



Кристаллическая и магнитная структура ViMnO_3 : ab initio расчет

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First principle calculations

One-particle Kohn-Sham equation:

$$[T_e + V_{ne} + V_{ee} + V_{xc}]\psi_i(r) = \varepsilon_i\psi_i(r)$$

T_e – kinetic energy of electron

V_{ne} – core-electron interaction

V_{ee} – electron-electron Coulomb interaction

V_{xc} – exchange-correlation interaction of electrons

Density Functional Theory

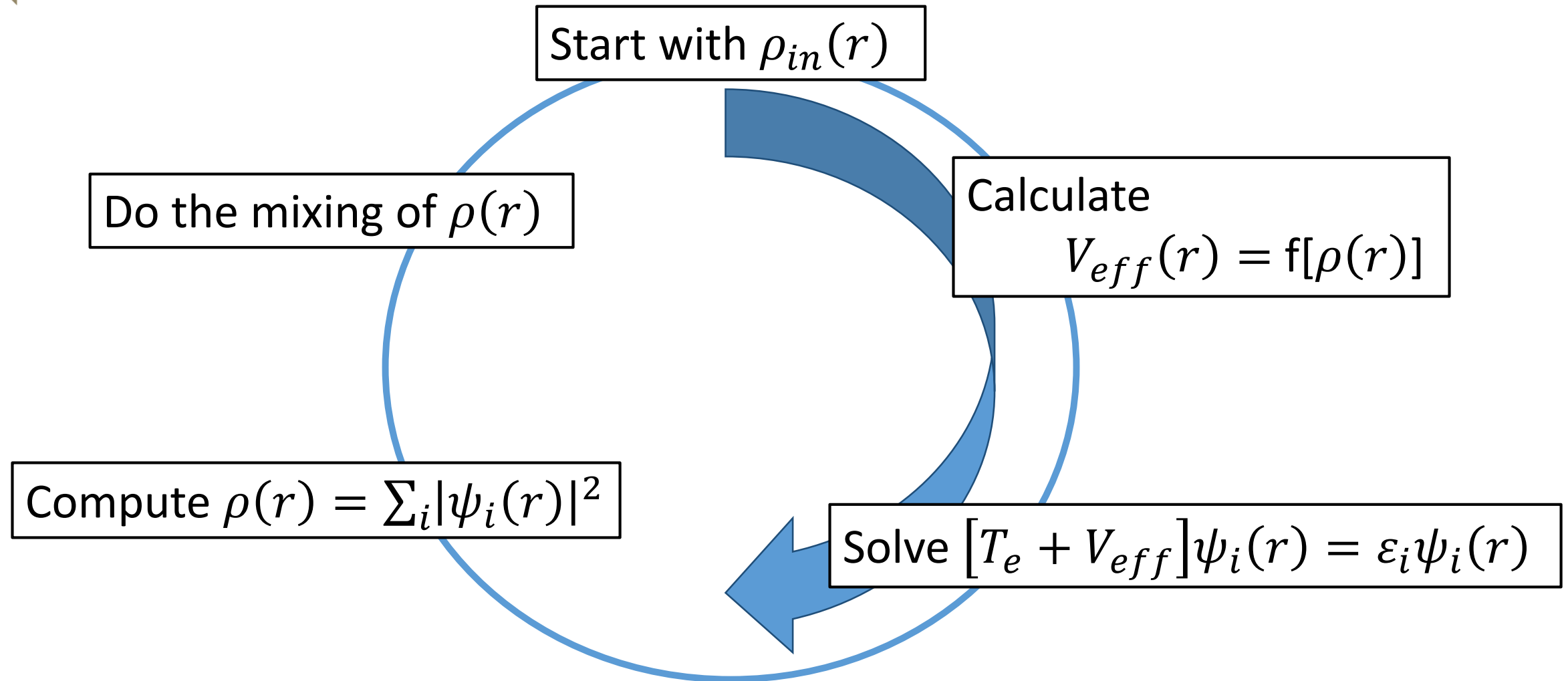
Self-consistent field (SCF)

$$\rho(r) = \sum_i |\psi_i(r)|^2 \quad (1)$$

$$V_{eff}(r) = V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + V_{xc}[\rho(r)] \quad (2)$$

$$[T_e + V_{eff}] \psi_i(r) = \varepsilon_i \psi_i(r) \quad (3)$$

SCF cycles



Approximations of DFT

- Adiabatic approximation
- $T = 0\text{K}$
- Ions \rightarrow **Basis sets, pseudopotentials**

$$\psi_i(r) = \sum_j c_{ij} \varphi_j(r)$$

Basis functions $\varphi_j(r)$: Plain waves

Gauss functions (CO LCAO)

- Exchange-correlation functional

$$H = T_e + V_{ne} + V_{ee} + V_{xc}$$

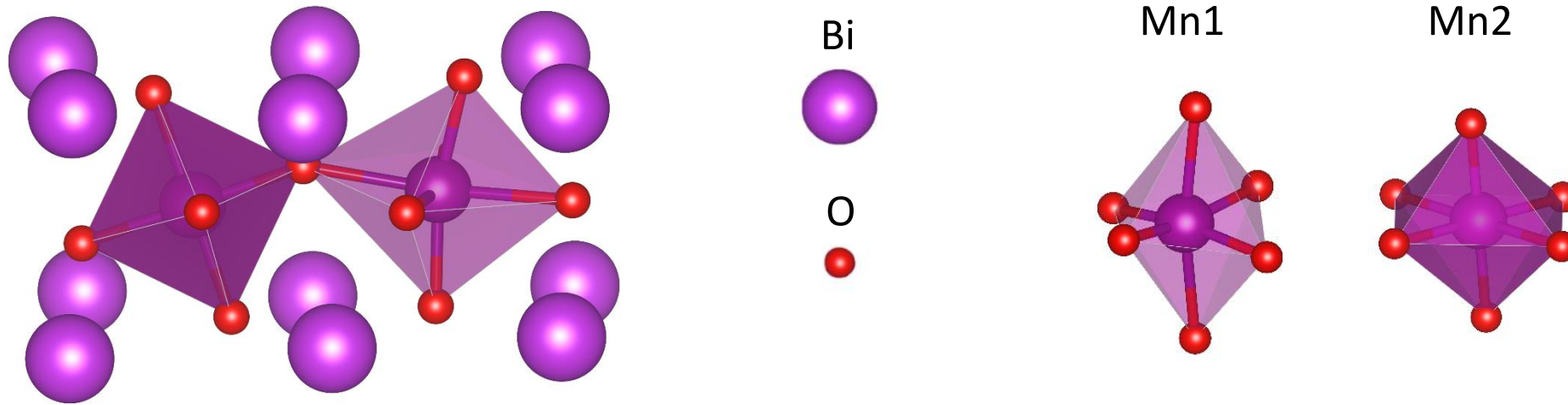


Calculation details

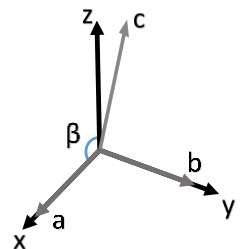
- *CRYSTAL14* [1] package
- Crystal orbitals LCAO approximation
- Hybrid DFT/Hartree-Fock
 - *WC1LYP* exchange-correlation functional
 - with 16% Hartree-Fock exchange energy
- All-electron Gauss-type basis sets for Mn^{3+} and O^{2-}
- Bi^{3+} pseudopotential, $6s^2$ not included in core
- Spin polarized mode, high-spin state $S=2$ for Mn^{3+}

Crystal structure of BiMnO_3

Monoclinic phase: space group $C2/c$, $Z=4$



Lattice constant	a	b	c	β
Value, Å	9.484(9.569)	5.589(5.602)	9.799(9.879)	110.96(111.02)



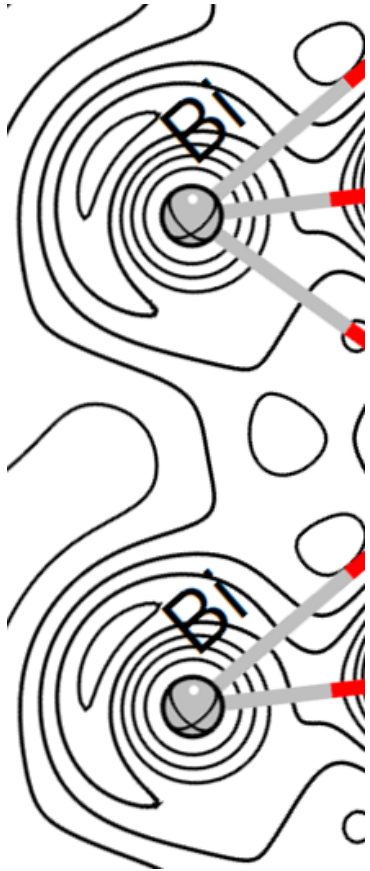
Crystal structure of BiMnO₃

Calculated and experimental [2] (in brackets) crystal structure parameters

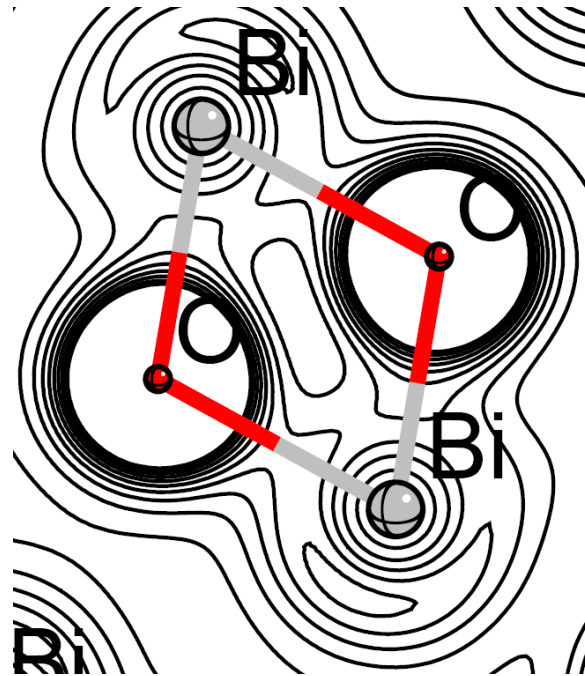
Atom coordinates in cell				
Atom	Wyckoff symbol	x/a	y/b	z/c
Bi	8f	0.1351(0.1365)	-0.230(-0.217)	0.1181(0.1269)
Mn1	4e	0	0.2014(0.2113)	0.25
Mn2	4c	0.25	0.25	0
O1	8f	0.0993(0.0991)	0.1666(0.1776)	0.0794(0.0815)
O2	8f	0.3510(0.3524)	0.4496(0.4567)	0.1662(0.1646)
O3	8f	0.1447(0.1443)	0.4161(0.4342)	0.3782(0.3639)
Bond lengths, Å				
Mn1-O1	2.20(2.20)	Mn2-O1	1.91(1.93)	
Mn1-O2	1.91(1.90)	Mn2-O2	2.24(2.23)	
Mn1-O3	1.95(1.97)	Mn2-O3	1.92(1.95)	

Charge density map around Bi ions

BiFeO₃



BiMnO₃



- Antiferroelectric ordering of dipole moments in BiMnO₃

Magnetic moment of Mn³⁺ ions

Experimental [3] Mn³⁺ magnetic moment 3.92 μ_B

- High-spin state S=2
 - locked spins during all SCF cycles: **3.81** μ_B
 - locked spins only during first two SCF cycles: **3.81** μ_B
 - Mid-spin state S=1: 1.93 μ_B
 - Low-spin state S=0: 3.71 μ_B
 - Paramagnetic phase -
- lowest energy

Orbital ordering in $\text{Lu}_2\text{V}_2\text{O}_7$

Calculated exchange coupling constant: $J = 8.18 \text{ meV}$ [4]

Experimental (spin waves): $J = 8.22 \text{ meV}$ [5]

Orbital ordering obtained using the polarized neutron diffraction technique [6]

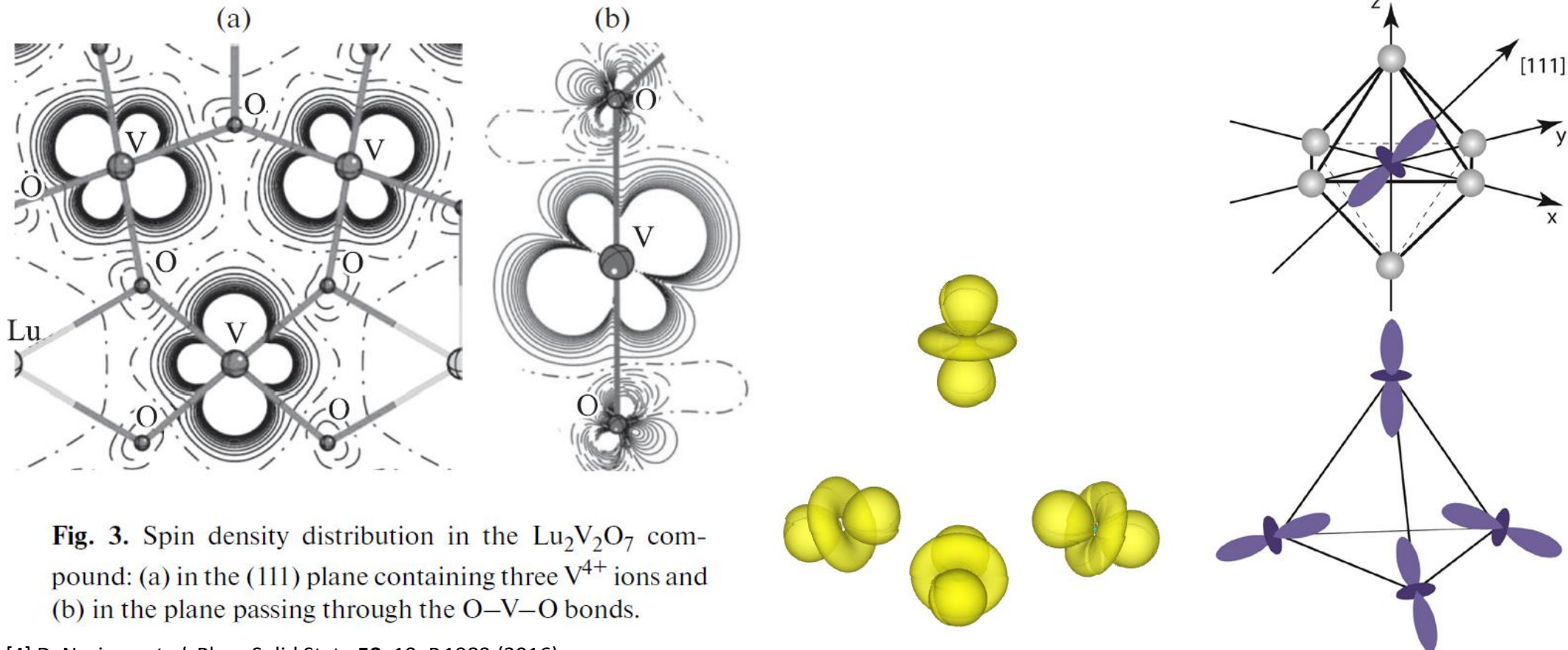


Fig. 3. Spin density distribution in the $\text{Lu}_2\text{V}_2\text{O}_7$ compound: (a) in the (111) plane containing three V^{4+} ions and (b) in the plane passing through the O–V–O bonds.

[4] D. Nazipov *et al.* Phys. Solid State **58**, 10, P.1989 (2016)

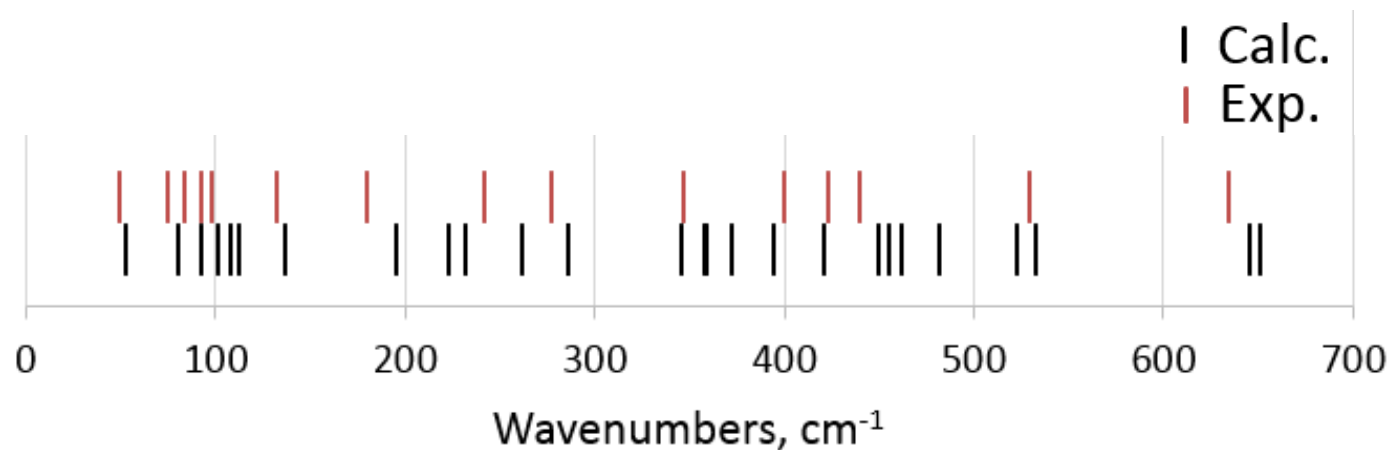
[5] H. Ichikawa *et al.* J. Phys. Soc. Japan **74**, 3, P.1020 (2005)

[6] M. Mena *et al.*, Phys. Rev. Lett. 113, 047202 (2014)

Phonon spectra of BiMnO₃

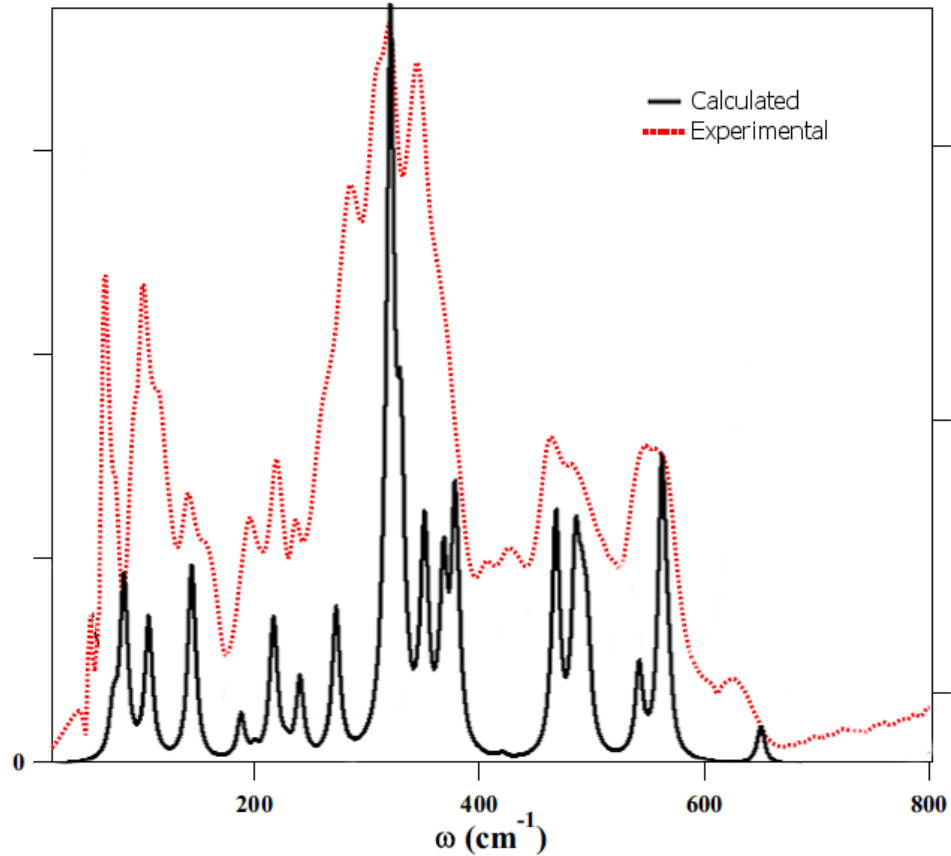
$$\Gamma = (13A_g + 14B_g)^{Ram} + (14A_u + 16B_u)^{IR} + (A_u + 2B_u)^{Acoust}$$

Raman active modes



Frequencies of Raman active modes			
№	Irr. repr.	Calc.	Exp. [6]
4	A _g	53	50
7	B _g	81	75
10	B _g	93	84
11	B _g	102	93
13	A _g	108	99
14	A _g	113	
15	B _g	137	133
18	A _g	196	180
21	B _g	223	
23	B _g	232	
26	A _g	262	242
28	A _g	287	278
29	B _g	287	
34	B _g	346	347
36	A _g	358	
37	A _g	360	
39	B _g	373	
42	B _g	395	400
44	A _g	422	424
45	A _g	450	440
46	B _g	456	
47	A _g	462	
49	B _g	482	
53	A _g	523	
54	B _g	533	530
58	B _g	646	635
60	A _g	652	

Infrared absorption spectrum



Infrared active modes

N_0	Irr. repr.	Freq. Calc.	Freq. Exp. [6]	Calc. Intensity (normalized)
5	A_u	74	68	16
6	B_u	76	75	59
8	B_u	85	92	255
9	A_u	88	101	0.5
12	A_u	107	115	200
16	B_u	145	143	282
17	A_u	189	159	64
19	B_u	201	196	14
20	B_u	218	219	200
22	A_u	229	-	11
24	B_u	241	237	112
25	A_u	244	-	2
27	B_u	273	261	213
30	A_u	291	-	1
31	B_u	316	284	66
32	B_u	321	308	1000
33	A_u	331	321	374
35	A_u	351	345	312
38	B_u	368	369	249
40	B_u	379	-	335
41	A_u	381	407	34
43	A_u	421	426	7
48	B_u	468	463	341
50	A_u	485	486	261
51	A_u	490	-	141
52	B_u	495	508	159
55	B_u	542	541	128
56	B_u	562	561	401
57	A_u	567	604	87
59	A_u	649	628	54

[6] W. S. Mohamed *et al.* Phys. Rev. B **92**, 054306 (2015)



Conclusions

- Calculated crystal structure and phonon spectra confirm the inversion presence in BiMnO_3 crystal symmetry
- Antiferroelectric ordering of dipole moments is predicted

Thank you for attention!

Infrared absorption spectrum

In CRYSTAL package the intensity of modes I_p in infrared spectrum is computed according to:

$$I_p = \frac{\pi N_A}{3 c^2} d_p |\vec{Z}_p|^2$$

where N_A is the Avogadro's number, c is the speed of light, d_p is the degeneracy of the mode, \vec{Z}_p is the mass-weighted effective mode Born charge vector.

The infrared absorbance spectrum $A(\omega)$ is calculated using following model:

$$A(\omega) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\omega - \omega_p)^2 + \gamma_p^2/4}$$

where ω_p is TO frequency, γ_p is the damping factor that equals 8 cm^{-1}