Center for Solid State Physics & New Materials

LATTICE DYNAMICS IN FERRIMAGNETIC LAYERED VAN DER WAALS MATERIAL $Mn_3Si_2Te_6$

JELENA PEŠIĆ

INSTITUTE OF PHYSICS BELGRADE,
UNIVERSITY OF BELGRADE,
SERBIA

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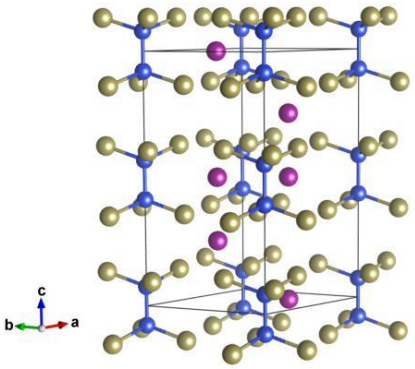
MOTIVATION

first objective	Layered magnetic van der Waals materials have lately received widespread attention due to their potential application in spintronics, magneto-electronics, data storage and biomedicine
second objective	This study provides a comprehensive insight to the lattice properties, their temperature dependence and shows arguments for existence of the competing short-range magnetic phases in $Mn_3Si_2Te_6$.

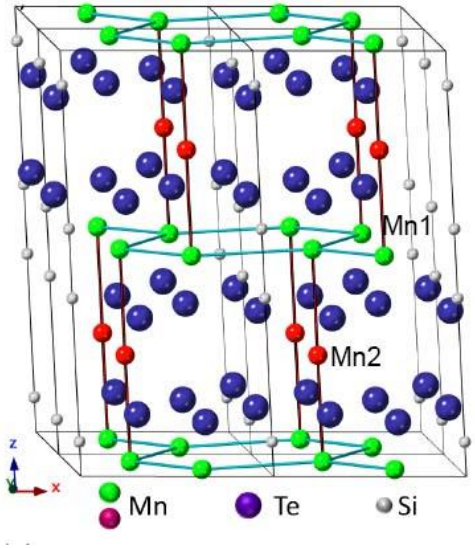
$Mn_3Si_2Te_6$ – structure

H. Vincent, D. Leroux, and D. Bijaoui, Crystal structure of Mn3Si2Te6, Journal of Solid State Chemistry 63, 349 (1986).
R. Rimet, C. Schlenker and H. Vincent, Journal of Magnetism and Magnetic Materials 25 (1981) 7-10 (1981)



The layered framework is analogous to that of $CrSiTe_3$, which is hexagonal and has a van der Waals gap between the layers. In $Mn_3Si_2Te_6$, the layers are linked by the filling of one-third of the octahedral holes within the van der Waals gap by Mn atoms at the Mn2 site, yielding a composition of $Mn_3Si_2Te_6$. **The multiplicity of Mn1 is twice that of Mn2.**

The lattice consists of planes of Mn^{2+} ions (S = 5/2, L = 0) alternating with planes of Te and Si atoms along the *c*-axis



Trigonal space group
SG 163 P-31c
Lattice parameters - experimental:
a= 7.03456 Å c = 14.2435 Å
The first principles calculations depict a strong relationship of physical structure to the magnetism.

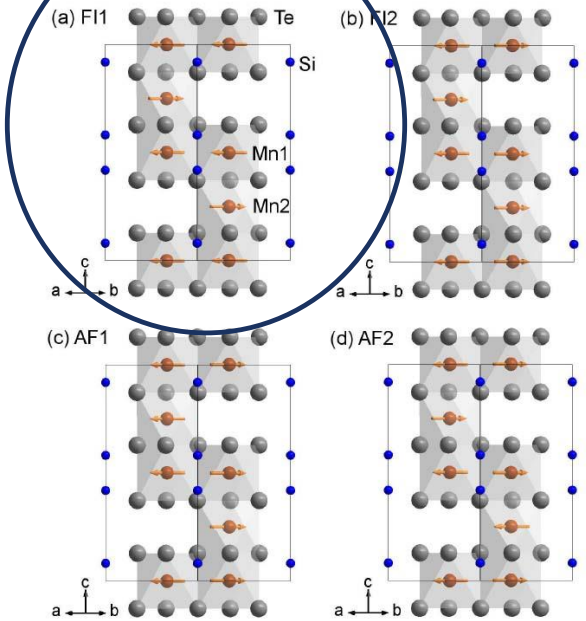
One layer of Mn atoms (Mn1 on the 4 *f* site) has a honeycomb structure, shown as green spheres, and the other layer of Mn atoms (Mn2 on the 2*c* site) are arranged in a triangular lattice, red spheres.

$Mn_3Si_2Te_6$ - MAGNETIC STRUCTURE

First principle calculations suggested a competition between ferrimagnetic ground state and three additional magnetic configurations, originating from antiferromagnetic exchange for the three nearest Mn-Mn pairs.

Ground state

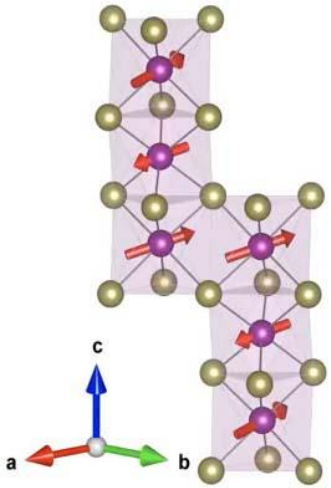
FI2=32.6 meV/Mn



AF1=20.8 meV/Mn AF2=33.8 meV/Mn

*relative to ground state FI1,, and. [1]

Ferrimagnet, $T_C = 78$ K



The magnetic spins are ferromagnetically aligned within the *ab*-plane and antiferromagnetically aligned along the *c* axis below. Neutron diffraction experiment gives that $Mn_3Si_2Te_6$ is a ferrimagnet below Tc ≈ 78K

[1] A. May et al, Phys. Rev. B 95, 174440, 2017

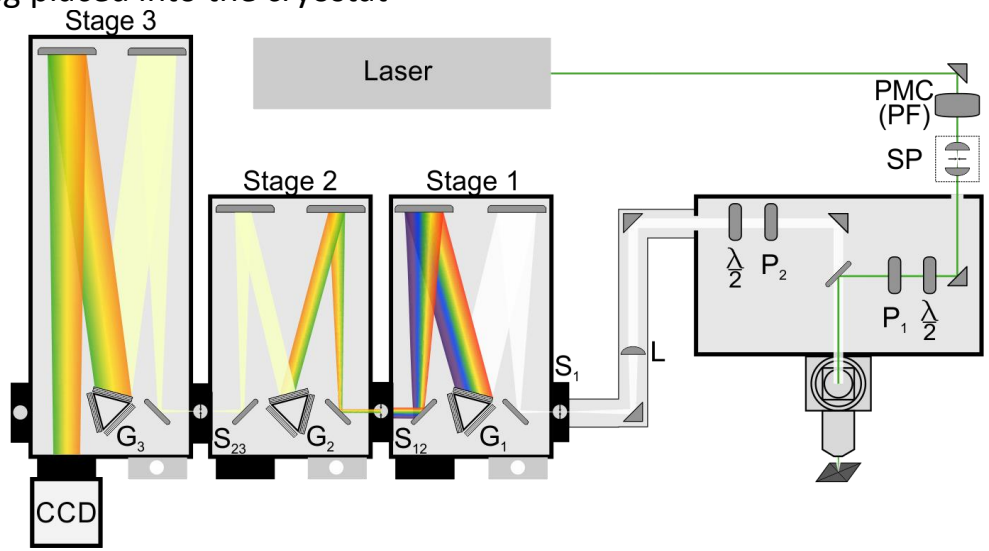
CALCULATIONS

- The calculations are based on the density functional theory formalism as implemented in Vienna Ab initio Simulation Package (VASP), with the plane wave basis truncated at a kinetic energy of 520 eV, using Perdew-Burke-Ernzehof (PBE) exchange-correlation functional and projector augmented wave (PAW) method.
- The Monkhorst and Pack scheme of k point sampling is employed to integrate over the first Brillouin zone with 12 × 12 × 10 at the Γ-centered grid. The convergence criteria for energy and force have been set to 10^{-6} eV and 0.001 eVÅ^{-1}, respectively. The DFT-D2 method of Grimme is employed for van der Waals (vdW) corrections.
- The vibrational modes are calculated using density functional perturbation theory implemented in VASP and Phonopy. It is found the energy of the ferrimagnetic state to be well above an eV per Mn below that of the non-magnetic state thus this configuration is considered in this study.

EXPERIMENTAL SETUP

Tri Vista 557 spectrometer

- backscattering micro-Raman configuration
- 1800/1800/2400 groves/mm diffraction grating combination
- measurements under high vacuum (10^{-6} mbar)
- The 514 nm line of a Coherent Ar+/Kr+ ion laser
- The samples are cleaved in air before being placed into the cryostat



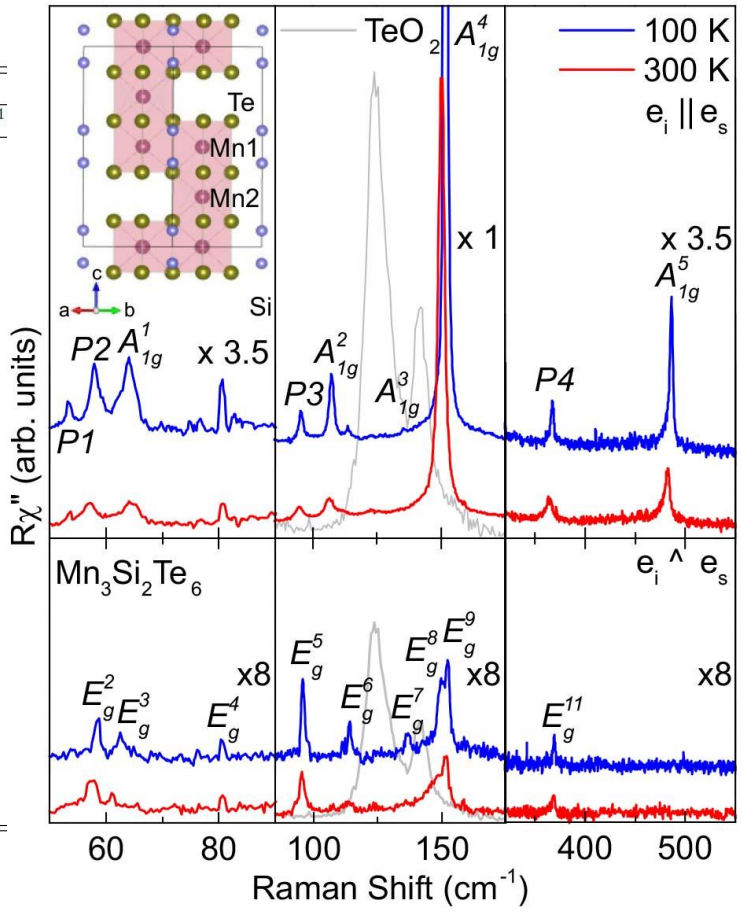
RAMAN SPECTRA

- According to the symmetry analysis there are sixteen Raman-active modes ($5A_{1g} + 11E_g$) and seventeen infrared-active modes ($6A_{2u} + 11E_u$)

- E_g symmetry modes can be observed in the Raman spectra measured in both parallel and crossed polarization configurations, whereas A_{1g} modes arise only for those in parallel polarization configuration

- Four excess modes at 53.3 cm^{-1}, 57.9 cm^{-1}, 95.3 cm^{-1} and 366.7 cm^{-1} marked with **P and attributed to overtones.**

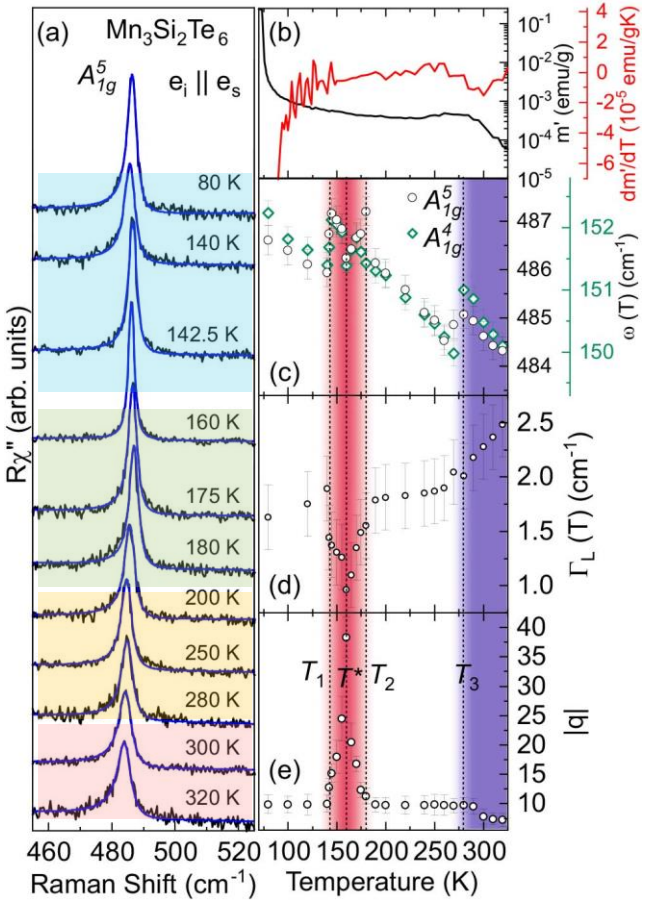
Space group $P\bar{3}1c$			
n_0	Symm.	Exp. (cm^{-1})	Calc. (cm^{-1}
1	E_g^1	-	53.1
2	$P1$	53.3	-
3	$P2$	57.9	-
4	E_g^2	58.7	58.5
5	E_g^3	62.6	61.8
6	A_{1g}^1	64.2	62.3
7	E_g^4	80.4	82.7
8	$P3$	95.3	-
9	E_g^5	95.9	90.3
10	A_{1g}^2	107.3	104.3
11	E_g^6	114.0	106.5
12	A_{1g}^3	135.4	134.2
13	E_g^7	136.6	136.1
14	E_g^8	149.8	143.4
15	A_{1g}^4	151.8	147.3
16	E_g^9	152.6	146.6
17	E_g^{10}	-	352.7
18	$P4$	366.7	-
19	E_g^{11}	368.7	354.5
20	A_{1g}^5	486.7	475.83



discrepancy between theory and experiment below 8% for all observed modes

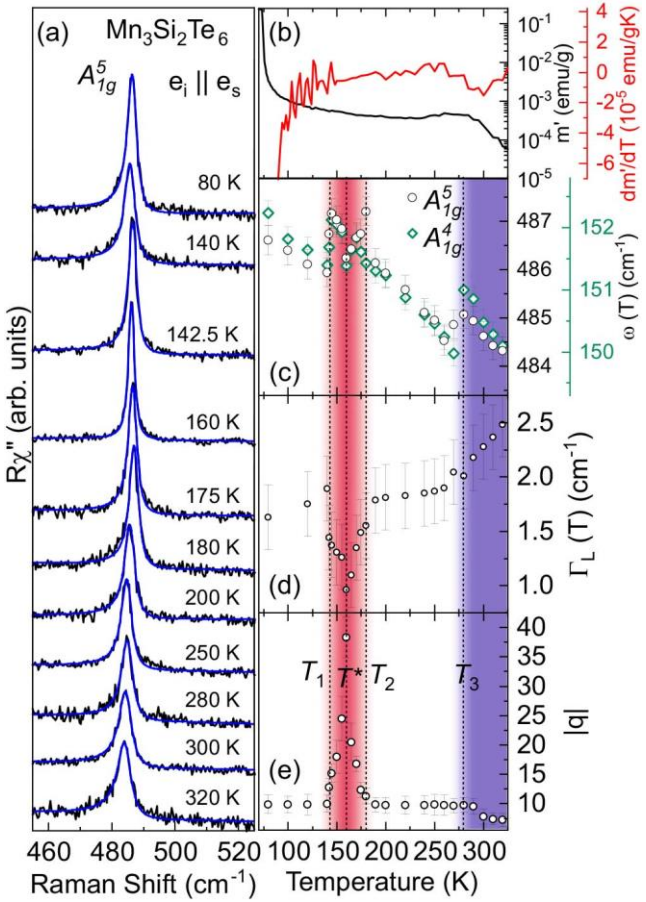
TEMPERATURE DEPENDENCE

- Some of the modes exhibit an asymmetric lineshape.
- Asymmetry may arise from coupling between phonon and other elementary excitations
- By increasing the temperature above 80 K, the A^5_{1g} mode broadens and softens up to T_1 = 142.5 K, where it abruptly narrows and shifts to higher energies followed by further softening and narrowing up to T∗ = 160 K. Additional heating leads to a broadening and hardening before the drop in phonon energy at ∼ T_2 = 190 K. In the region T_2 the mode softens and broadens with additional jump in phonon energy at T_3= 285 K
- This intriguing temperature dependence is also manifested in the asymmetry i.e. Fano parameter.
- While the **ferrimagnetic** order in $Mn_3Si_2Te_6$ is established **only** at Tc= 78 K, the **asymmetry** of the mode can be observed at **all experimental temperatures.**
- the most probably, asymmetry can be traced to enhanced spin-phonon interaction related to short-range correlations, that can survive up to temperatures well above Tc



TEMPERATURE DEPENDENCE

This unconventional temperature evolution of the A^5_{1g} Raman mode reveal three successive, *possibly magnetic*, phase transitions that may have significant impact on the strength of the spin-phonon interaction in $Mn_3Si_2Te_6$.
These are likely caused by the competition between the *various magnetic states*, close in energy



CONCLUSION

- We present an experimental and theoretical Raman scattering study of $Mn_3Si_2Te_6$ single crystals, with the focus on phonon properties in the temperature range from 80 K to 320 K.
- Phonon energies are in a good agreement with the theoretical predictions.
- Two most prominent Raman modes, A^4_{1g} and A^5_{1g} are used to study the temperature evolution of phonon properties, and reveal three subsequent phase transitions at T_1= 142.5 K, T_2= 190 K and T_3= 285 K.
- The A^5_{1g} mode exhibits strong asymmetry, most likely originating from enhanced spin-phonon coupling.

PEOPLE

Spin-phonon interaction and short range order in Mn3Si2Te6 **- S. Djurdjic Mijin, A.Solajic, J. Pesic, Y. Liu, C. Petrovic, M. Bockstedte, A. Bonanni, Z. V. Popovic and N. Lazarevic**
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- SAMPLES

Brookhaven National Laboratory

Cedomir Petrovic
Yu Liu

- RAMAN SPECTROSCOPY

Center for Solid State Physics and New Materials

IPB
UNIVERSITY OF BELGRADE | INSTITUTE OF PHYSICS | BELGRADE
NATIONAL INSTITUTE OF THE REPUBLIC OF SERBIA

Sanja Djurdjić
Nenad Lazarević
Zoran V. Popović

- CALCULATIONS

Center for Solid State Physics and New Materials

IPB
UNIVERSITY OF BELGRADE | INSTITUTE OF PHYSICS | BELGRADE
NATIONAL INSTITUTE OF THE REPUBLIC OF SERBIA

Jelena Pešić
Andrijana Šolajić

MAG Quantum Materials Group

JKU JOHANNES KEPLER UNIVERSITÄT LINZ

Michel Bockstedte
Alberta Bonanni

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