Magnetoelastic interactions in the two-dimensional magnetic material $MnPS_3$

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Summary

It belongs to the **family of magnetic van der Waals** systems
cousins and **siblings** of the graphene and the dichalcogenides.
Can be exfoliated to study 2D magnetism in single-layers, bilayers, three-layer.
Promising playground for fundamental physics studies and applications.

This work : $MnPS_3$

Experiments

Raman experiments versus T revealing magnetoelastic interactions

Theory

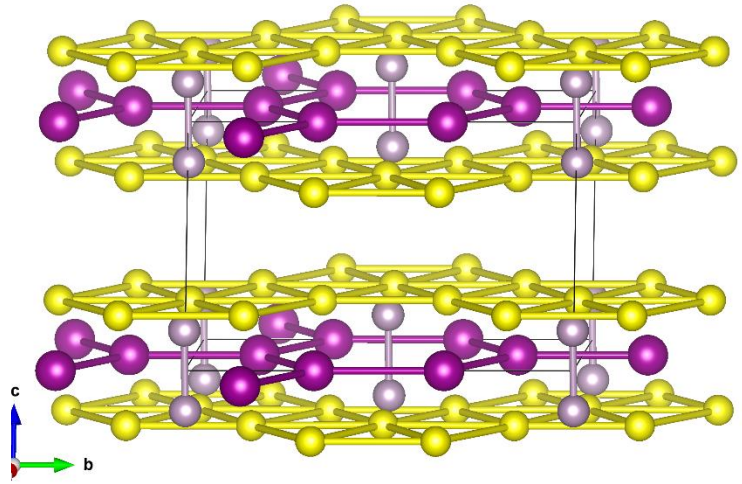
DFT calculations of the exchange interactions
DFT calculations of the Raman modes

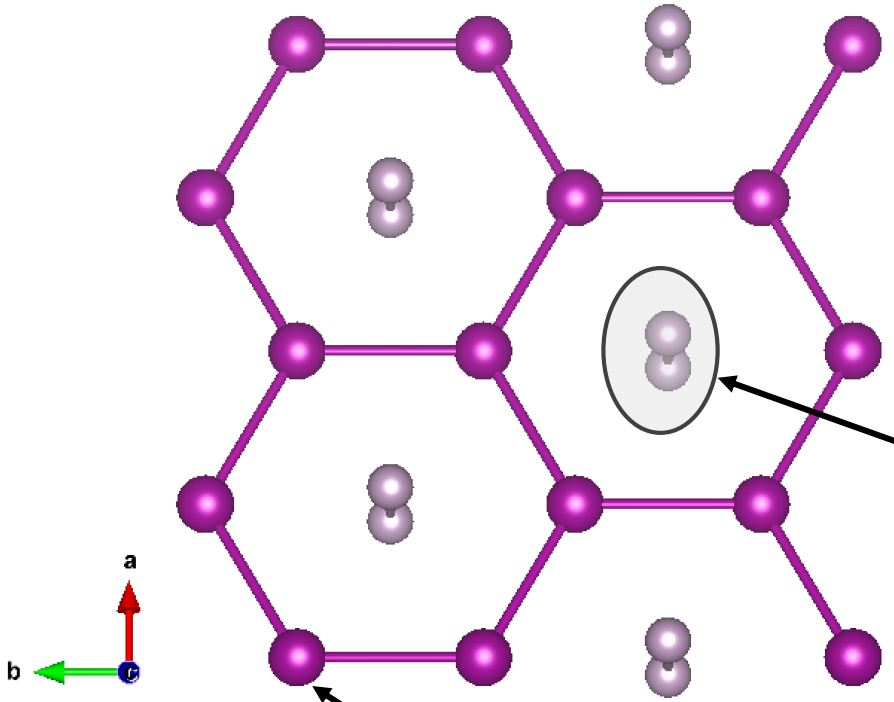
Discussion

Interpretation : putting all together

$MnPS_3$

Transition metal phosphorous tri-calchogenide
Monoclinic structure C2/m



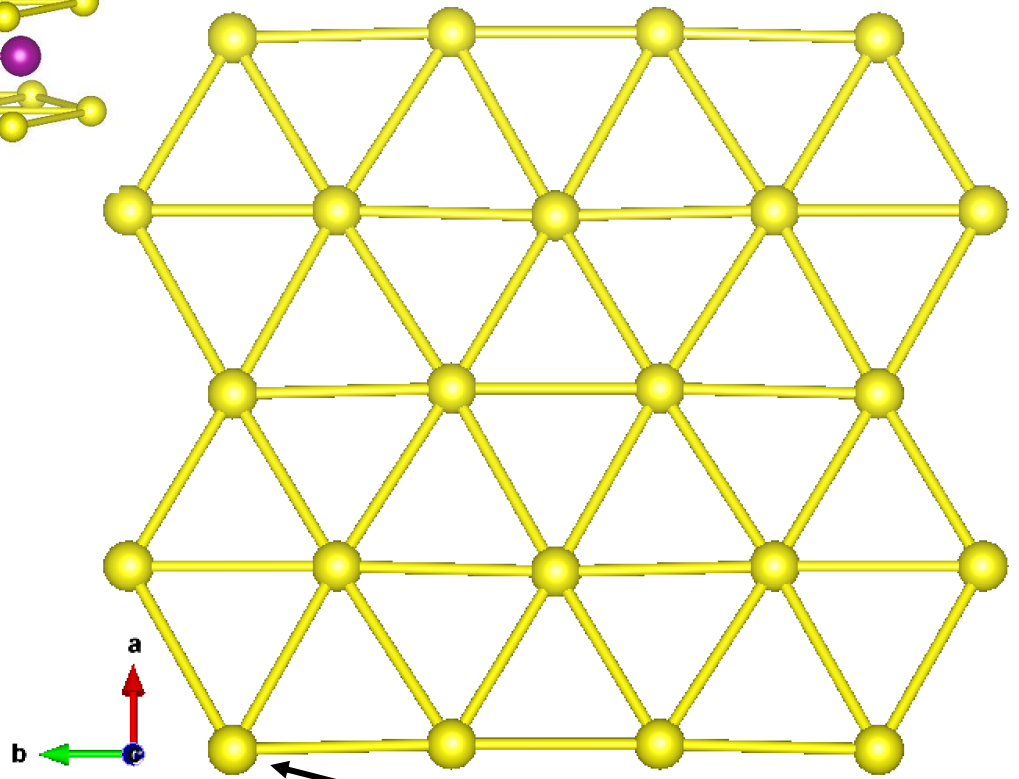


P_2 dimers

Mn

distorted honeycomb lattice

Mn^{2+} : $3d^5$



S

distorted triangular lattice

Magnetic ground state of $MnPS_3$

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Vol. 55, No. 12, December, 1986, pp. 4456–4463

Magnetic Properties of Layered Compound $MnPS_3$

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$Mn^{2+} : 3d^5$

$S = 5/2 - L = 0$

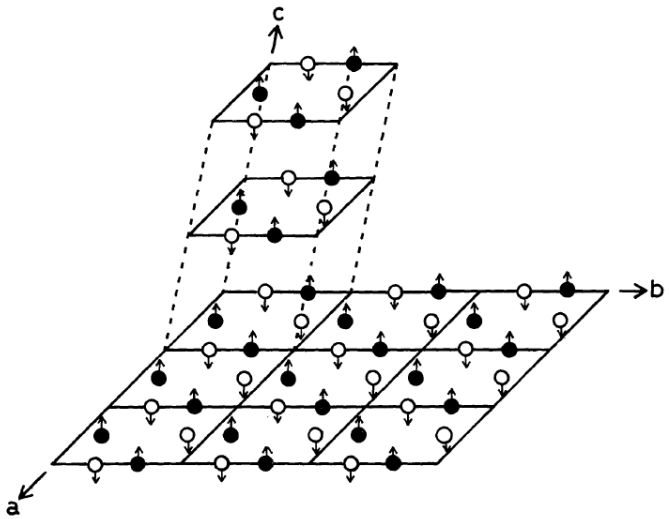


Fig. 2. Magnetic structure of $MnPS_3$. Close and open circles denote up- and down-moments, respectively.

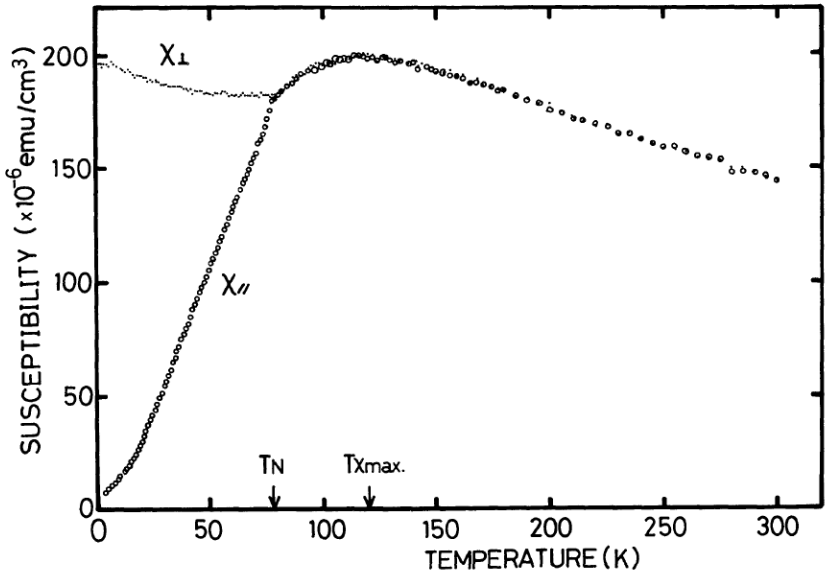
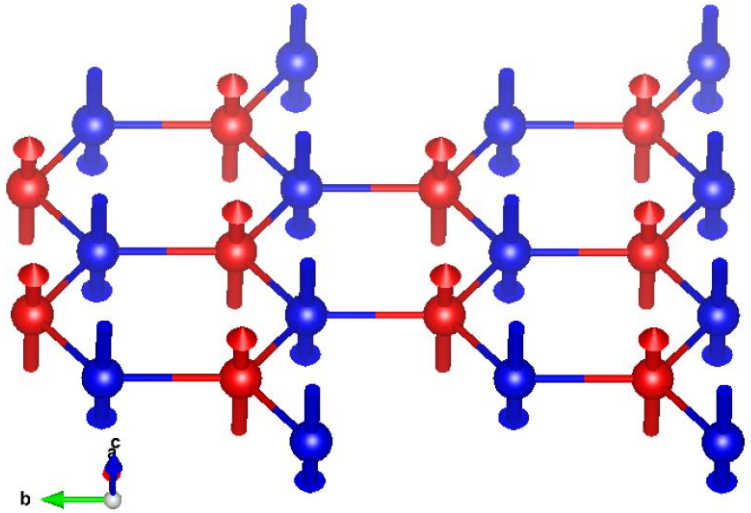


Fig. 4. Temperature dependence of magnetic susceptibility of $MnPS_3$ for two directions, parallel ($\chi_{//}$) and perpendicular ($\chi_{\perp}$) to the z-axis.

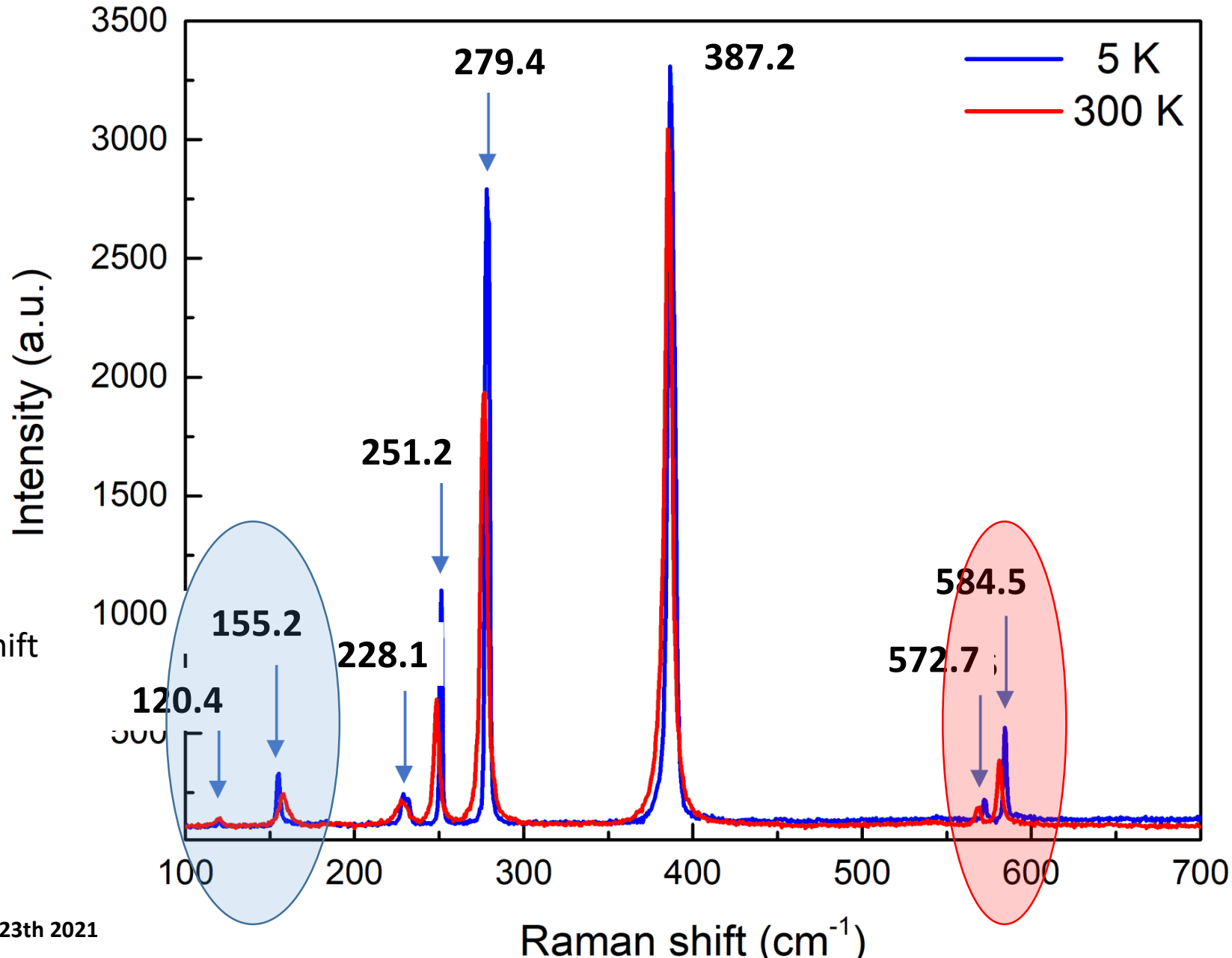
In-plane AFM order
FM order along c
T_N = 78 K
Easy axis along c



2D long range order and anisotropy due to a single ion anisotropy and/or dipolar interactions.

$MnPS_3$: Raman spectroscopy

Diana Vaclavkova
Marek Potemski
Clement Faugeras
LNCMI
CNRS Grenoble



"anomalous" **blue** shift

"normal" **red** shift

$MnPS_3$: Raman spectroscopy

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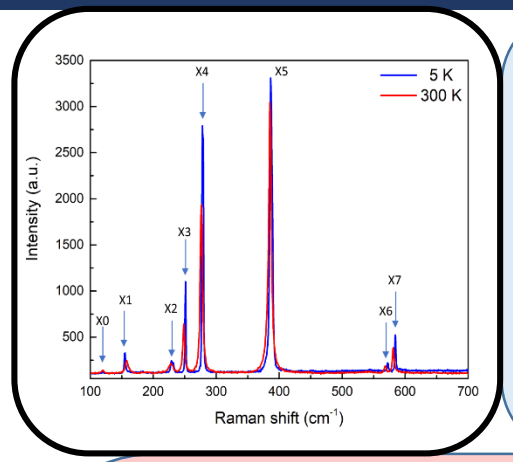
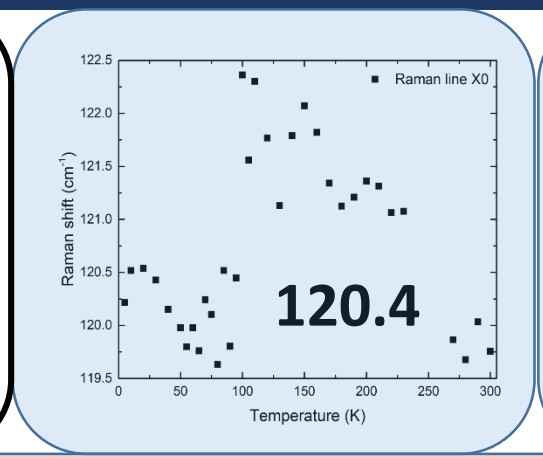
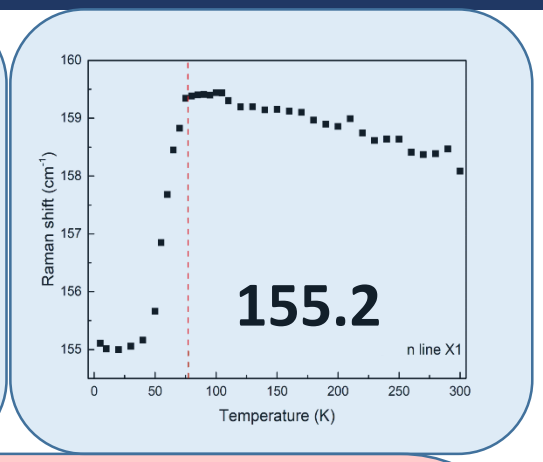
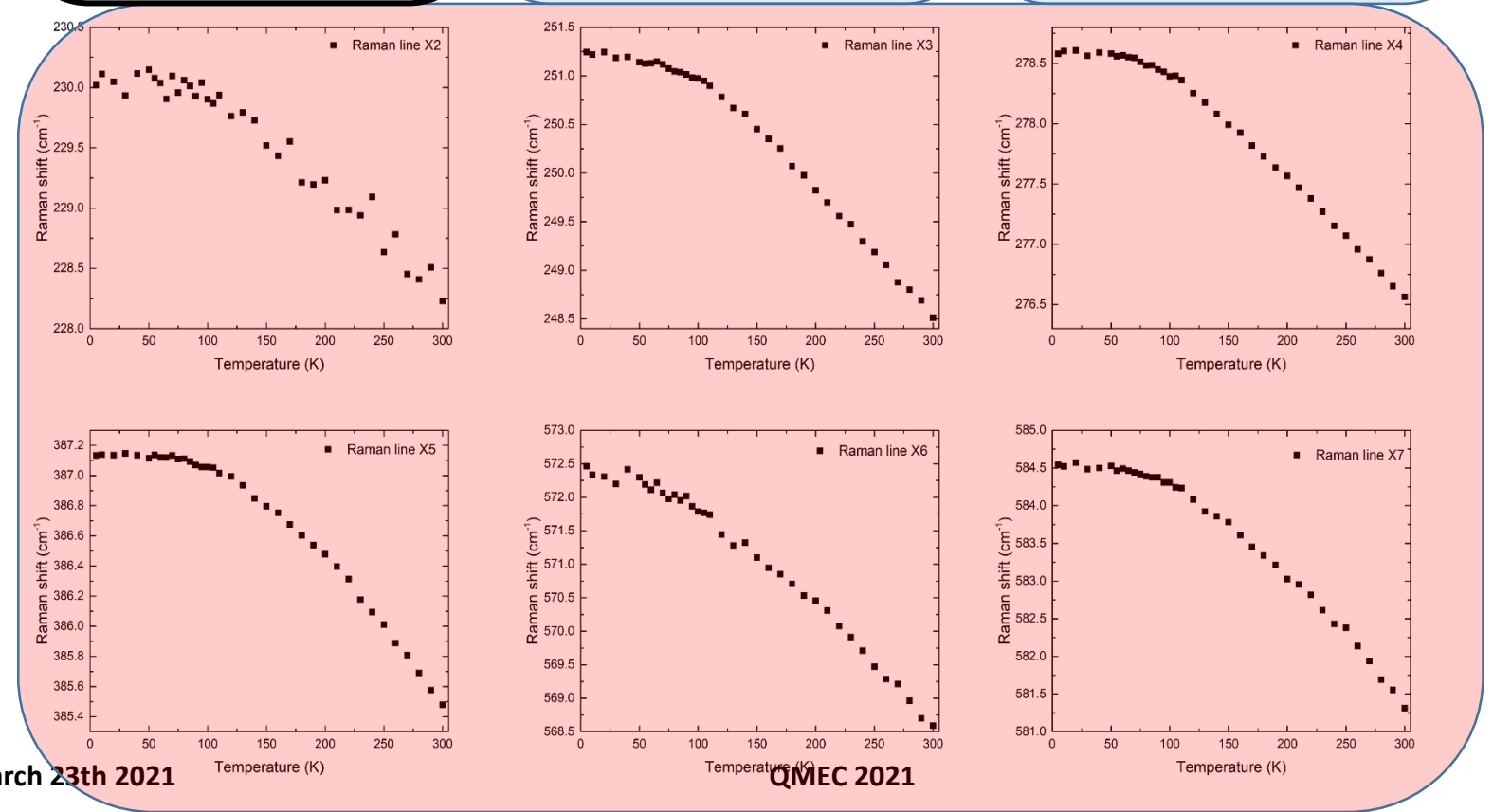






Blue shift of 5cm^{-1} at T_N
Sensitive to the magnetic order.
Magnetoelastic interaction



Normal
Red shift
Softening of the modes with temperature

Effective exchange interactions

$$\hat{H} = \hat{H}_0 + \sum_{i>j} J_{ij} \hat{S}_i . \hat{S}_j$$

Interactions classified by the **Mn-Mn distance**

Intra-layer

J1 : 3.500 Å

J2 : 3.524 Å

J3 : 6.076 Å

J4 : 6.077 Å

J7 : 7.000 Å

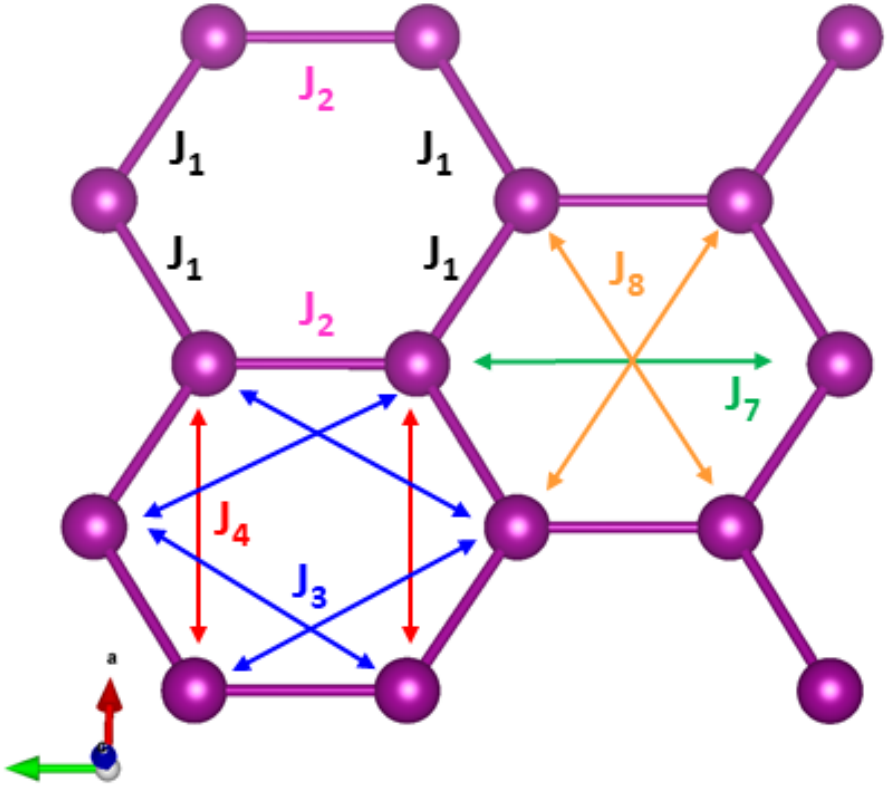
J8 : 7.025 Å

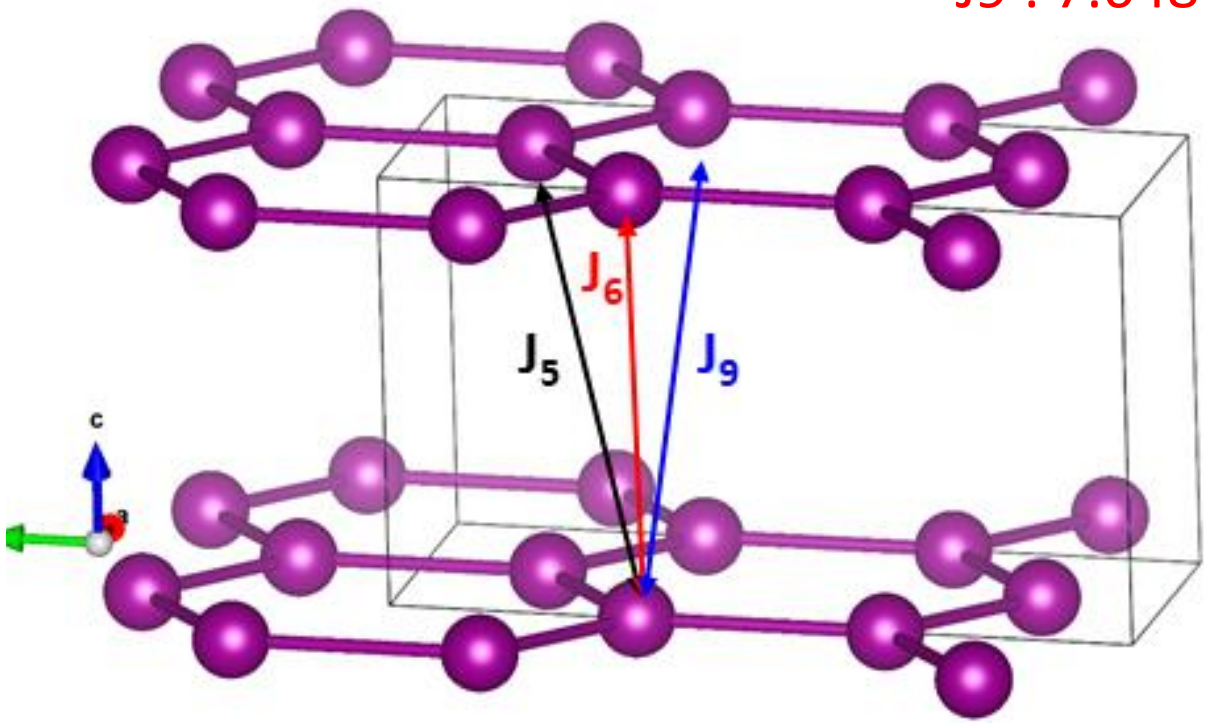
Inter-layer

J5 : 6.792 Å

J6 : 6.796 Å

J9 : 7.648 Å





Effective exchange interactions

Exchange interactions calculated using a **broken-symmetry formalism** within **DFT**.

Intra-layer

J1 : 3.500 Å
J2 : 3.524 Å

J3 : 6.076 Å
J4 : 6.077 Å

J7 : 7.000 Å
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Inter-layer

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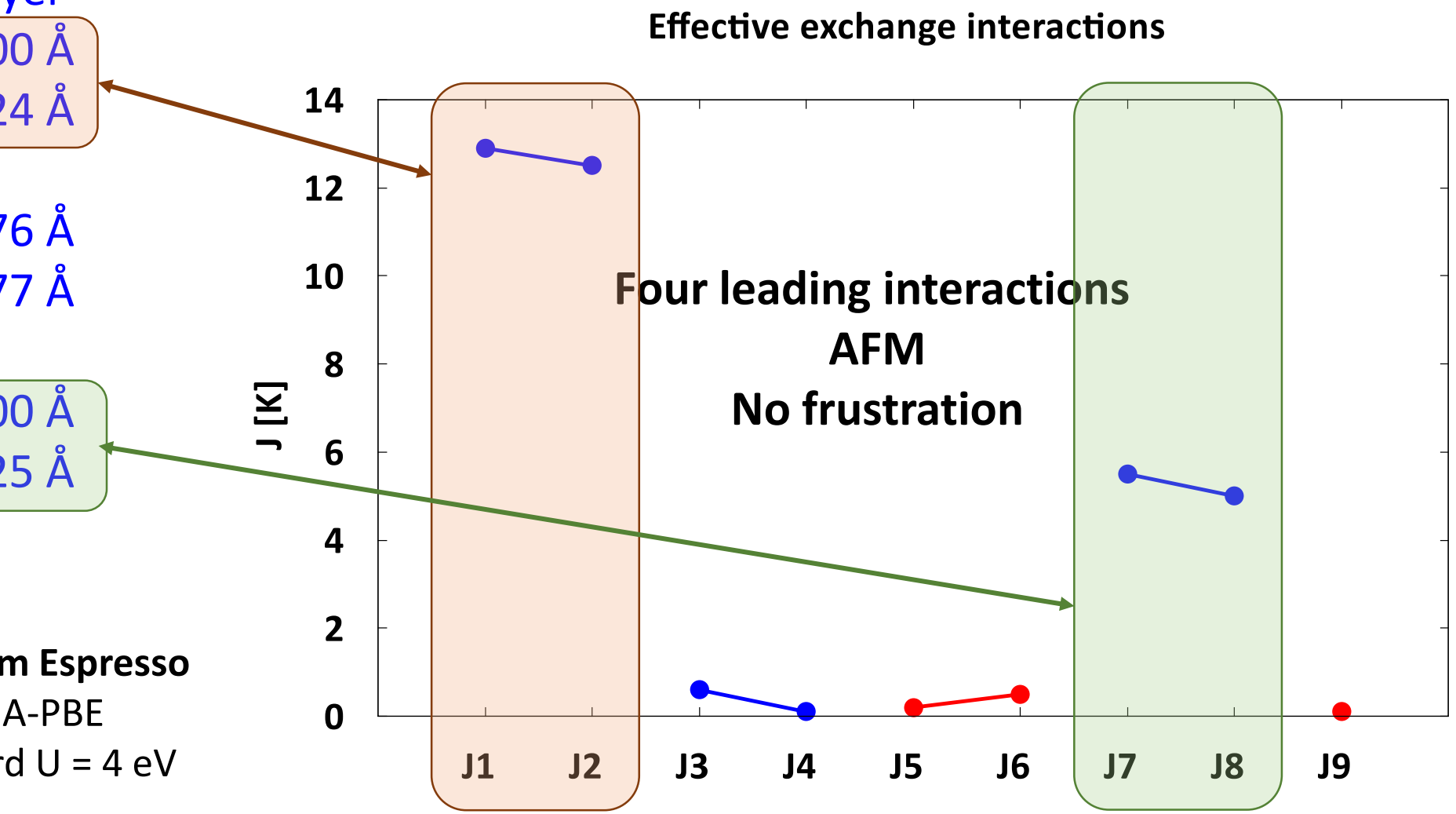


Quantum Espresso
GGA-PBE
Hubbard U = 4 eV

Effective exchange interactions

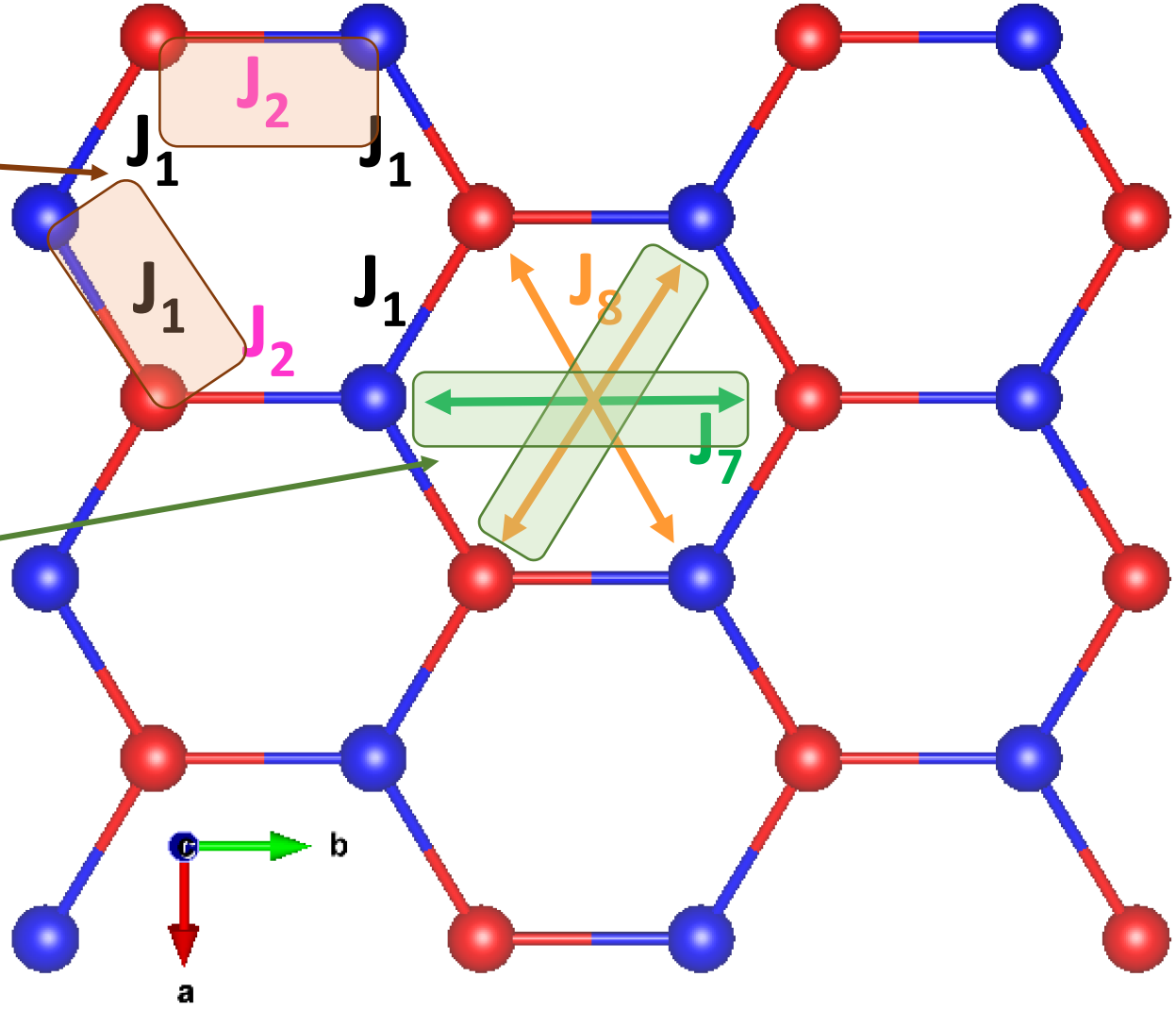
Interactions classified by the **Mn-Mn distance: 9** different interactions up to 7.647 A

Intra-layer

J1 : 3.500 Å
J2 : 3.524 Å

J3 : 6.076 Å
J4 : 6.077 Å

J7 : 7.000 Å
J8 : 7.025 Å

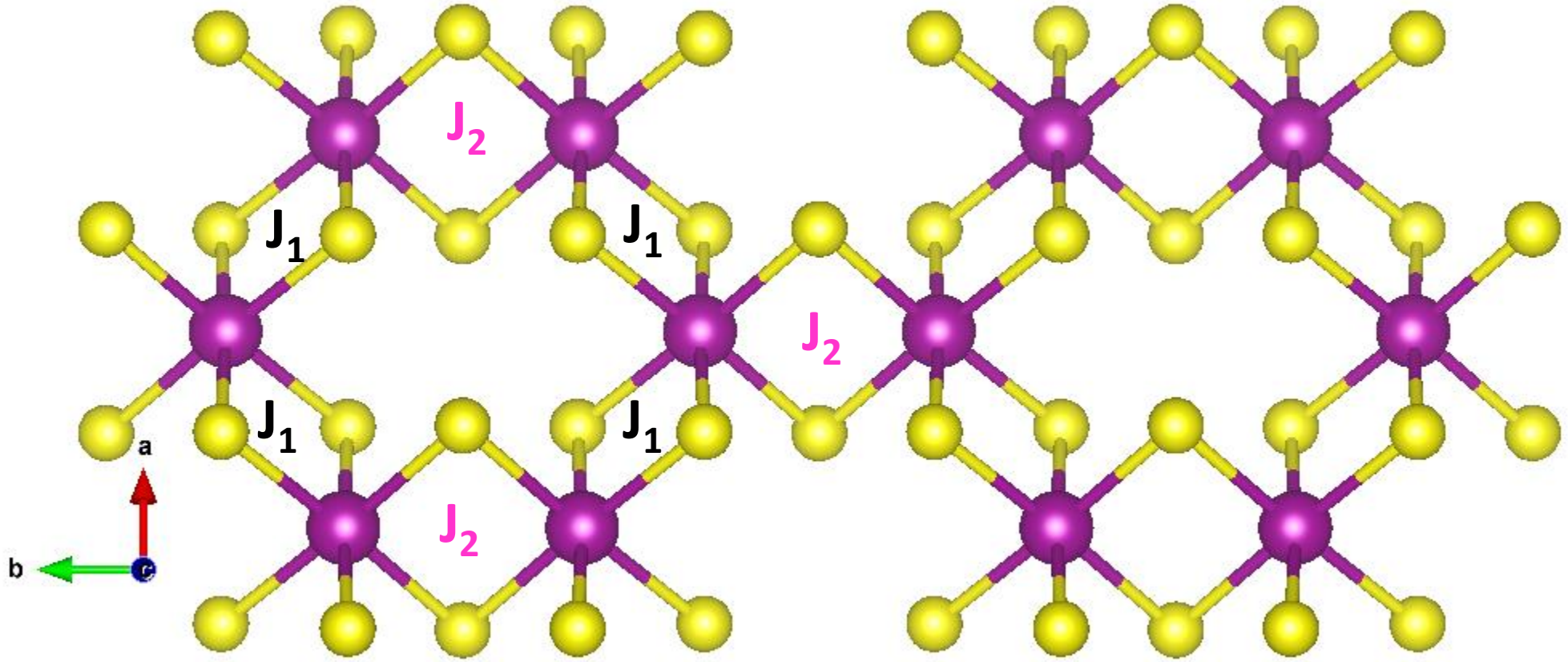


Inter-layer

J5 : 6.792 Å
J6 : 6.796 Å

J9 : 7.648 Å

Super exchange path



J1 = 12.9 K **Mn-Mn distance : 3.500 Å** **Mn-S-Mn angle : 83.5627 deg.**

J2 = 12.5 K **Mn-Mn distance : 3.524 Å** **Mn-S-Mn angle : 84.4573 deg.**

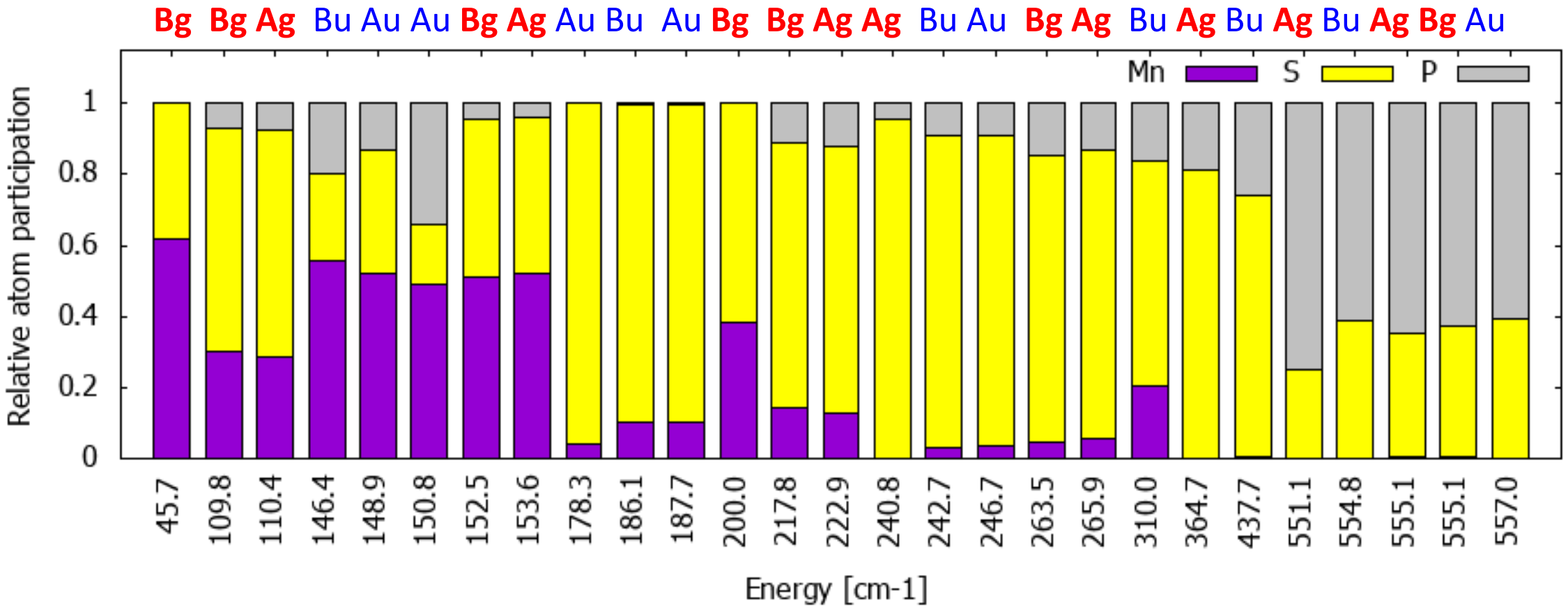
Calculation of the phonon modes

Phonon modes calculated at the Γ point in the **10 atoms C2/m monoclinic cell**

Group analysis : Γ_{tot} : **8 A_g** + 6 A_u + **7 B_g** + 9 B_u = **30**

Only **Ag** and **Bg** are **Raman** active

Quantum Espresso
GGA-PBE
Hubbard U = 4 eV



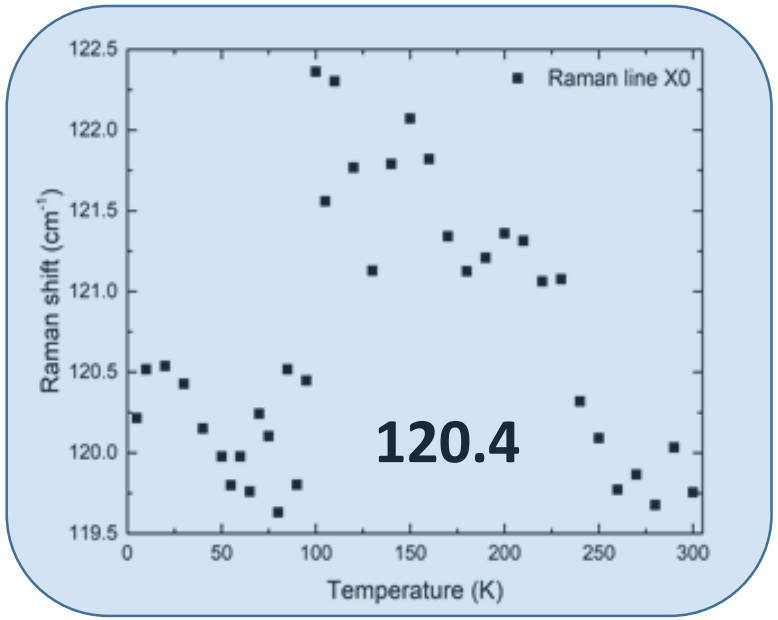
Raman spectroscopy

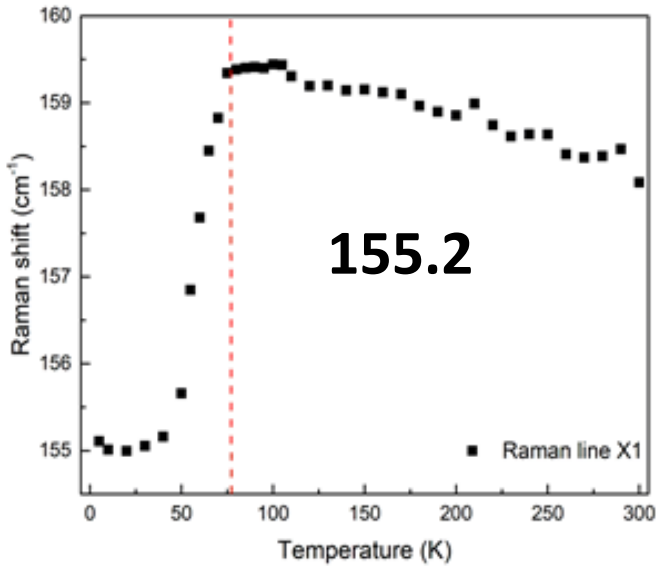
Table 2. Comparison between the calculated Raman active modes versus experimentally observed phonon modes (see figure 2 and Supplementary Material figure **S1**).

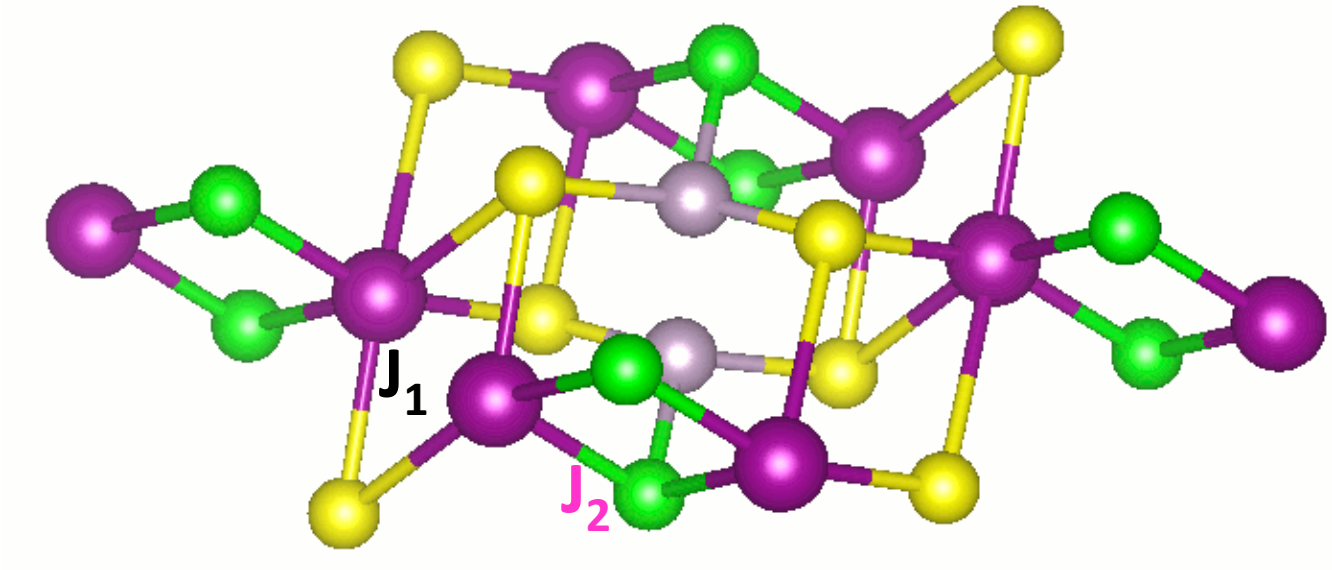
Calculations		Experiments	
Symmetry	Energy (cm^{-1})	Energy (cm^{-1})	Feature
Bg	45.7		
Bg Ag	109.8 110.4	120.2	X1
Bg Ag	152.5 153.6	155.1	X2
Bg	200.0		
Bg Ag	217.8 222.9	228.1 231.9	X3
Ag	240.8	251.2	X4
Bg Ag	263.5 265.9	278.6	X5
Ag	364.7	387.1	X6
Ag	551.1	572.5	X7
Ag Bg	555.1 555.1	584.5	X8

The two experimental modes sensitive to the magnetic order correspond to two pairs of almost degenerate modes.

The phonon modes





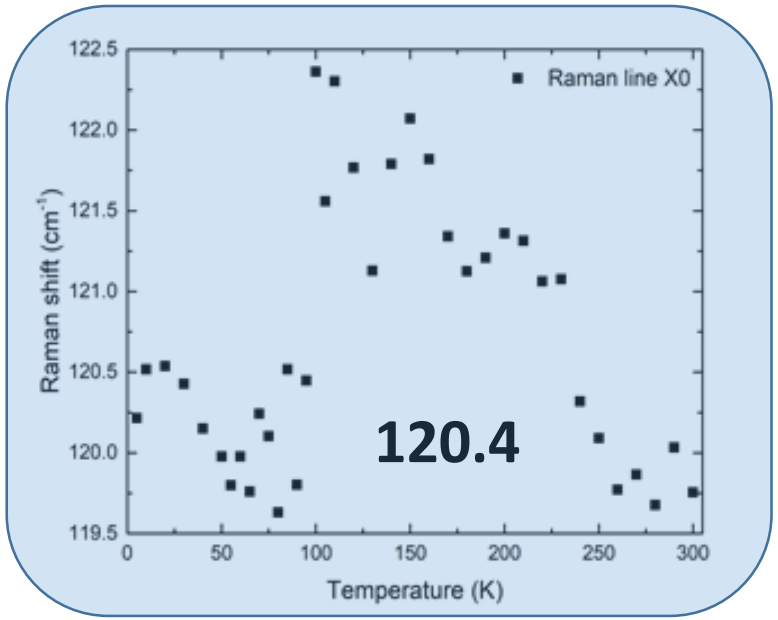


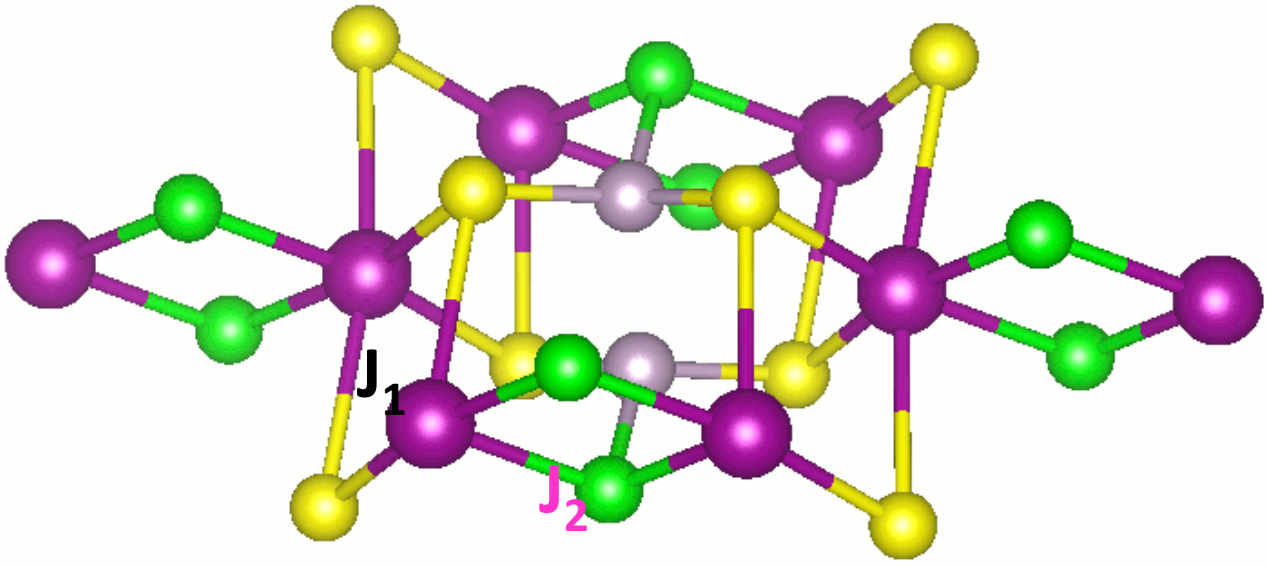
Bg mode 109.8 cm^{-1}

Movement changes the angle associated with J1.

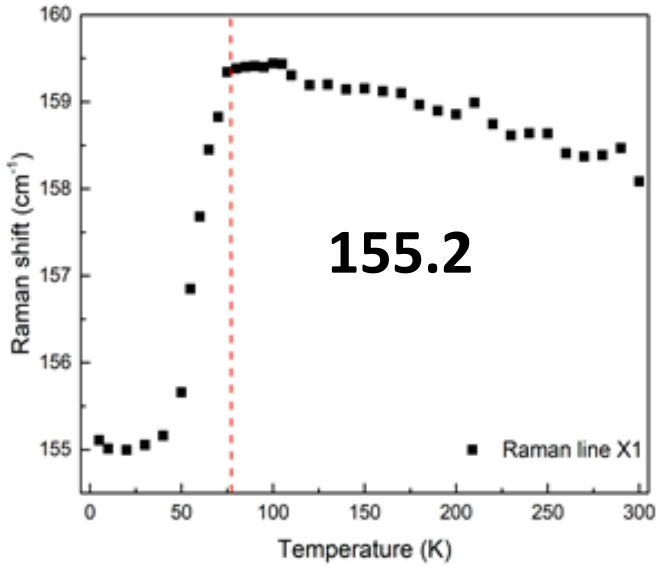
Almost rigid rotation of the structure associated with J2

The phonon modes



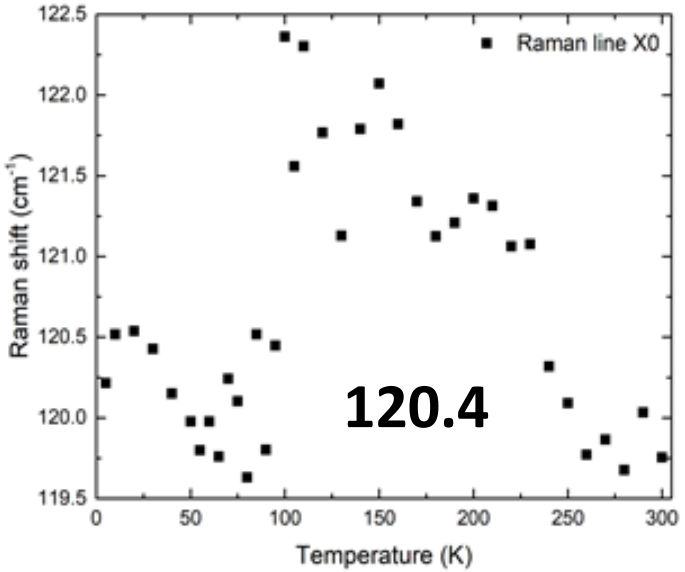


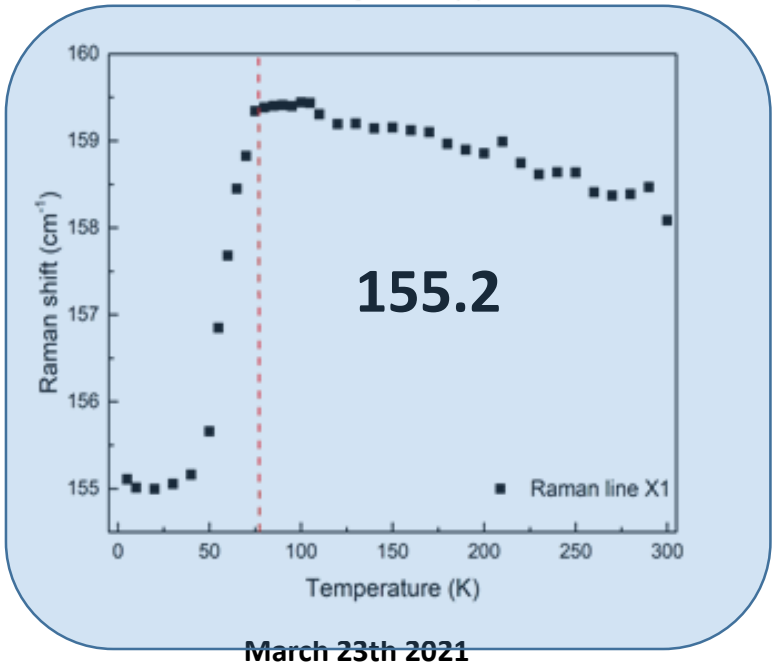
Ag mode 110.4 cm^{-1}

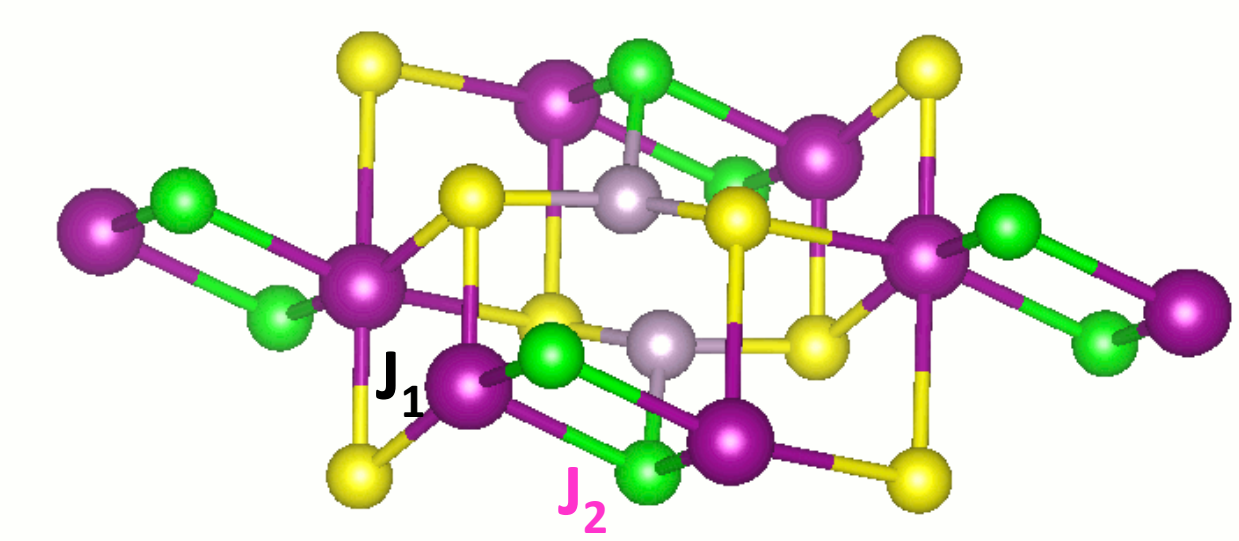


Movement changes the angle associated with J1 and J2.

The phonon modes





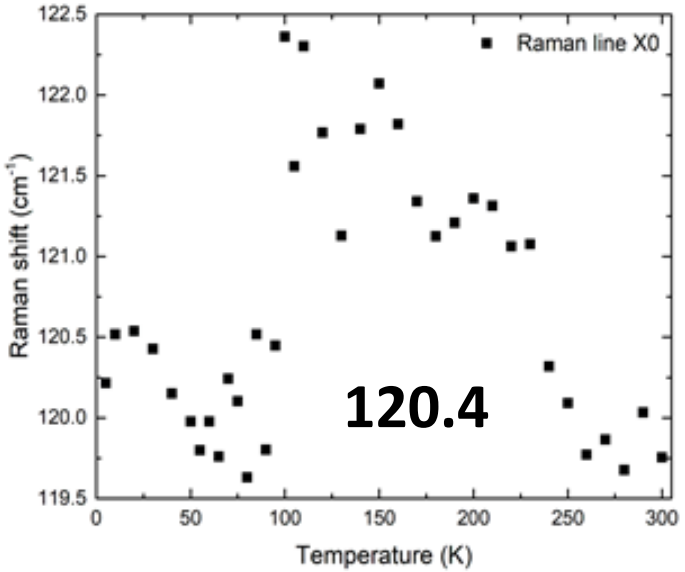


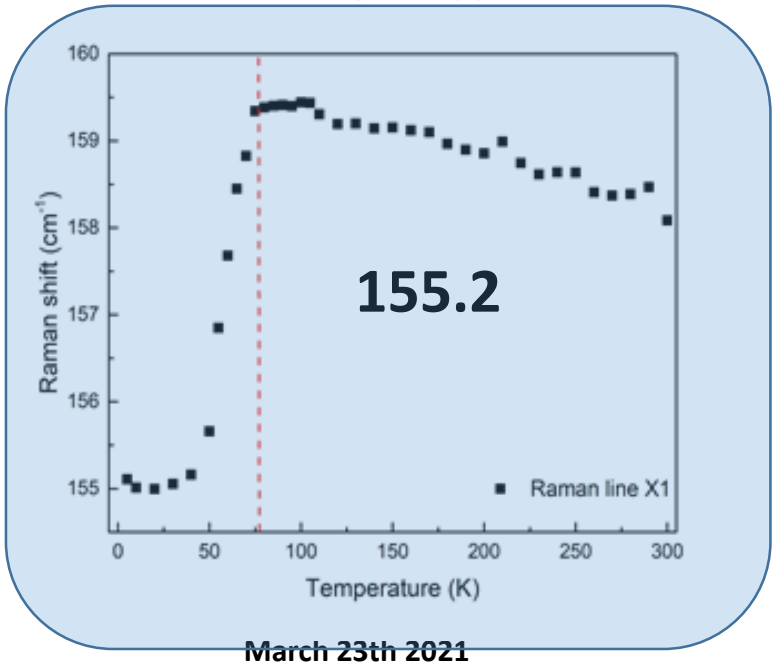
Bg mode 152.5 cm^{-1}

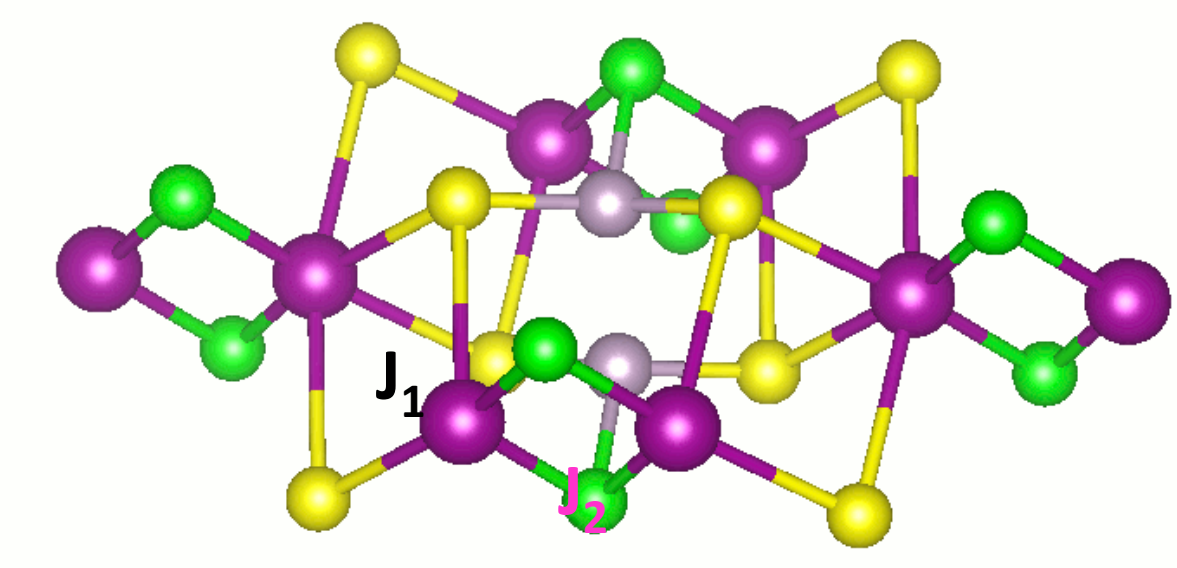
Movement changes the angle associated with J1.

Almost rigid rotation of the structure associated with J2

The phonon modes





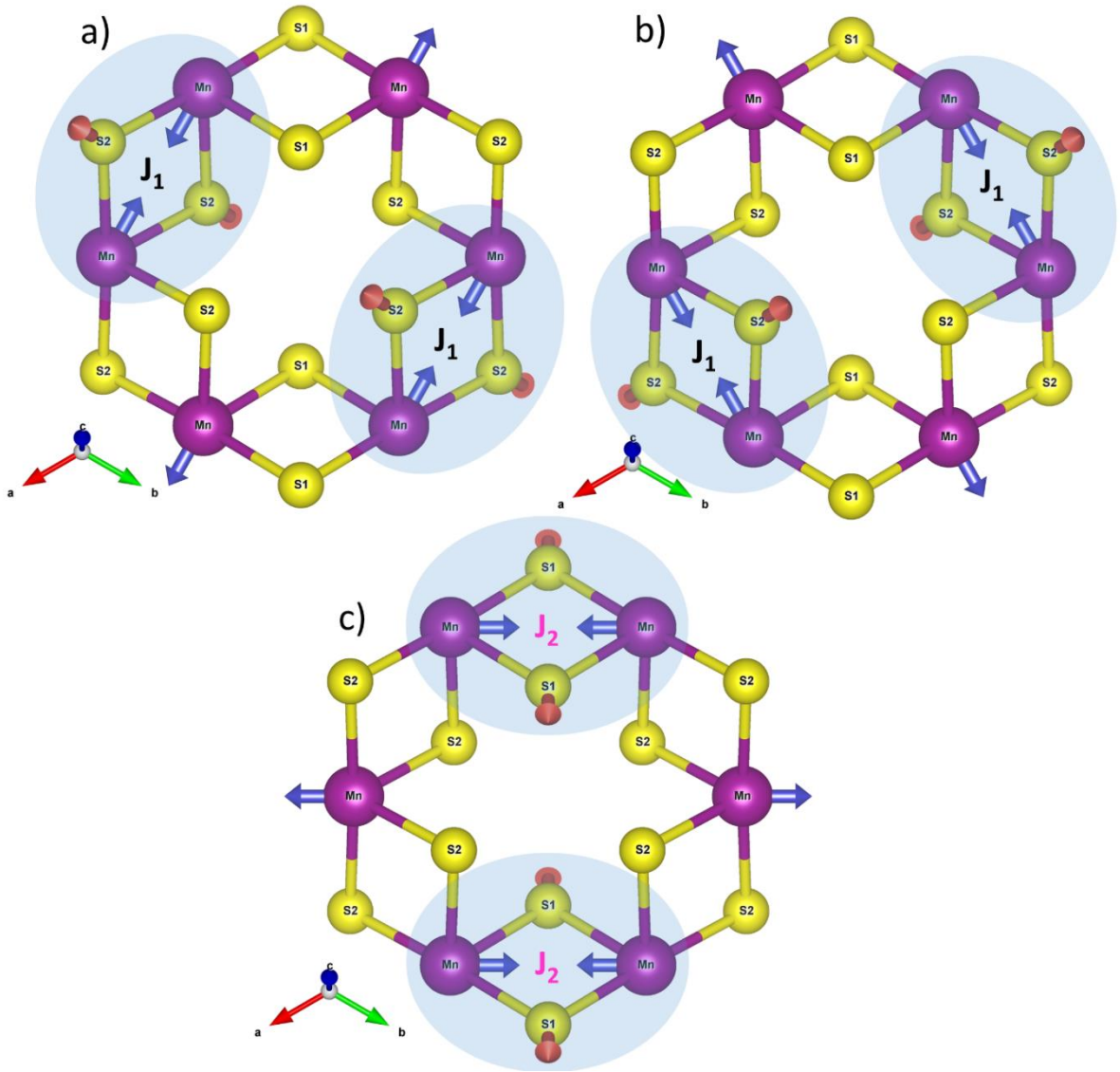


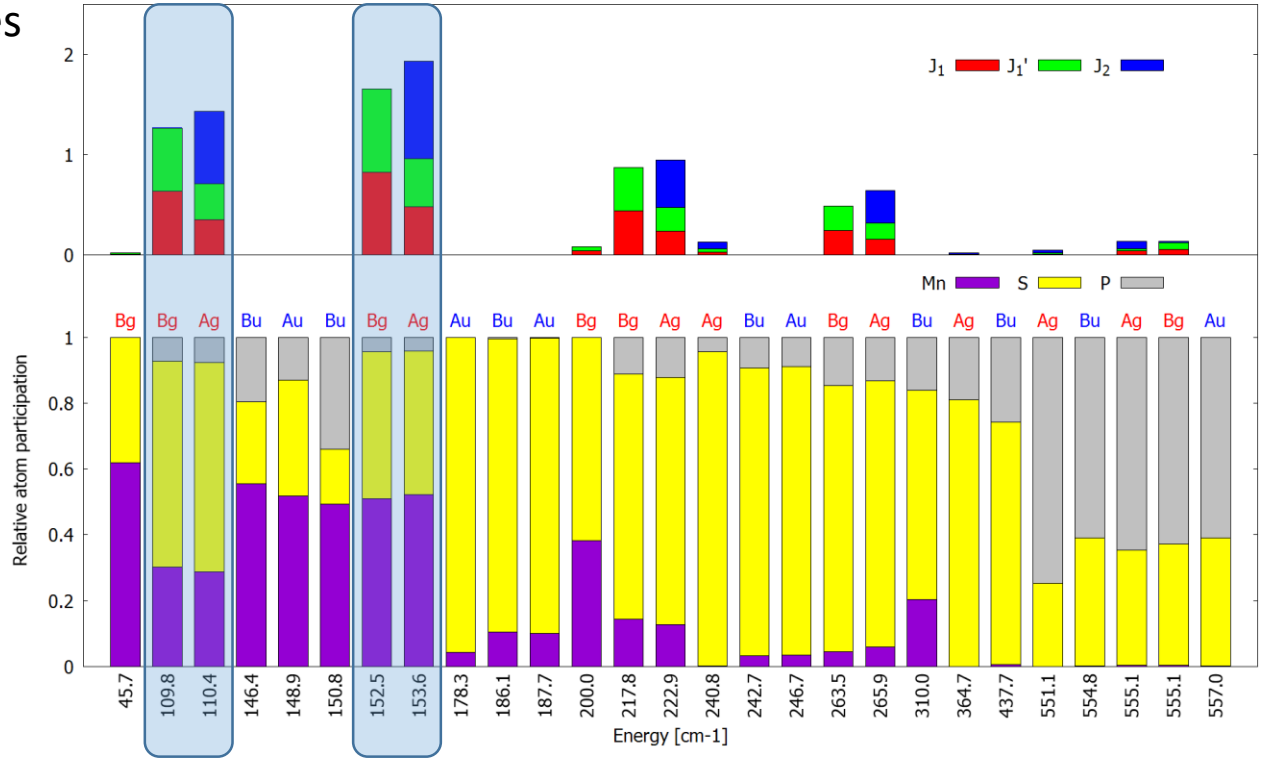
Ag mode 153.6 cm^{-1}

Movement changes the angle associated with J1 and J2.

Projection in modes associated with the super exchange angles

Virtual phonons modes, each one affecting one pair of angles





Four pairs of modes have significant projections to the virtual modes.

The projections are larger for the two modes at 120 and 155 cm^{-1} which are sensitive to the magnetic order.

Conclusion

In systems with a few **leading AFM interactions,** due to **thermal excitations**
the **atoms associated to** the **super-exchange paths**
will like to **move to decrease** the corresponding effective exchange interaction **J**

The **Raman modes** associated with these angles are **sensitive** to this effect and can give information about the magnetic transitions.

Collaborations

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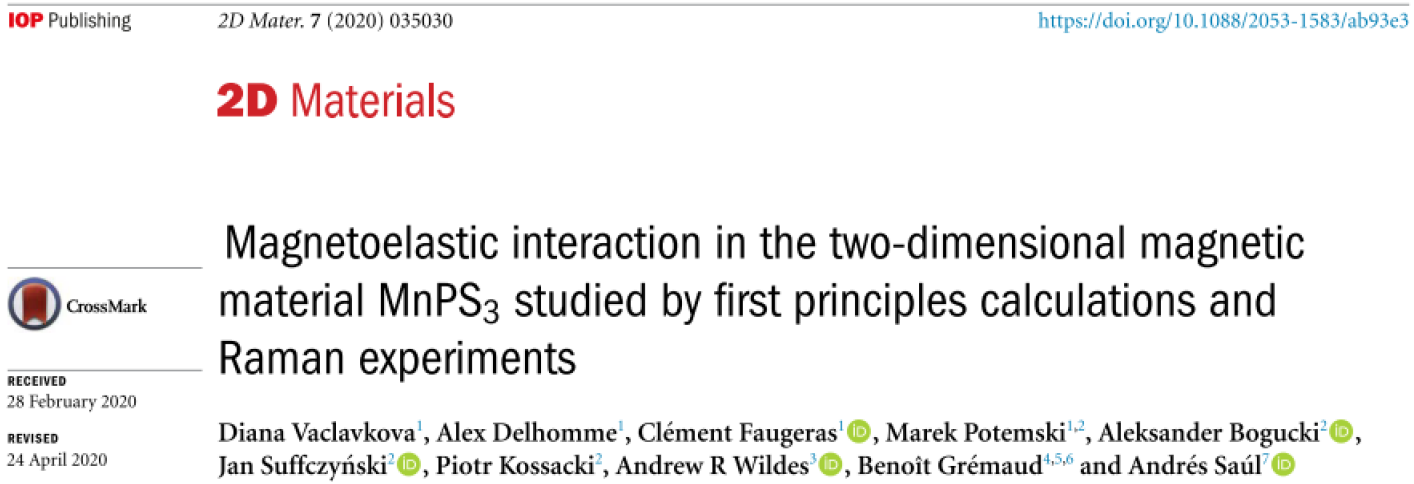

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2D Materials

Magnetoelastic interaction in the two-dimensional magnetic material $MnPS_3$ studied by first principles calculations and Raman experiments

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