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Incommensurately modulated structure of morpholinium tetrafluoroborate and configurational *versus* chemical entropies at the incommensurate and lock-in phase transitions

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The incommensurate phase at $T = 130$ K

The structure model for the incommensurate phase (phase II) at $T = 130$ K incorporates atomic coordinates and atomic displacement parameters (ADPs) for the atoms of the morpholinium anion (Tables S1 and S2) and atomic coordinates for a single $[BF_4]^-$ ion (Table S3). Furthermore, it contains parameters describing the orientation, position and occupation of each of two orientations (Ma and Mb) of the $[BF_4]^-$ ion, as well as their ADPs within the TLS formalism (Tables S4 and S5). Two more orientations are generated by symmetry. Most of the parameters are modulated. The structure refinement has resulted in a good match between observed and calculated structure factors (Fig. S1).

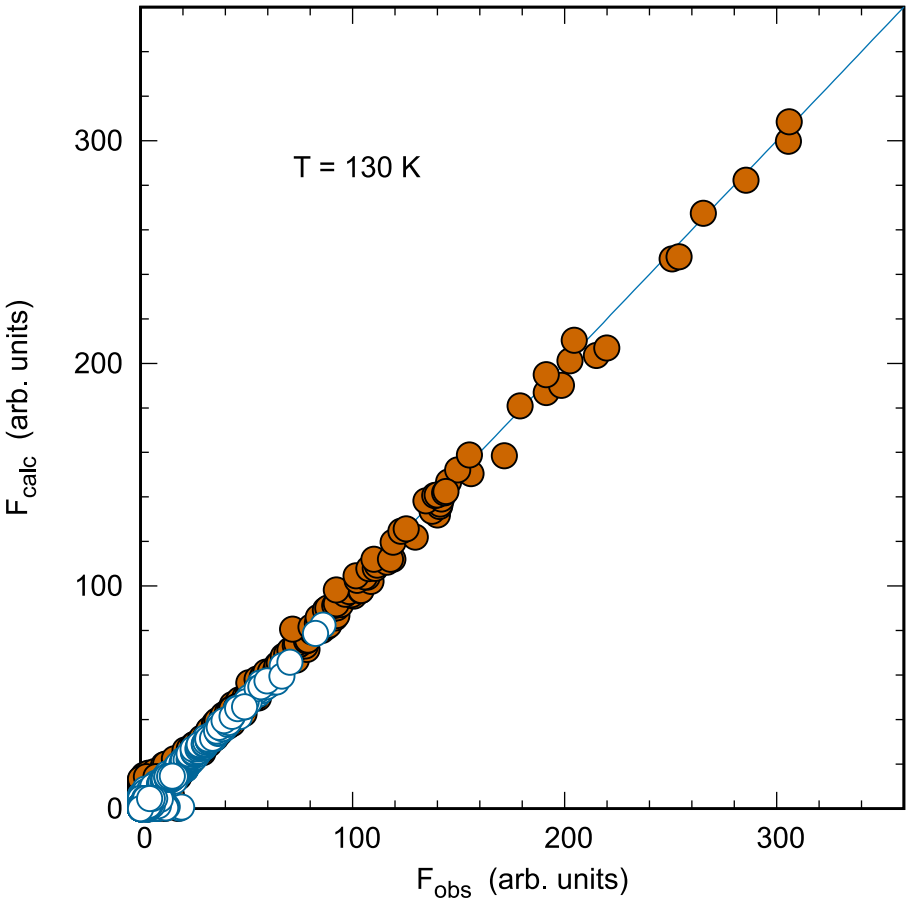

Figure S1: Plot of calculated *vs* observed structure factors for the final structure model at $T = 130$ K. Red circles represent main refections; white circles represent satellite reflections.

Table S1: Fractional atomic coordinates x, y, z and the equivalent isotropic ADP (U_{iso}) of the basic structure, together with the first-order harmonic parameters describing displacive modulation. For each atom is given the basic-structure coordinates (first line), sine coefficients of the modulation function (s,1), and cosine coefficients (c,1). Values of the parameters of the atoms B1a–F4b of the two orientations, Ma and Mb, of the $[BF_4]^-$ molecule have been obtained by transformation of the refined pseudo-rigid-body parameters (see Tables S4 and S5). Standard uncertainties are given in parentheses.

Atom		x	y	z	U_{iso}
O1		0.03326(8)	0.76034(6)	0.25	0.03003(19)
	s,1	0	0	0.01918(9)	
	c,1	0	0	-0.01460(8)	
N1		0.26956(7)	0.53856(5)	0.25	0.0238(2)
	s,1	0	0	0.01582(8)	
	c,1	0	0	-0.00039(8)	
C1		0.12672(7)	0.72981(6)	0.37320(6)	0.03110(19)
	s,1	-0.00815(7)	-0.00623(7)	0.01779(8)	
	c,1	-0.00769(7)	0.00799(7)	-0.01218(8)	
C2		0.17310(7)	0.57458(6)	0.37769(5)	0.02729(17)
	s,1	-0.00942(7)	-0.00588(7)	0.01197(6)	
	c,1	-0.00769(7)	0.00899(7)	-0.00257(7)	
H1c		0.2935	0.4431	0.25	0.035634
	s,1	0	0	0.0152	
	c,1	0	0	0.0066	
H2b		0.239	0.5565	0.4591	0.032749
	s,1	-0.0173	-0.0069	0.0147	
	c,1	-0.0099	0.0154	-0.0011	
H2a		0.0748	0.5178	0.3807	0.032749
	s,1	-0.0073	-0.0082	0.0048	
	c,1	-0.0104	0.0077	-0.0019	
H1d		0.367	0.5887	0.25	0.035634
	s,1	0	0	0.022	
	c,1	0	0	-0.0074	
H1b		0.0625	0.7531	0.4543	0.037326
	s,1	-0.0111	-0.0124	0.0185	
	c,1	-0.0152	0.011	-0.0137	
H1a		0.225	0.7867	0.374	0.037326
	s,1	-0.0098	-0.0041	0.0214	
	c,1	-0.0051	0.009	-0.0176	
B1a		0.1760(9)	0.1454(7)	0.2623(5)	0.0262(17)
	s,1	0.0003(8)	0.0005(6)	0.0087(5)	
	c,1	-0.0053(8)	-0.0023(7)	0.0011(6)	
F1a		0.2321(13)	0.2578(10)	0.3422(9)	0.039(3)
	s,1	-0.0119(13)	0.0008(9)	0.0137(9)	
	c,1	-0.0038(14)	-0.0004(10)	-0.0036(10)	
F2a		0.3049(11)	0.0576(10)	0.2264(8)	0.042(3)
	s,1	0.0065(11)	0.0089(10)	0.0076(10)	
	c,1	-0.0076(11)	-0.0055(11)	-0.0007(11)	
F3a		0.0601(12)	0.0705(10)	0.3387(11)	0.040(3)
	s,1	0.0059(11)	-0.0090(11)	0.0026(9)	
	c,1	-0.0023(12)	-0.0044(12)	0.0043(10)	
F4a		0.0999(13)	0.1976(12)	0.1440(7)	0.061(3)
	s,1	0.0000(12)	0.0015(11)	0.0092(7)	
	c,1	-0.0071(13)	-0.0050(12)	0.0024(8)	
B1b		0.1542(4)	0.1250(2)	0.2631(4)	0.0220(6)
	s,1	-0.0003(3)	-0.0012(2)	0.0021(3)	
	c,1	0.0007(4)	0.0039(3)	0.0008(3)	
F1b		0.298(3)	0.047(4)	0.2510(12)	0.0351(15)
	s,1	0.0014(5)	0.0022(5)	0.0025(5)	
	c,1	-0.0019(5)	0.0025(5)	-0.0126(6)	
F2b		0.0646(19)	0.118(3)	0.1411(10)	0.0432(15)
	s,1	0.0020(5)	-0.0134(6)	0.0012(4)	
	c,1	-0.0018(5)	0.0175(6)	0.0017(5)	
F3b		0.062(3)	0.071(3)	0.3728(11)	0.0257(15)
	s,1	-0.0006(5)	0.0040(5)	0.0046(5)	
	c,1	0.0018(5)	-0.0072(6)	-0.0032(5)	
F4b		0.194(5)	0.2638(19)	0.2943(12)	0.0498(16)
	s,1	-0.0040(5)	0.0010(4)	-0.0022(6)	
	c,1	0.0048(6)	-0.0006(5)	0.0169(6)	

Table S2: Anisotropic atomic displacement parameters (anisotropic ADPs) U_{ij} (Å^2) of the non-hydrogen atoms. Values of the parameters of the atoms B1a–F4b of the two orientations, Ma and Mb, of the $[BF_4]^-$ molecule have been obtained by transformation of the TLS parameters of the pseudo-rigid-body model. Standard uncertainties are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0273(3)	0.0225(3)	0.0403(4)	0.0070(2)	0	0
N1	0.0228(4)	0.0139(3)	0.0346(4)	0.0002(2)	0	0
C1	0.0326(4)	0.0250(3)	0.0358(3)	0.0039(2)	-0.0019(3)	-0.0079(2)
C2	0.0319(3)	0.0243(3)	0.0256(3)	0.0005(2)	-0.0023(2)	-0.0003(2)
B1a	0.012(3)	0.035(3)	0.031(3)	0.0059(16)	-0.0047(18)	-0.0092(17)
F1a	0.055(7)	0.020(4)	0.041(6)	-0.016(4)	-0.002(4)	0.004(4)
F2a	0.034(4)	0.041(5)	0.050(7)	0.022(4)	0.015(4)	0.011(4)
F3a	0.021(5)	0.042(6)	0.057(6)	-0.017(4)	0.007(4)	-0.029(4)
F4a	0.074(6)	0.072(7)	0.038(4)	0.050(5)	-0.019(4)	-0.014(4)
B1b	0.0256(10)	0.0141(10)	0.0263(13)	-0.0017(6)	-0.0011(7)	0.0008(8)
F1b	0.0259(18)	0.028(3)	0.051(3)	0.0027(19)	-0.001(2)	-0.005(2)
F2b	0.039(2)	0.071(3)	0.020(2)	0.011(2)	-0.0007(19)	0.0016(19)
F3b	0.033(3)	0.022(3)	0.022(2)	-0.002(2)	-0.002(2)	0.003(2)
F4b	0.049(3)	0.0148(19)	0.086(3)	-0.0101(18)	0.013(3)	-0.005(2)

Table S3: Fractional coordinates of the atoms of the single $[BF_4]^-$ molecule of the structure of phase II at $T = 130$ K. Standard uncertainties are given in parentheses.

Atom	x	y	z
B1	0	0	0
F1	0.0560(9)	0.1124(6)	0.0799(8)
F2	0.1288(7)	-0.0878(7)	-0.0359(7)
F3	-0.1160(8)	-0.0749(8)	0.0764(9)
F4	-0.0761(10)	0.0522(10)	-0.1183(4)

Table S4: Basic-structure parameters and modulation functions for translation and rotation of the two $[BF_4]^-$ ions, Ma and Mb, within the pseudo-rigid-body model at $T = 130$ K. Molecular rotations (angles ϕ, χ and ψ) and their harmonic modulation amplitudes (sine coefficients s,1; cosine coefficients, c,1) are given in degree. Molecular translations (x_{trans}, y_{trans}, z_{trans}) and their harmonic modulation amplitudes are given as relative coordinates. Standard uncertainties are given in parentheses.

Molecule		ϕ	χ	ψ	x_{trans}	y_{trans}	z_{trans}
Ma		0	0	0	0.1760(9)	0.1454(7)	0.2623(5)
	s,1	0.0049(7)	-0.0021(6)	0.0077(7)	0.0003(8)	0.0005(6)	0.0087(5)
	c,1	-0.0025(9)	0.0009(7)	0.0007(8)	-0.0053(8)	-0.0023(7)	0.0011(6)
Mb		-67.7(14)	72.2(4)	16.4(13)	0.1542(4)	0.1250(2)	0.2631(4)
	s,1	-0.0031(3)	-0.0048(5)	0.0014(2)	-0.0019(4)	-0.0002(3)	0.0017(2)
	c,1	0.0032(4)	0.0127(5)	-0.0014(3)	-0.0021(4)	0.0011(3)	-0.0034(3)

Table S5: Parameters for occupation fractions of the molecular orientations Ma and Mb, along with their harmonic occupational modulation functions. Values are given for individual atoms, as they have been obtained by transformation of the pseudo-rigid-body model. Given are the average occupancy [$P^0(\mu)$] and the sine [$P^s(\mu)$] and cosine [$P^c(\mu)$] amplitudes of the harmonic modulation functions.

Atom	$P^0(\mu)$	$P^s(\mu)$	$P^c(\mu)$
B1a	0.183	0.1482	-0.1243
F1a	0.183	0.165	-0.101
F2a	0.183	0.1813	-0.0675
F3a	0.183	0.1036	-0.1634
F4a	0.183	0.1203	-0.1515
B1b	0.317	0.1462	-0.1437
F1b	0.317	0.1892	-0.079
F2b	0.317	0.1083	-0.174
F3b	0.317	0.1072	-0.1747
F4b	0.317	0.1604	-0.1276

Rigid body refinement of the crystal structure at 160 K

The crystal structure of phase I at $T = 160$ K has been refined against X-ray diffraction data measured on the same crystal as that which has been used for structural analysis of the incommensurate structure of phase II at $T = 130$ K.

X-ray diffraction data have been measured on a 2-circle MAR345 imaging-plate diffractometer. The crystal was kept at a temperature of $T = 160$ K employing an open flow nitrogen cryostat by Oxford Cryosystems. The procedure of measurement was similar to that followed for the data measured at $T = 130$ K, except that for 160 K only a single run at $2\theta_{\text{offset}} = 0$ deg has been measured (Table S6). The software EVAL15 [2] was used for indexing and determination of integrated intensities of Bragg reflections. All Bragg reflections could be indexed on a primitive orthorhombic lattice (Table S6). The integrated intensities were scaled and absorption correction was applied by the software SADABS [3], employing point group mmm defining equivalent reflections.

An initial structure refinement has been performed of the model reported by [4] against the presently measured data. Within this model disorder of $[BF_4]^-$ is described by employing two positions for B and seven positions for F, all of which atoms were independently refined. Therefore, we call this the atomic model. A good fit to the diffraction data has been obtained (Table S6).

In an alternative approach, disorder of $[BF_4]^-$ is described by a single molecule $[BF_4]^-$ that is placed in two orientations/positions (Ma and Mb). The orientations and positions of Ma and Mb have been independently refined (Table S7). Thermal motion is described by independent TLS parameters for Ma and Mb. Symmetry generates two more orientations (Ma′ and Mb′), resulting in a description of the

Table S6: Crystal data and refinement details

	Rigid body model	Atomic model[a]
Temperature (K)	160	
Chemical formula	$C_4NOH_{10}\ BF_4$	
Formula weight	174.93	
Space group	$Pnam$	
a (Å)	8.13100(12)	
b (Å)	9.40719(22)	
c (Å)	9.58445(29)	
V (Å^3)	733.11(3)	
Z	4	
D_{calc} ($g\,cm^{-3}$)	1.5849	
Crystal color	Colorless	
Radiation type	Mo-Kα	
Wavelength (Å)	0.71069	
Scan mode	ϕ	
Theta range (deg)	3.03 to 39.09	
Range of h	-10 to 10	
Range of k	-13 to 16	
Range of l	-17 to 16	
μ (mm^{-1})	0.173	
Absorption corr.	SADABS	
T_{min}, T_{max}	0.4473, 0.7477	
No. of reflections		
Measured	13271	
Independent	1797	
Observed	997	
$R_{int}(obs, all)$ averaged in mmm	4.41, 5.31	
Criterion for observed reflections	$I > 3\sigma(I)$	
Refinement, Software	on F, JANA2006	
GOF^{obs},GOF^{all}	3.14, 2.44	3.14, 2.43
R_F^{obs}, wR_F^{all}	0.0495, 0.0690	0.0473, 0.0685
No. of parameters	93	111
$\Delta\rho_{max}$, $\Delta\rho_{min}$(e Å^{-3})	0.26, -0.30	0.34, -0.29

[a]Refinement of the model of [4] against the data measured in Bayreuth.

Table S7: Rotational and translational parameters defining the orientations/positions Ma and Mb of the molecule $[BF_4]^-$ in the pseudo-rigid-body approach to the structure at $T = 160$ K.

Molecule	ϕ	χ	ψ	x_{trans}	y_{trans}	z_{trans}
Ma	0	0	0	0.1760(14)	0.1503(14)	0.2613(11)
Mb	-77.5(11)	50.8(6)	5.1(9)	0.1539(9)	0.1233(6)	0.2354(8)

Table S8: Fractional atomic coordinates of the boron and fluor atoms defining the pseudo-rigid-body $[BF_4]^-$ in the structure at $T = 160$ K. Standard uncertainties are given in parentheses.

Atom	x	y	z
B1	0	0	0
F1	0.0575(19)	0.1103(14)	0.0799(17)
F2	0.1238(14)	-0.0942(14)	-0.0316(13)
F3	-0.1226(19)	-0.0701(15)	0.071(2)
F4	-0.059(3)	0.0529(19)	-0.1239(9)

disorder by four orientations. This description is completely equivalent to the description employed for the average structure of the incommensurate phase II (Section 2.2). Refinement of the pseudo-rigid-body model for the structure at $T = 160$ K furthermore incorporated atomic coordinates for the single molecule $[BF_4]^-$ (Table S8), and atomic coordinates and anisotropic atomic displacement parameters (ADPs) for the non-hydrogen atoms of the morpholinium moiety (Table S9). Similar orientations have been found for Ma and Mb in phases I and II (compare Tables S3 and S8 as well as Tables S4 and S7).

Employing JANA2006 [1], the positions have been refined of all atoms of the morpholinium and the $[BF_4]^-$ molecules, of the parameters defining two independent orientations, Ma and Mb, of the $[BF_4]^-$ molecule, and of the ADPs for morpholinium and TLS tensors for Ma and Mb (Tables S7 and S8). Furthermore, the refinement incorporated the the occupancies of Ma and Mb, whereby occ[Ma′] = occ[Ma], occ[Mb′] = occ[Mb] and occ[Ma]+occ[Mb]=0.5. Refined values at 160 K are occ[Ma] = 0.188(13) and occ[Mb] = 0.312. An excellent fit to the diffraction data has been obtained (Table S6). Geometrical properties of the structure model are given in Tables S11 and S12.

Table S9: Fractional atomic coordinates and equivalent isotropic ADP (Å^2) for the rigid-body model $T = 160$ K. Atomic coordinates of the atoms of Ma and MB have been obtained by transformation of the refined molecular model (Tables S8 and S7). Standard uncertainties are given in parentheses.

Atom	x	y	z	U_{iso}
O1	0.02967(14)	0.76002(11)	0.25	0.0369(4)
N1	0.26669(14)	0.53944(11)	0.25	0.0278(4)
C1	0.12308(14)	0.73029(12)	0.37276(13)	0.0373(4)
C2	0.17054(14)	0.57537(11)	0.37765(12)	0.0326(3)
H1c	0.2908	0.4439	0.25	0.041659
H2b	0.2366	0.5579	0.4589	0.039106
H2a	0.073	0.518	0.381	0.039106
H1d	0.3638	0.5897	0.25	0.041659
H1b	0.059	0.7535	0.4538	0.044757
H1a	0.2206	0.7878	0.3733	0.044757
B1a	0.17599	0.15029	0.26131	0.0271
F1a	0.23348	0.26056	0.34119	0.0526
F2a	0.29979	0.05607	0.22969	0.0506
F3a	0.05337	0.08019	0.33274	0.0608
F4a	0.11679	0.20315	0.13743	0.0799
B1b	0.15392	0.12328	0.23544	0.0251
F1b	0.29524	0.04599	0.25401	0.0443
F2b	0.06020	0.06825	0.12894	0.0321
F3b	0.06382	0.12205	0.35715	0.05739
F4b	0.19459	0.26022	0.19933	0.0654

Table S10: Anisotropic atomic displacement parameters (anisotropic ADPs) U_{ij} (Å^2) of the non-hydrogen atoms. ADPs of B and F atoms have been calculated on the basis of the refined TLS parameters. Standard uncertainties are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0284(6)	0.0262(5)	0.0560(8)	0.0082(4)	0	0
N1	0.0239(7)	0.0155(5)	0.0439(7)	-0.0005(4)	0	0
C1	0.0360(7)	0.0310(6)	0.0449(7)	0.0035(4)	-0.0010(5)	-0.0112(5)
C2	0.0387(7)	0.0292(5)	0.0299(5)	0.0007(4)	-0.0024(5)	0.0002(4)
B1a	0.030(4)	0.017(3)	0.034(4)	0.001(2)	-0.004(3)	-0.001(2)
F1a	0.077(11)	0.024(8)	0.058(10)	-0.026(8)	-0.009(9)	-0.001(7)
F2a	0.040(8)	0.056(10)	0.056(12)	0.022(7)	0.006(8)	0.001(9)
F3a	0.037(8)	0.055(12)	0.090(10)	-0.027(8)	0.021(7)	-0.023(9)
F4a	0.099(12)	0.103(13)	0.038(5)	0.058(10)	-0.022(6)	-0.005(6)
B1b	0.0262(19)	0.015(2)	0.034(2)	-0.0026(11)	0.0002(10)	-0.0010(16)
F1b	0.032(4)	0.031(7)	0.070(7)	0.006(4)	-0.008(4)	-0.007(5)
F2b	0.036(5)	0.032(7)	0.028(6)	-0.007(5)	0.000(4)	-0.001(5)
F3b	0.049(7)	0.091(7)	0.032(6)	0.003(5)	0.006(5)	-0.016(4)
F4b	0.057(7)	0.018(6)	0.122(7)	-0.015(4)	-0.015(5)	0.012(5)

Table S11: Selected bond lengths (Å) for the pseudo-rigid-body model for the crystal structure of phase I at $T = 160$ K. Standard uncertainties are given in parentheses. Symmetry operator (i) is x, y, $-z+1/2$.

Atom pair	Bond length
O1-C1	1.4281(14)
C1-C2	1.5083(15)
C1-H1a	0.96
C1-H1b	0.96
C2-H2a	0.96
C2-H2b	0.96
N1-C2	1.4907(13)
N1-H1c	0.92
N1-H1d	0.92
B1a-F1a	1.37(2)
B1a-F2a	1.37(2)
B1a-F3a	1.38(2)
B1a-F4a	1.37(2)
B1b-F1b^i	1.36(3)
B1b-F2b	1.37(2)
B1b-F3b	1.38(2)
B1b-F4b	1.37(2)

Table S12: Selected bond angles (deg) for the pseudo-rigid-body model for the crystal structure of phase I at $T = 160$ K. Standard uncertainties are given in parentheses. Symmetry operator (i) is x, y, $-z+1/2$.

Atom triplet	Bond angle
C1-O1-C1^i	110.95(10)
C2-N1-C2^i	110.31(9)
C2-N1-H1c	109.47
C2-N1-H1d	109.47
C2^i -N1-H1c	109.47
C2^i -N1-H1d	109.47
H1c-N1-H1d	108.62
O1-C1-C2	110.54(10)
O1-C1-H1b	109.47
O1-C1-H1a	109.47
C2-C1-H1b	109.47
C2-C1-H1a	109.47
H1b-C1-H1a	108.38
N1-C2-C1	109.13(9)
N1-C2-H2b	109.47
N1-C2-H2a	109.47
C1-C2-H2b	109.47
C1-C2-H2a	109.47
H2b-C2-H2a	109.81
F1a-B1a-F2a	111.2(13)
F1a-B1a-F3a	109.3(14)
F1a-B1a-F4a	109.1(15)
F2a-B1a-F3a	109.3(14)
F2a-B1a-F4a	107.4(13)
F3a-B1a-F4a	110.4(15)
F1b-B1b-F2b	111.2(15)
F1b-B1b-F3b	109.3(15)
F1b-B1b-F4b	109.1(18)
F2b-B1b-F3b	109.3(14)
F2b-B1b-F4b	107.4(15)
F3b-B1b-F4b	110.4(15)

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