Magnetic phase diagram in rare-earth orthoferrite $HoFeO_3$ from single crystal neutron diffraction in external magnetic field.

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Introduction

Rare earth orthoferrites $RFeO_3$

Multiferroics - materials that exhibit more than one of the ferroic properties in the same phase.

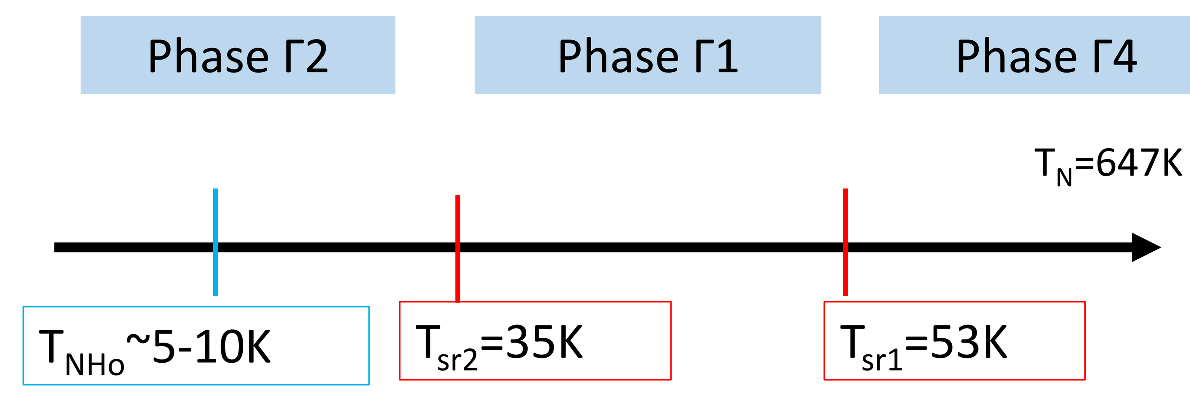
Multiferroicity at room temperature has been reported for some representatives of the rare-earth orthoferrites family RFeO3 (e.g. YFeO3, LuFeO3, SmFeO3)[1-4]. Dzyaloshinskii-Moriya interaction (DMI), which leads to a weak ferromagnetism (WF) in the Fe sublattice is proposed as one of possible reasons for the electric polarization in this materials. A spontaneous electric polarization in HoFeO3 occurs at elevated temperatures ~ 210 K

Magnetocaloric effect (MCE) - the temperature change in compounds by external magnetic field in an adiabatic process. Usually it describe by magnetic entropy change ΔS_M.

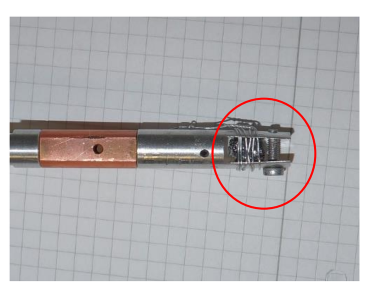
With applied magnetic field, a strong magnetocaloric effect was found in HoFeO3 at lower temperatures. Three peaks in the entropy-change occur for a field variation of 0-7 T: ΔSM=9 J/Kg K at 53 K, ΔSM=15 J/Kg K at 10 K and ΔSM=18 J/Kg K at 3 K [5]. The first peak is associated with a spin reorientation in the Fe subsystems solely. The last one should related to the Ho ordering. While the second peak may be related with some processes including both the Ho and Fe magnetic subsystems.

Magnetic structure $HoFeO_3$ in zero field

The crystal structure of $HoFeO_3$ is described by the space group Pnma - #62.
Neel temperature T_N = 647K, below which the Fe moments are ordered antiferromagnetically with a weak ferromagnetic component order with representation Γ_4.
The spin-reorientation phase transition to antiferromagnetic structure Γ_1 takes place at T_{SR1} = 53K, Fe spin rotate in plana ac at T_{SR2} = 35K.
The Ho sublattice spontaneously ordered below $T_{NR} \approx$ 10 K.[6]



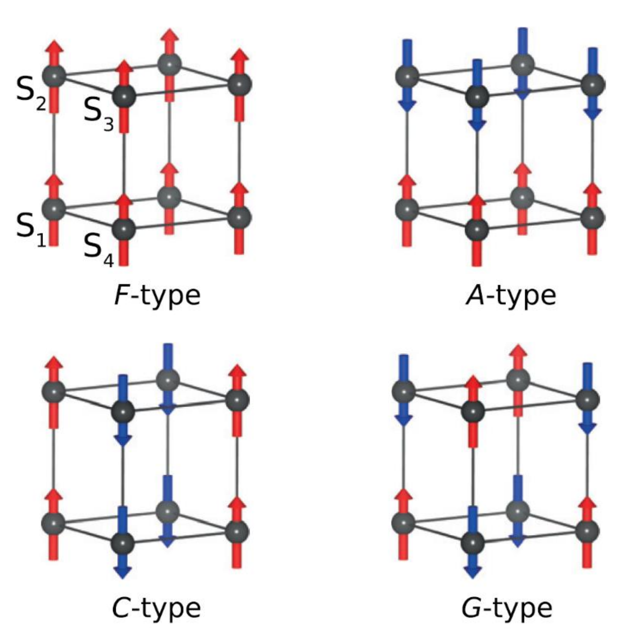
Neutron diffraction



High quality single crystal of $HoFeO_3$, dimensions 5x6x7 mm³. Neutron diffraction experiments were performed at MLZ on two axes single crystal diffractometer POLI using a new 8T magnet. Crystal was slowly cooling in the magnet with zero field.

- Temperature range 2-66K with 2 K steps.
- 8 peaks (two peaks for each types A, F, C, G)
- 7 discrete constant fields: 0.5, 1.25, 2.25, 3.5, 5, 6.5, 8T, along b direction.

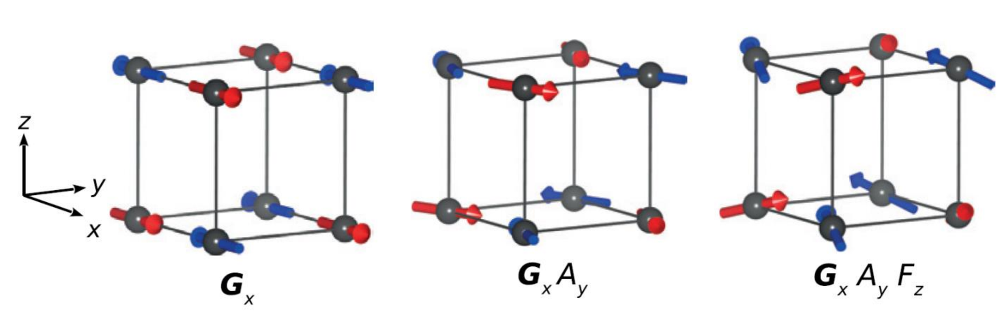
4 types of possible collinear ordering of the Fe subsystem [7,8]: F - FM ordering, A - AFM order of FM planes, C - AFM order of FM chains and G- 'full' AFM ordering, type:



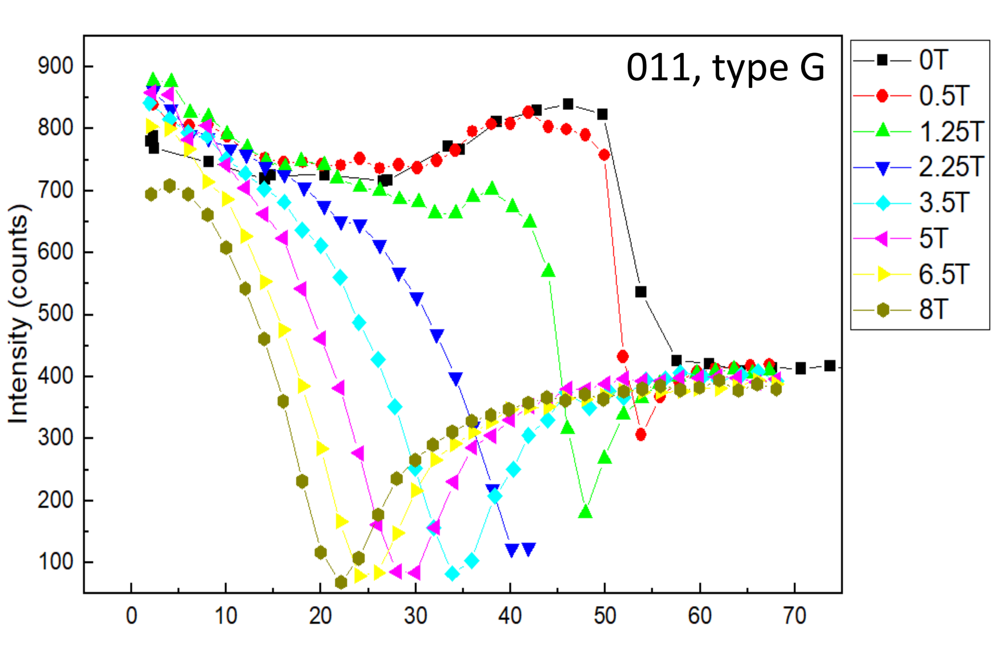
Each type of ordering will contribute to the intensity of different reflections:

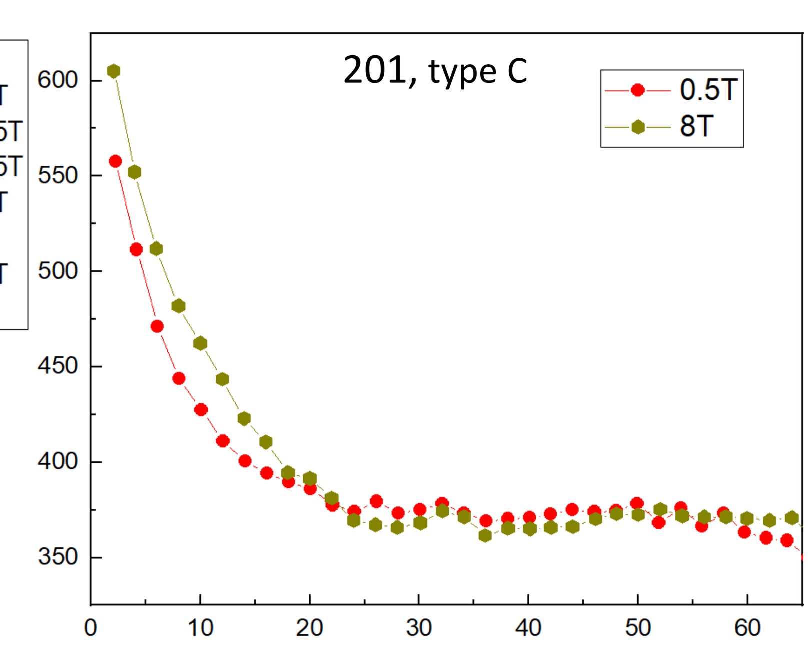
Type	even	odd	experiment	
F	h+l; k		002	200
A	h+l;	k	113	311
C	k	h+l;	201	102
G		h+l; k	011	110

DM interactions leads to canting:

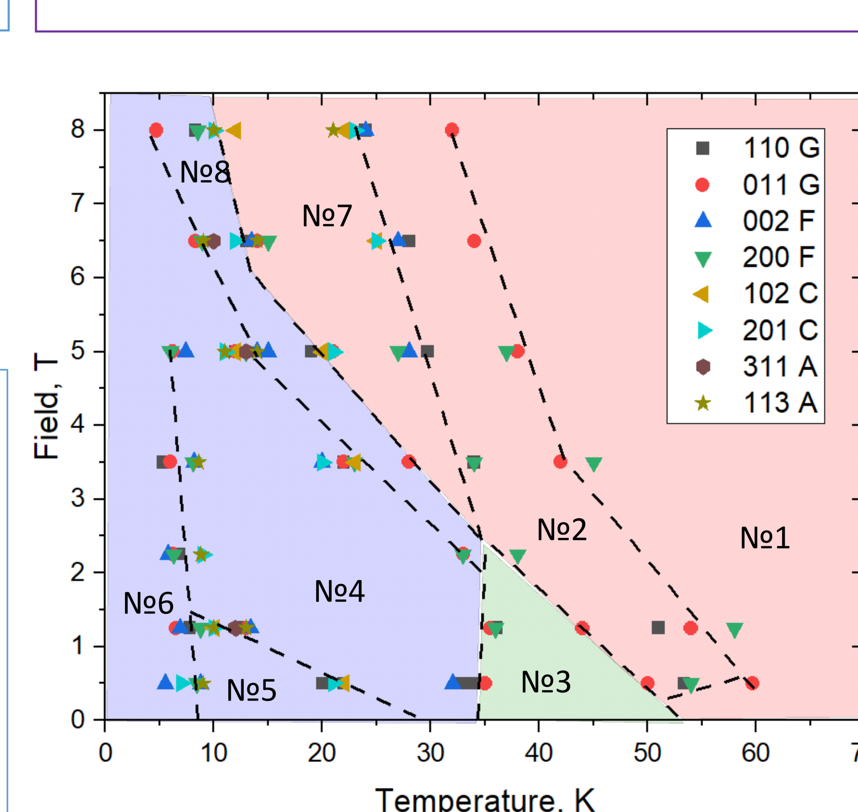


Temperature dependence of the reflections 011, type G and 201, type C in an external magnetic field. Colors – different magnetic fields. Errors bar less than symbol.





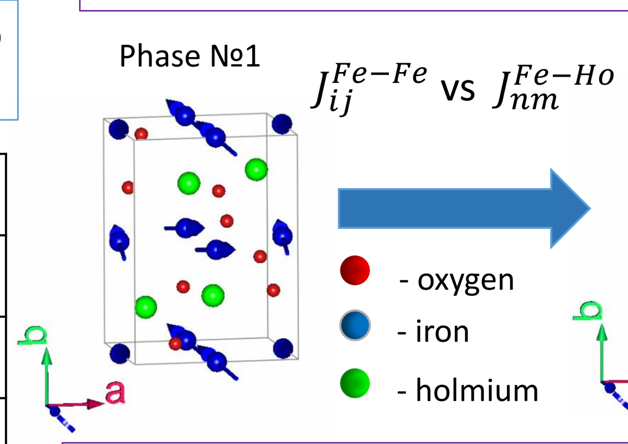
Results



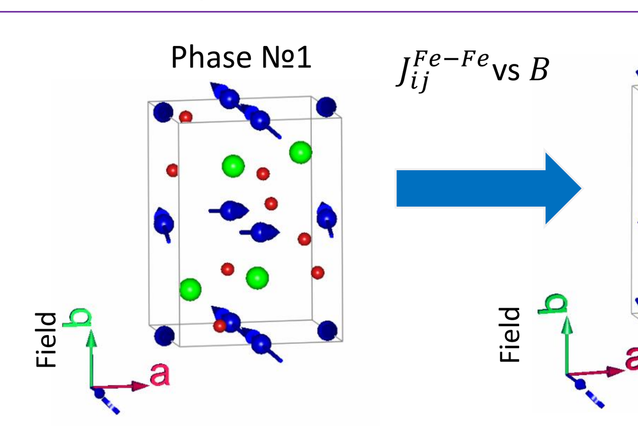
Magnetic phase diagram of $HoFeO_3$. Dotted line – phase boundaries. Color area – region that are describe by different magnetic representation: red – Γ_4, green – Γ_1, blue – Γ_2. The numbers indicate phases.

- All phase transitions are described by magnetic representation as in zero field.
- Magnetic phases 3 and 5 are suppressed by the field.
- New intermediate phases appear

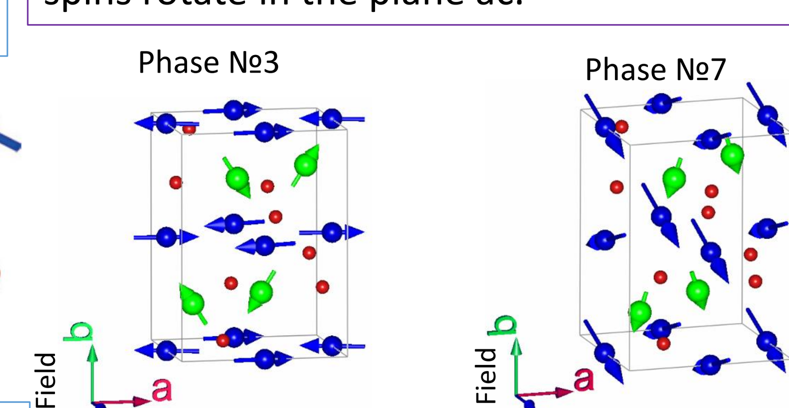
All spin-orientation transitions can be described using competition between exchange interactions inside the crystal and an external magnetic field. For example :



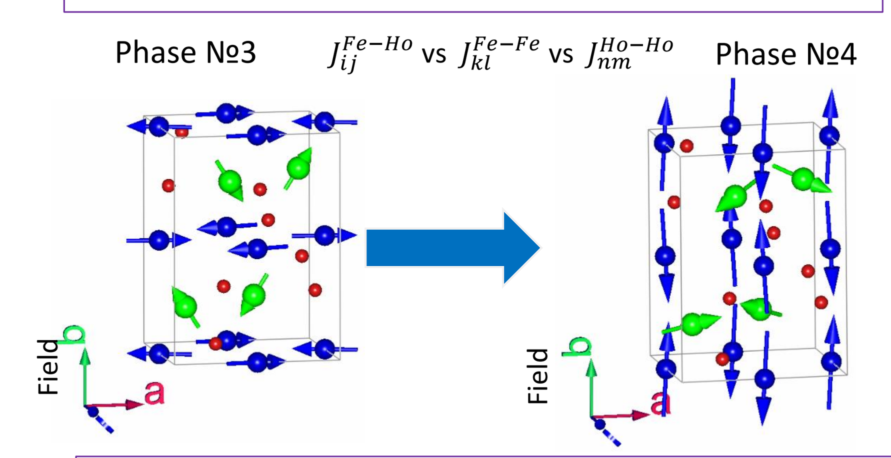
Ho ion in an external field from the Fe -> Fe polarized Ho -> appears J_{nm}^{Fe-Ho} -> the Fe spins rotate in the plane ac.



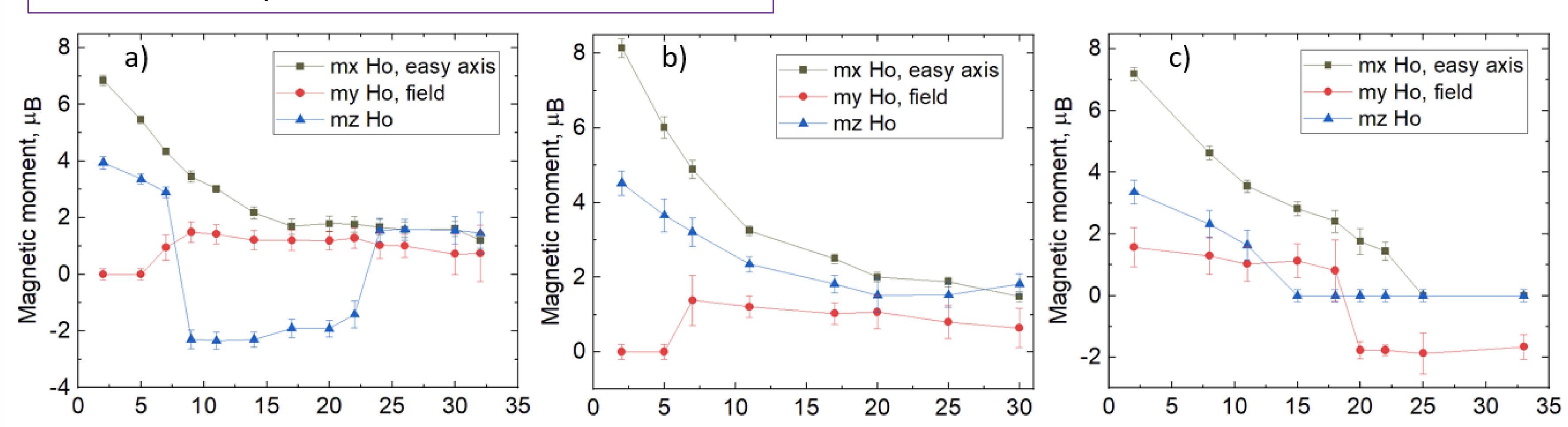
The external field compensates field from Fe sublattice. The total field is not enough to create a magnetic moment on Ho ion.



In the phase 3 energy of J_{nm}^{Fe-Ho} > B and J_{nm}^{Fe-Ho} rotate the Fe spins in the plane ac.
In the phase 7 energy of J_{nm}^{Fe-Ho} < B and B holds the Fe spins.



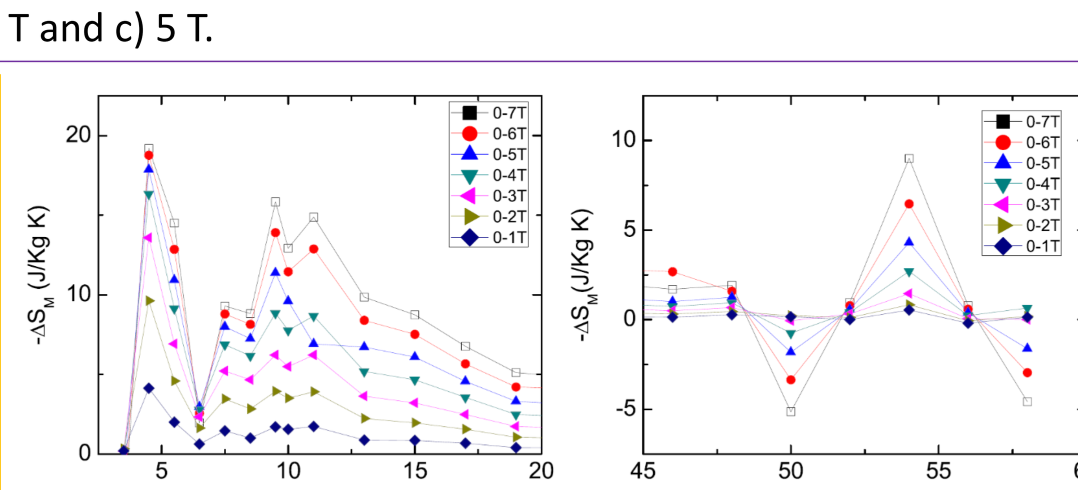
The exchange J_{nm}^{Ho-Ho} has opposite sign with exchange J_{ij}^{Fe-Ho}. This leads to rebalancing of energy [9].



Temperature dependence of the *x*, *y* and *z* components of the Ho magnetic moments in fields of a) 0.5 T, b) 1.25 T and c) 5 T.

Concluding remarks:

The $HoFeO_3$ has a rich phase diagram in an external magnetic field. The competition between the external magnetic field, the antisymmetric DMI and isotropic exchange interactions between the Fe and Ho sublattice and within the Fe sublattice leads to a complex picture of phase transitions in the rare-earth orthoferrite $HoFeO_3$. According to our considerations we can outline 8 different magnetic phases, induced or suppressed by the magnetic field. The richness of this phase diagram is the result of a very delicate balance of exchange interactions in the crystal and the external magnetic field. Such complex behavior may cause the useful functionality of rare-earth orthoferrites. The obtained results are in good agreement with the results from inelastic neutron scattering experiments[9], from which the values of exchange interactions were calculated and also with measurements of the magnetic entropy change where peaks of ΔS_M lie near the spin reorientation transition between phases 1 or 2 and 3; phases 4, 5 and 6[10].



Magnetic entropy change ΔS_M of HoFeO3 as a function of temperature for a field variation from 0–1 to 0–7 T.

References: [1]J.-H. Lee, et al., Phys. Rev. Lett. 107, 117201, 2011; [2] P. Mandal, et al., Phys. Rev. Lett. 107, 137202, 2011; [3]U. Chowdhury, et al., Appl. Phys. Lett. 105, 052911, 2014.; [4]Ke, Y.-J. et al. Sci. Rep. 6, 2016; [5]M. Shao et al. Solid State Communications 152, 947–950, 2012; [6]T. Chatterji, et al., AIP ADVANCES 7, 045106, 2017;[7] E. Bousquet, A. Cano J. Phys.: Condens. Matter **28** (2016) [8]J. Mareschal and J. Sivardi`ere, J.de Physique **30**, 967 (1969);[9]A.K.Ovsianikov et al., JMMM, Volume 507, 166855, 2020 ; [10] M. Shao et al. / Solid State Communications 152 (2012) 947–950

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