



# Article Lattice Dynamics of Ni<sub>3-x</sub>Co<sub>x</sub>B<sub>2</sub>O<sub>6</sub> 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  $NiCo_2B_2O_6$  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 Ni<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and Co<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and solid solutions of Ni<sub>3-x</sub>Co<sub>x</sub>B<sub>2</sub>O<sub>6</sub> were obtained in the 1990s [1-5]. These compounds are interesting both from the fundamental point of view and as promising anode materials for lithium-ion and sodium-ion batteries [6]. The compounds  $Ni_3B_2O_6$  and  $Co_3B_2O_6$  are antiferromagnets, but their easy axis of magnetization is different [7,8]. 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 [9-15]. 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  $Ni_3B_2O_6$  shows several new phonon modes to appear at the antiferromagnetic ordering temperature [16]. In  $Co_3B_2O_6$ , such effects are not observed [17]. 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<sub>3-x</sub>Co<sub>x</sub>B<sub>2</sub>O<sub>6</sub> 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 [18-20]. 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 Ni<sub>2</sub>CoB<sub>2</sub>O<sub>6</sub> and Co<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub> solid solutions and an experimental study of the Raman spectra of Co<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub>.

## 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). The unit cell of kotoite contains six transition



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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 BO<sub>3</sub> group. In the solid solutions Ni<sub>2</sub>CoB<sub>2</sub>O<sub>6</sub> and NiCo<sub>2</sub>B<sub>2</sub>O<sub>6</sub>, nickel and cobalt ions can randomly occupy both positions (2a and 4f). Lattice dynamics have been calculated for the cation ordered state. In Ni<sub>2</sub>CoB<sub>2</sub>O<sub>6</sub>, the cobalt ions occupy the 2a crystallographic position, while the nickel ions occupy the 4f position. In NiCo<sub>2</sub>B<sub>2</sub>O<sub>6</sub>, the cobalt ions occupy the 4f crystallographic position, while the nickel ions occupy the 2a position.



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

The first-principles calculations were carried out using the projector-augmented wave (PAW) method [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) parametrization [24]. Electronic configurations were chosen as follows: Ni,  $3d^94s^1$ ; Co,  $3d^84s^1$ ; B,  $2s^22p^1$ ; and O,  $2s^22p^4$ . 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], 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].

The lattice parameters and ion coordinates were optimized until the residual forces acting on the ions became less than 0.02 eV/Å. 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 Ni<sub>3-x</sub>Co<sub>x</sub>B<sub>2</sub>O<sub>6</sub> (x = 0, 1, 2, 3) are presented in Table 1. Here, good agreement 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.

Compounds		a (Å)	b (Å)	c (Å)
Co <sub>3</sub> B <sub>2</sub> O <sub>6</sub> -	exp. [16]	4.5290	5.4620	8.4360
	calc.	4.4956	5.4594	8.4071
NiCo <sub>2</sub> B <sub>2</sub> O <sub>6</sub> –	exp. [4]	4.504 (1)	5.444 (8)	8.404 (0)
	calc.	4.4814	5.3946	8.4098
Ni <sub>2</sub> CoB <sub>2</sub> O <sub>6</sub> –	exp. [5]	4.478 (8)	5.419 (9)	8.352 (0)
	calc.	4.4905	5.3686	8.2444
Ni <sub>3</sub> B <sub>2</sub> O <sub>6</sub> –	exp. [15]	4.459	5.396	8.297
	calc.	4,4480	5.3484	8.2667

#### 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]. The decomposition of the complete vibrational representation into irreducible representations at the center of the Brillouin zone has the following form [16]:

 $\Gamma = 8A_g + 8B_{1g} + 7B_{2g} + 7B_{3g} + 7A_u + 7B_{1u} + 11B_{2u} + 11B_{3u}$ , 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 and 3. The experimental phonon frequencies of  $Ni_3B_2O_6$  and  $Co_3B_2O_6$  from [16,17] are also given in the tables for comparison.

**Table 2.** The calculated phonon frequencies (g-symmetry) for  $Ni_{3-x}Co_xB_2O_6$  (x = 0, 1, 2, 3). The experimentally measured frequencies are presented for comparison.

Mode	Co <sub>3</sub> I	$B_2O_6$	Co <sub>2</sub> NiB <sub>2</sub> O <sub>6</sub>	Ni <sub>2</sub> CoB <sub>2</sub> O <sub>6</sub>	Ni <sub>3</sub> l	B <sub>2</sub> O <sub>6</sub>
	calc.	exp. [17]	calc.	calc.	calc.	exp. [16]
	218.823	205.6	220.277	233.985	234.541	238
	246.300	248.4	257.783	258.942	271.995	278
٨	314.787	304.8	329.223	337.229	351.245	351
	378.206	382.4	422.192	397.743	401.149	403
Ag	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
	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
B1.	396.303	335.2	403.110	410.896	412.032	415
D <sub>1g</sub>	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
	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
B <sub>2g</sub>	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 <sub>3g</sub>	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 BO<sub>3</sub> groups. The frequencies of normal vibrations for an isolated  $[BO_3]^{3-}$  anion are 672 cm<sup>-1</sup>, 765 cm<sup>-1</sup>, 939 cm<sup>-1</sup> and 1260 cm<sup>-1</sup> [27]. In [15], the correlational analysis was carried out, showing that each Raman-active vibration of the free BO<sub>3</sub> group generates a Raman combination of mode in the crystal, either (A<sub>g</sub> + B<sub>1g</sub>) or (B<sub>2g</sub> + B<sub>3g</sub>), but each IR-active vibration transforms into either a combination mode (B<sub>2u</sub> + B<sub>3u</sub>) or a simple mode B<sub>1u</sub> in the infrared spectrum of the crystal [28]. The IR spectrum data of Co<sub>2</sub>Ni(BO<sub>3</sub>)<sub>2</sub> and CoNi<sub>2</sub>(BO<sub>3</sub>)<sub>2</sub> are presented in [4,5]. The comparison of the IR spectrum data [4,5] with the calculated frequencies of

	Co <sub>3</sub> I	B <sub>2</sub> O <sub>6</sub>	Co <sub>2</sub> NiB <sub>2</sub> O <sub>6</sub>	Ni <sub>2</sub> CoB <sub>2</sub> O <sub>6</sub>	Ni <sub>3</sub> l	B <sub>2</sub> O <sub>6</sub>
	calc.	exp. [17]	calc.	calc.	calc.	exp. [16]
	136.525		151.267	135.729	157.822	
	193.487		197.641	203.412	206.968	
	287.366		283.441	310.643	315.534	
Au	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	
	173.946	190.8	196.489	171.755	201.160	200
	301.179	256	316.769	328.449	341.500	340
B.	335.321	331.4	338.665	344.310	350.869	354
$D_{1u}$	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
Ba	360.533	305	362.851	367.989	375.145	372
$D_{2u}$	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
	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
Ba	350.095	352	354.441	363.642	372.059	375
D3u	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  $Ni_{3-x}Co_xB_2O_6$  (x = 0, 1, 2, 3). The experimentally measured frequencies are presented for comparison.

**Table 4.** The comparison of the IR spectrum data [4,5] with the calculated frequencies of  $Co_2Ni(BO_3)_2$  and  $CoNi_2(BO_3)_2$ .

The Vibrations	Co <sub>2</sub> Ni(BO <sub>3</sub> ) <sub>2</sub>		CoNi <sub>2</sub> (BO <sub>3</sub> ) <sub>2</sub>	
of BO <sub>3</sub> Group	exp. [4]	calc.	exp. [5]	calc.
v <sub>3</sub> (BO <sub>3</sub> )	1255	1233,3	1253	1232.0
v <sub>3</sub> (BO <sub>3</sub> )	1170	1134,3	1180	1158.1
v <sub>2</sub> (BO <sub>3</sub> )	707	661,6	712	667.2
v <sub>2</sub> (BO <sub>3</sub> )	668	657,3	688	658.9
$v_4(BO_3)$	615	585,2	622	582.3

As one can see from Tables 1 and 2, some frequencies are similar in all the compounds, while other frequencies differ by more than 40 cm<sup>-1</sup>. 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.

Position	Ions	The Eigenvector of B <sub>2u</sub> Mode		
		$Co_3B_2O_6$	Ni <sub>3</sub> B <sub>2</sub> O <sub>6</sub>	
B <sub>2u</sub> (cm <sup>-1</sup> )		286.8	331.6	
0.	Co/Ni	(0.42 0 0.04)	(0.34 0 0.09)	
Za	Co/Ni	(0.42 0 -0.04)	(0.34 0 -0.09)	
	Co/Ni	(0.10 0 -0.06)	(0.16 0 -0.05)	
16	Co/Ni	(0.10 0 0.06)	(0.16 0 0.05)	
4t	Co/Ni	(0.10 0 -0.06)	(0.16 0 -0.05)	
	Co/Ni	(0.10 0 0.06)	(0.16 0 0.05)	

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

Figure 2 shows 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  $Co_2Ni(BO_3)_2$  and  $CoNi_2(BO_3)_2$  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<sub>2</sub>Ni(BO<sub>3</sub>)<sub>2</sub> (a) and CoNi<sub>2</sub>(BO<sub>3</sub>)<sub>2</sub> (b).

## 4. Raman Spectra of Co<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub>

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]. A single crystal of  $Co_2NiB_2O_6$  is shown in Figure 3. The plane of the figure corresponds to the (110) crystallographic plane.



**Figure 3.** A single crystal of Co<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub>.

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<sup>-1</sup> grooves and 100 m slits was about 2 cm<sup>-1</sup>. The micro-Raman system based on an Olympus BX41 microscope with a 50× 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).

Two series of experiments were performed with parallel and cross-(parallel) polarization 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 exciting radiation was no more than 2  $\mu$ m in a complete 2 $\pi$  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). A detailed description of the experimental technique is provided in [30–32]. 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,b present two regions of the angular dependence of Raman spectra of  $Co_2NiB_2O_6$ .



**Figure 4.** The angular dependence of the Raman spectra of  $Co_2NiB_2O_6$  (**a**) low-wavenubers region (**b**) high-wavenumbers region.

The strong modes are located near 400 cm<sup>-1</sup> and 900 cm<sup>-1</sup> (Figure 4). According to the calculation, two modes of different symmetry ( $B_{1g}$ ,  $B_{2g}$ ) were calculated in the 400 cm<sup>-1</sup> region (Table 2). The calculation showed that in the 900 cm<sup>-1</sup> region, there are also two modes of different symmetry ( $A_g$ ,  $B_{1g}$ ).

Figure 5 shows the calculated modes of the vibrational spectrum at 400 and 900 cm<sup>-1</sup> for the Co<sub>3</sub>B<sub>2</sub>O<sub>6</sub> 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<sup>-1</sup> region, deformation modes were obtained in BO<sub>3</sub> where oxygen and boron atoms vibrate (Figure 5a). In Figure 5b, vibrations of cobalt atoms are added to the BO<sub>3</sub> deformations. This vibrational mode can change when the cobalt atoms are replaced by nickel and changes during the magnetic transition. Stretching modes are observed in BO<sub>3</sub> around 900 cm<sup>-1</sup>. Figure 5d shows how oxygen atoms are displaced toward boron atoms.



**Figure 5.** The forms of the vibrational modes of the  $Co_3B_2O_6$  crystal near 400 and 900 cm<sup>-1</sup>. (**a**) mode  $B_{1g}$  396.3 cm<sup>-1</sup>; (**b**) mode  $B_{2g}$  396.4 cm<sup>-1</sup>; (**c**) mode  $B_{1g}$  898.2 cm<sup>-1</sup>; (**d**) mode  $A_{1g}$  897.4 cm<sup>-1</sup>.

The comparison of the experimental Raman spectra of  $Ni_3B_2O_6$  and  $Co_2NiB_2O_6$  in the parallel polarizer–analyzer configuration is presented in Figure 6. 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<sup>-1</sup>, corresponding to B-O stretching, are almost identical (Figure 6b), but the deformation of BO<sub>3</sub> with B in the plane demonstrates a slight difference (Figure 6a). In  $Ni_3B_2O_6$  the lengths of the B-O bonds are 1.35, 1.39 and 1.39 Å, while in  $Co_2NiB_2O_6$ , all the B-O bonds are almost equal: 1.38, 1.39 and 1.39 Å. In  $Co_3B_2O_6$ , the BO<sub>3</sub> 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 [4,5] with the calculated frequencies of  $Co_2Ni(BO_3)_2$ is presented in Table 6. 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). This is due to the metal ions being involved in these vibrations. The black dashed line in Figure 6 denotes the calculated frequencies of  $Co_2NiB_2O_6$ . Here, good agreement between the theoretical and experimental results is observed.



**Figure 6.** The comparison of the experimental Raman spectra of  $Ni_3B_2O_6$  and  $Co_2NiB_2O_6$  in the parallel polarizer–analyzer configuration. (a) 100–500 cm<sup>-1</sup>, (b) 500–1300 cm<sup>-1</sup>. The angle 0° 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 [4,5] with the calculated frequencies of  $Co_2Ni(BO_3)_2$ .

The Vibrations of BO. Crown	Co <sub>2</sub> Ni(BO <sub>3</sub> ) <sub>2</sub>		
	exp.	calc.	
$v_1(BO_3)$	916	890.6	
$v_1(BO_3)$	912	894.4	
υ <sub>2</sub> (BO <sub>3</sub> )	767	690.6	
υ <sub>2</sub> (BO <sub>3</sub> )	779	720.4	
υ <sub>3</sub> (BO <sub>3</sub> )	1130	1123.9	
υ <sub>3</sub> (BO <sub>3</sub> )	1155	1139.6	
υ <sub>3</sub> (BO <sub>3</sub> )	1238	1243.9	

### 5. Conclusions

The theoretical study of the lattice dynamics of the Ni<sub>3-x</sub>Co<sub>x</sub>B<sub>2</sub>O<sub>6</sub> 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<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub> were obtained. The theoretical and experimental data are observed to be in good agreement. The spectra of the compounds Ni<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, Co<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, Ni<sub>2</sub>CoB<sub>2</sub>O<sub>6</sub> and Co<sub>2</sub>NiB<sub>2</sub>O<sub>6</sub> are very similar. The phonon spectra contain the modes which correspond to the BO<sub>3</sub> 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.

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