# Experimental report

21/09/2018

**Proposal:** 5-31-2388 **Council:** 10/2014

**Title:** Modification of AF structure in La2O3(Fe(1-x)Mnx)2Se2 under pressure

**Research area:** Physics

**This proposal is a new proposal**


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**Samples:** La2O3(Fe1-x,Mnx)2Se2, x=0.90
La2O3(Fe1-x,Mnx)2Se2, x=0.95

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D20 | 4 | 4 | 13/07/2015 | 17/07/2015 |


## Abstract:

In the proposed experiment we suggest to study two La2O3(Fe1-xMnx)2Se2 x = 0.9 and x =0.95 systems that exhibit different AF structures at low temperatures using D20 and Paris-Edinburgh pressure cell. The two AF structures that have nearly the same phase transition temperature, differ in the direction of the Fe/Mn moments with respect to the tetragonal axis. Electronic structure calculations suggest that it should be possible to change the moment directions under pressure. It is the aim to determine the pressure dependence of crystallographic parameters (especially of the interatomic distances and bond angles) and bring the in relation with magnetic structure. We would like to know whether it would be possible to switch the direction of Fe/Mn moments under pressure before eventually destroying the AF order or modifying the crystal structure. We ask for 4 days on D20.

The subject of the study were two representative concentrations of polycrystalline samples with the composition $La_2O_3(Fe_{1-x}Mn_x)_2Se_2$ investigated under high pressure up to ~9 GPa down to 5 K. These tetragonal systems (space group *I4/mmm* that are not superconducting) are closely related to very intensively studied superconducting iron pnictides and chalcogenides. In the known iron pnictide and chalcogenide systems the Fe ion is tetrahedrally coordinated [1,2] and the environment is non-planar. The superconductivity in the latter systems appear either under pressure or via substitutions which alters the local Fe geometry. A large number of studies show that the highest superconducting phase transitions are achieved for X-Fe-X (X = pnictide/chalcogenide atom) bond angle that is close to the ideal value of 109.47 degrees. In $La_2O_3(Fe_{1-x}Mn_x)_2Se_2$, Fe has a planar Fe–O coordination with an additional non-planar Fe–Se bonding forming the iron oxyselenide layer as displayed in Fig. 1. $La_2O_3Fe_2Se_2$ is reported to be a Mott insulator and shows an AF magnetic order with a transition just below 90 K [4].

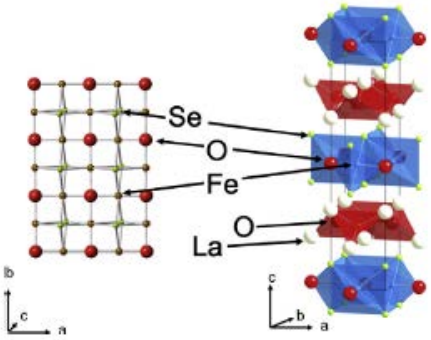


**Fig. 1:** Schematic representation of the crystal structure of $La_2O_3Fe_2Se_2$. The Mn takes the same position as Fe.

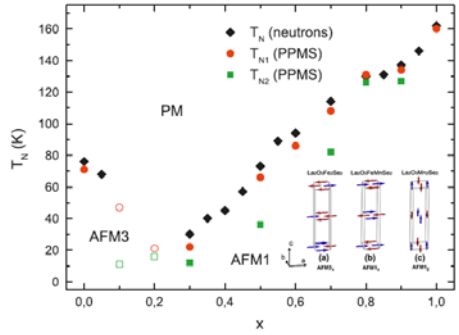


**Fig. 2:** Magnetic phase diagram of $La_2O_3(Fe_{1-x}Mn_x)_2Se_2$. In the inset the three different magnetic structures encountered for (a) $x < 0.1$, (b) $0.25 < x < 0.9$ and (c) $x > 0.9$ are shown, respectively. Note that x = 0 (AFM3) and x = 0.5 (AFM1) systems have different AF structure shown as insets a) and b) respectively. After [3].

The neutron diffraction experiment was carried out on the high-flux D20 diffractometer. For the experiment we have finally selected x = 0 and x = 0.5 concentrations that order antiferromagnetically at nearly identical temperatures (see Fig. 2) and stand at the two opposite sides of a region with no magnetic order. About 40 mg of samples were enclosed together with deuterated methanol/ethanol mixture inside the Paris-Edinburgh cell attached to a closed-cycle refrigerator and cooled under a semi-constant pressure generated by a compressor as fast as possible to ~ 80-100 K while collecting data. At this temperature few data sets were collected to resolve the crystal structure before cooling down to ~5 K. On warming up the data were also collected before increasing the pressure at high temperature. For the x = 0.5 sample, we have performed three pressure runs, at ~ 1.7 GPa, 4.4 GPa and at 7.8 GPa. For the x = 0.0 system we have collected data at ~ 2.4 GPa, ~5.7 GPa and ~8.9 GPa. The pressure has been monitored in-situ by following Bragg reflections of small amount of Pb and using its equation of state.

It appears that while the x = 0.5 system exhibits under pressures neither structural nor magnetic structure modifications, the x = 0 system shows a severe magnetic structure change already at the lowest applied pressure.

In Fig. 3 we show the best fit to experimental data (red points) taken at 5 K, 7.8 GPa on $La_2O_3FeMn_2Se_2$. The results suggest that while the c axis parameter decreases at a rate of ~ -0.13 Å/GPa, the a axis parameter only at a rate of ~ -0.006 Å/GPa resulting to a reduced c/a ratio at high pressure. This, in turn, with the La and Se positional paremeters changing only marginally, leads to a modified atomic distances and bonding angles involving Fe/Mn. Notably, the Se-Fe/Mn and La-Fe/Mn distances decrease significantly, but the angle Fe/Mn-Se-Fe/Mn increases from 96.1 at ambient pressure [3] to 98.1 degrees at 7.8 GPa, still well below the ideal value of 109.47 degrees for which many pnictides/chalcogenides exhibit highest superconducting transition temperatures. The distance

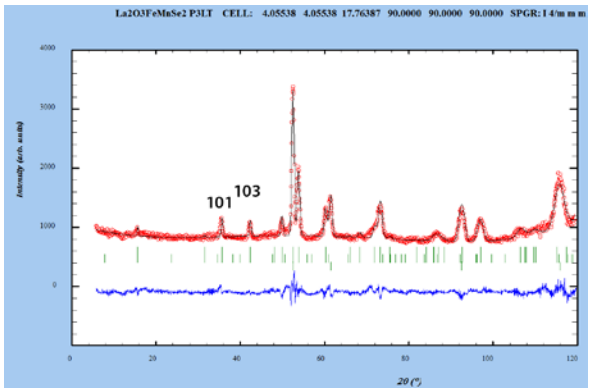


**Fig. 3:** The best fit (black line) to experimental data (red points) taken at 5 K, 7.8 GPa on $La_2O_3FeMnSe_2$. Ticks from the bottom denote positions of Bragg reflections belonging to Pb, the magnetic and nuclear structure of the sample, respectively. The blue line is the difference between experiment and the best fit.

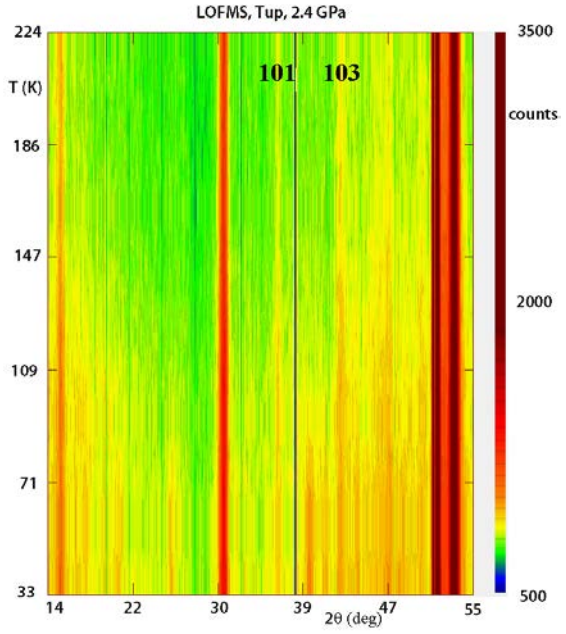


**Fig. 4:** Color coded temperature dependence of a portion of the diffracted intensity taken on the $La_2O_3Fe_2Se_2$ Sample under pressure of 2.4 GPa.

between Fe/Mn is reduced only marginally and the magnetic moment stays within the error bars constant and equal to about 3.3 $\mu_B$/Fe(Mn). We are not able to distinguish betwee possible different moment on Fe and Mn that are both assumed to be in a divalent state. We conclude that no evidence of any modification to the crystal or magnetic structure is found to pressure of ~ 8 GPa for the x = 0.5 system. The antiferromagnetic structure remains of the same type as shown in Fig. 2, inset b. However, we find an enhancement of the magnetic phase transition temperature that increases with pressure at a rate of ~ 2 K/GPa.

As mentioned above, the x = 0 system behaves (although we observe asimilar reduction of the a and the c axis parameters with pressure) from the point of view of magnetism differently. This is documented in Fig. 4 in which we show color-coded temperature dependence (increasing T) of the diffracted signal between 14 and 55 deg. Clearly, new Bragg reflections are present in the diffractogram at low temperatures (compare with Fig. 3). All the yet unindexed reflections disappear around 100 K, while the 101 and 103 reflections that are labeled in Fig. 4 decrease in intensity continuously up to ~160 K. In the high temperature limit only reflections belonging to the nuclear structure (I4/mmm) remain. The observation of new, uniandexed reflections and a significant increase of the transition temperature (actually a split of originally one transition into two) suggests a severe modification of exchange interactions in the system. Up to now we were unable to index the newly observed magnetic reflections and note that they are not indexable using commensurate propagation vectors. This part is not satisfactory and needs further work. We hope to be able to relate the change in the magnetic structure to the electronic structure calculations [5].

**References**

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