153.140	1141.805	1128

The crystal structure of the kotoite contains triangle $BO₃$ groups. The frequencies of normal vibrations for an isolated $[BO₃]^{3−}$ anion are 672 cm⁻¹, 765 cm⁻¹, 939 cm⁻¹ and 1260 cm⁻¹ [\[27\]](#page-10-11). In [\[15\]](#page-10-0), the correlational analysis was carried out, showing that each Raman-active vibration of the free $BO₃$ group generates a Raman combination of mode in the crystal, either $(A_g + B_{1g})$ or $(B_{2g} + B_{3g})$, but each IR-active vibration transforms into either a combination mode $(B_{2u} + B_{3u})$ or a simple mode B_{1u} in the infrared spectrum of the crystal [\[28\]](#page-10-12). The IR spectrum data of $Co_2Ni(BO_3)_2$ and $CoNi_2(BO_3)_2$ are presented in $[4,5]$ $[4,5]$. The comparison of the IR spectrum data $[4,5]$ $[4,5]$ with the calculated frequencies of

	$Co3B2O6$		$Co2NiB2O6$	$Ni2CoB2O6$	$Ni3B2O6$	
	calc.	exp. [17]	calc.	calc.	calc.	exp. [16]
A_{u}	136.525		151.267	135.729	157.822	
	193.487		197.641	203.412	206.968	
	287.366		283.441	310.643	315.534	
	331.036		344.134	344.019	360.098	
	429.832		446.587	446.064	456.276	
	567.895		564.034	570.299	569.288	
	1251.491		1244.483	1259.358	1243.797	
B_{1u}	173.946	190.8	196.489	171.755	201.160	200
	301.179	256	316.769	328.449	341.500	340
	335.321	331.4	338.665	344.310	350.869	354
	492.831	480	505.480	503.554	509.944	513
	574.690	591.5	568.443	586.237	584.770	603
	1142.891	1225	1134.254	1158.111	1146.298	1146
	132.186		135.920	143.068	147.366	132
	182.147	136.1	188.568	197.522	203.151	208
	223.536	173.7	225.049	247.549	250.657	245
	286.862	236.4	309.861	321.309	331.670	342
	360.533	305	362.851	367.989	375.145	372
B_{2u}	367.425	375	383.006	395.053	390.782	420
	586.068	419.2	587.511	580.977	581.661	575
	658.254	633.3	661.597	667.164	668.771	691
	878.269	735.6	875.944	882.204	880.292	896
	1254.988		1252.457	1243.510	1249.699	1244
B_{3u}	118.508	116	122.188	128.424	130.064	149
	177.081	180	191.195	193.158	205.371	202
	230.118	224.4	233.636	240.343	246.192	255
	306.416	314.5	330.273	342.077	341.825	327
	350.095	352	354.441	363.642	372.059	375
	391.129	411	401.574	417.168	416.259	396
	582.917	620	585.225	582.322	583.819	611
	653.186	681.6	657.250	658.940	660.475	696
	879.610	898.9	877.406	880.845	878.720	
	1235.500	1278	1233.260	1232.042	1239.359	1252

Table 3. The calculated phonon frequencies (u-symmetry) for $\text{Ni}_{3\times}\text{Co}_{\text{x}}\text{B}_2\text{O}_6$ (x = 0, 1, 2, 3). The experimentally measured frequencies are presented for comparison.

Table 4. The comparison of the IR spectrum data [\[4](#page-9-6)[,5\]](#page-9-1) with the calculated frequencies of $\rm{Co_2Ni(BO_3)_2}$ and $\text{CoNi}_2(\text{BO}_3)_2$.

As one can see from Tables [1](#page-1-1) and [2,](#page-2-0) some frequencies are similar in all the compounds, while other frequencies differ by more than 40 cm⁻¹. The vibration frequencies associated with the movement of metal ions undergo the greatest changes. In Table 5, a part of the eigenvector of the B_{2u} mode is presented. As is shown in the table, the direction and amplitude of vibration are changed.

 \overline{B} (Bo3) 668 \overline{B} (Bo3) 668 \overline{B} (Bo3) 668 \overline{B} (Bo3) 668.99

Position	Ions	The Eigenvector of B_{2u} Mode		
		$Co_3B_2O_6$	$Ni3B2O6$	
B_{2u} (cm ⁻¹)		286.8	331.6	
	Co/Ni	(0.42) θ 0.04)	(0.34) θ 0.09)	
2a	Co/Ni	(0.42) $\overline{0}$ -0.04	(0.34) $\overline{0}$ -0.09	
	Co/Ni	(0.10) $\overline{0}$ -0.06	(0.16) $\overline{0}$ -0.05	
	Co/Ni	(0.10) θ 0.06)	$\overline{0}$ (0.16) 0.05)	
4f	Co/Ni	(0.10) $\overline{0}$ -0.06	(0.16) θ -0.05	
	Co/Ni	(0.10) θ 0.06)	θ (0.16) 0.05)	

Table 5. A part of the eigenvector of the B_{2u} mode.

Figure 2 sho[ws](#page-5-0) the dispersion curves of frequencies for $Co_2Ni(BO_3)_2$ (a) and $CoNi_2(BO_3)_2$ (b). In both compounds, there are no "soft" modes. The crystal structures of $\rm{Co_2Ni(BO_3)_2}$ and $\text{CoNi}_2(\text{BO}_3)_2$ are stable. The cause of appearance of new modes is not a structural phase transition.

Figure 2. *Cont*.

Figure 2. The dispersion curves of frequencies for $Co_2Ni(BO_3)_2$ (a) and $CoNi_2(BO_3)_2$ (b).

4. Raman Spectra of Co2NiB2O6 4. Raman Spectra of Co2NiB2O⁶ 4. Raman Spectra of Co2NiB2O6

A sample for the experimental study of polarized Raman spectra was grown using the "flux" method by E. Moshkina in the L. V. Kirensky Institute of Physics SB RAS. The technique was described in [\[29\]](#page-10-13). A single crystal of $Co_2NiB_2O_6$ is shown in Figure [3.](#page-5-1) The plane of the figure corresponds to the (110) crystallographic plane. plane of the figure corresponds to the (110) crystallographic plane. plane of the figure corresponds to the (110) crystallographic plane.

Figure 3. A single crystal of $Co₂NiB₂O₆$.

Polarized Raman spectra were obtained in backscattering geometry using a Horiba Jobin-Yvon T64000 triple spectrometer (Horiba, France) operating in the dispersion subtraction mode. The Spectra-Physics Excelsior-532-300-CDRH (Albany, NY, USA) 532 nm diode-pumped visible CW solid-state single-mode laser with a power of 3 mW applied to the sample was used as the excitation light source. The Raman spectra resolution using gratings with 1800 mm^{-1} grooves and 100 m slits was about 2 cm^{-1} . The micro-Raman system based on an Olympus BX41 microscope with a $50 \times$ objective lens $f = 1.2$ mm with the numerical aperture N.A. = 0.75 provides a focal spot 4 lm in diameter on the sample. The sample under investigation was a single crystal, approximately 3 mm in size, of optical quality with natural faceting that was free from defects or visible inclusions under the microscope (Figure 3). microscope (Figure 3). microscope (Figure [3\)](#page-5-1).

Two series of experiments were performed with parallel and cross-(parallel) polariza-
tion of the incident on decettered has no to the late may be denoted by an of the interaction not of the incident and scattered beams to study the angular dependence of the intensities of Raman spectra, using the backscattering geometry. The shift of the incidence point of tion of the incident and scattered beams to study the angular dependence of the intensities exciting radiation was no more than 2 μ m in a complete 2π revolution.

The angular dependences of the Raman spectra of the unoriented sample make it possible to assign the lines to irreducible representations of the corresponding space group. Different representations have different values of the observed maximum, and they are possible at various rotations angles of the angular dependences on the intensities of the Raman spectra (see Figure [4\)](#page-6-0). A detailed description of the experimental technique is provided in [\[30–](#page-10-14)[32\]](#page-10-15). The angular dependences allow observing all the lines in the spectra, including very closely located ones, especially if they have the intensity maximum at different angles. Figure [4a](#page-6-0),b present two regions of the angular dependence of Raman emerent angles. Figure The angular dependences of the Raman spectra of the unoriented sample make it The angular dependences of the Kaman spectra of the unoriented samp

point of exciting radiation was no more than 2 µm in a complete 2π revolution.

Figure 4. The angular dependence of the Raman spectra of Co₂NiB₂O₆ (a) low-wavenubers region (**b**) high-wavenumbers region. (**b**) high-wavenumbers region.

The strong modes are located near 400 cm $^{-1}$ and 900 cm $^{-1}$ (Figure 4). According [to](#page-6-0) the calculation, two modes of different symmetry (B_{1g}, B_{2g}) were calculated in the 400 cm⁻¹ region (Table 2). The cal[cu](#page-2-0)lation showed that in the 900 cm⁻¹ region, there are also two modes of different symmetry (A_g, B_{1g}) .

> Figure [5](#page-7-0) shows the calculated modes of the vibrational spectrum at 400 and 900 cm−¹ for the $Co₃B₂O₆$ crystal. Blue arrows indicate the vibrational directions. Oxygen atoms

are shown in red, cobalt atoms in dark pink and boron in light pink. In the 400 cm⁻¹ region, deformation modes were obtained in BO₃ where oxygen and boron atoms vibrate (Figure [5a](#page-7-0)). In Figure [5b](#page-7-0), vibrations of cobalt atoms are added to the BO₃ deformations. This vibrational mode can change when the cobalt atoms are replaced by nickel and changes brational mode can change when the cobalt atoms are replaced by nickel and changes during the magnetic transition. Stretching modes are observed in BO₃ around 900 cm⁻¹. Figure [5d](#page-7-0) shows how oxygen atoms are displaced toward boron atoms. Figure 5d shows how oxygen atoms are displaced toward boron atoms.

Figure 5. The forms of the vibrational modes of the Co₃B₂O₆ crystal near 400 and 900 cm⁻¹. (a) mode B_{1g} 396.3 cm⁻¹; (**b**) mode B_{2g} 396.4 cm⁻¹; (**c**) mode B_{1g} 898.2 cm⁻¹; (**d**) mode A_{1g} 897.4 cm⁻¹.

The comparison of the experimental Raman spectra of $Ni₃B₂O₆$ and $Co₂NiB₂O₆$ in the parallel polarizer–analyzer configuration is presented in Figure [6.](#page-8-0) Here, the angle 0° denotes the initial position of the crystal and that of 90° denotes the position where the crystal is rotated by 90◦ around the axis of the incident light direction.

The spectra of the compounds $Ni_3B_2O_6$ and $Co_2NiB_2O_6$ are very similar. The vibrations of 916 cm−¹ , corresponding to B-O stretching, are almost identical (Figure [6b](#page-8-0)), but the deformation of $BO₃$ with B in the plane demonstrates a slight difference (Figure [6a](#page-8-0)). In $Ni₃B₂O₆$ the lengths of the B-O bonds are 1.35, 1.39 and 1.39 Å, while in Co₂NiB₂O₆, all the B-O bonds are almost equal: 1.38, 1.39 and 1.39 Å. In $Co₃B₂O₆$, the BO₃ group is more distorted. The lengths of the B-O bonds are 1.41, 1.36 and 1.36 Å. The comparison of the measured Raman spectrum data [\[4](#page-9-6)[,5\]](#page-9-1) with the calculated frequencies of $Co₂Ni(BO₃)₂$ is presented in Table [6.](#page-8-1) One can observe good agreement between the theoretical and experimental data for both IR and Raman spectra.

In the low-wavelength region, we observe significant differences in the positions of the Raman lines (Figure [6a](#page-8-0)). This is due to the metal ions being involved in these vibrations. The black dashed line in Figure [6](#page-8-0) denotes the calculated frequencies of $Co₂NiB₂O₆$. Here, good agreement between the theoretical and experimental results is observed.

Figure 6. The comparison of the experimental Raman spectra of $Ni₃B₂O₆$ and Co₂NiB₂O₆ in the parallel polarizer-analyzer configuration. (a) 100–500 cm $^{-1}$, (b) 500–1300 cm $^{-1}$. The angle 0 $^{\circ}$ denotes the initial position and 90° denotes the position of the crystal rotated by 90° to the incident light polarization.

Table 6. The comparison of the Raman spectrum data [\[4,](#page-9-6)[5\]](#page-9-1) with the calculated frequencies of Co-Ni(BO_2) deformation of BO3 with B in the plane demonstrates a slight difference (Figure 6a). In the plane demonstrates a slight difference (Figure 6a). In the plane demonstrates a slight difference (Figure 6a). In the plane demon $Co₂Ni(BO₃)₂$.

	$Co2Ni(BO3)2$		
The Vibrations of $BO3$ Group	exp.	calc.	
$v_1(BO_3)$	916	890.6	
$v_1(BO_3)$	912	894.4	
$v_2(BO_3)$	767	690.6	
$v_2(BO_3)$	779	720.4	
$v_3(BO_3)$	1130	1123.9	
$v_3(BO_3)$	1155	1139.6	
$v_3(BO_3)$	1238	1243.9	

5. Conclusions

The theoretical study of the lattice dynamics of the $\text{Ni}_{3-x}\text{Co}_{x}\text{B}_{2}\text{O}_{6}$ solid solutions for $x = 0$, 1, 2, 3 was carried out in the VASP code. The experimental Raman spectra at the center of the Brillouin zone for $Co_2NiB_2O_6$ were obtained. The theoretical and experimental data are observed to be in good agreement. The spectra of the compounds $Ni₃B₂O₆$, $Co₃B₂O₆$, $Ni₂CoB₂O₆$ and $Co₂NiB₂O₆$ are very similar. The phonon spectra contain the modes which correspond to the $BO₃$ vibration group with the calculated and experimental (IR and Raman) modes being in good agreement. The most significant differences in the positions of the Raman lines are observed in the low-wavelength region, where the vibrations involve transition metal ions. The simulation of the lattice dynamics of the solid solutions showed the decreasing temperature; these compounds should not experience phase transitions, because unstable modes (soft modes) were not obtained.

The study of the lattice dynamics of the four compounds helped us to establish that the solid solution structures are stable and to determine the general trends in the substitution of nickel for cobalt. However, in order to understand the processes in the antiferromagnetic transition, low-temperature studies should be carried out. Therefore, we plan to perform low temperature Raman studies of the oxyborates and evaluate the effect of nickel substitution for cobalt on the antiferromagnetic transition.

Author Contributions: Conceptualization, S.N.S. and A.S.K.; methodology, A.S.K., M.S.P. and S.N.K.; funding, S.N.S.; writing draft, S.N.S. and A.S.K.; writing, A.N.V. and S.N.K.; software S.N.K., A.N.V. and M.S.P.; formal analysis, S.N.S. and M.S.P.; investigation, A.S.K.; data curation, S.N.K. and A.N.V.; writing—review and editing, A.S.K. and S.N.K.; visualization, S.N.S., S.N.K. and A.S.K.; supervision, S.N.S.; project administration, S.N.S. All authors have read and agreed to the published version of the manuscript.

Funding: The research was supported by Russian Science Foundation and Krasnoyarsk Regional Science Foundation, project № 23-12-20012 [\(https://rscf.ru/en/project/23-12-20012/,](https://rscf.ru/en/project/23-12-20012/) accessed on 13 November 2024).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The experimental investigations were carried out in the Center for Collective Use of the Krasnoyarsk Regional Center of Research Equipment of Federal Research Center "Krasnoyarsk Science Center SB RAS".

Conflicts of Interest: The authors declare no conflicts of interest.

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