Experimental report

11/04/2019

Proposal:	**5-31-2600**	**Council:**	4/2018
Title:	Magnetic Structures of Pillared Honeycomb Diferrites K2-x Fe4-y My O7 (M = Si, Ge, Ti, Mn, Ir, Rh)		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Jens HUNGER**
Experimental team:	Thomas DOERT Jens HUNGER
Local contacts:	Emmanuelle SUARD

Samples:

K1.52 Fe3.95 Ir0.05 O7
K1.66 Fe3.82 Rh0.18 O7
K1.69 Fe3.69 Ti0.31 O7
K1.45 Fe3.52 Si0.48 O7
K1.22 Fe2.00 Mn2.00 O7
K1.56 Fe3.56 Ge0.44 O7

Instrument	Requested days	Allocated days	From	To
D2B	4	2	12/10/2018	14/10/2018

Abstract:

The new ferrate K2-xFe4O7 (x = 0.3 - 0.5, P-31m) is composed of honeycomb layers of edge sharing [FeO6] octahedra which are interconnected to a three-dimensional framework by [Fe2O7] diferrate units with tetrahedrally coordinated Fe cations. The potassium cations are located in the two-dimensionally linked cavities of the framework. Magnetisation measurements suggest complex antiferromagnetic behaviour of K2-xFe4O7. First powder neutron diffraction data revealed a magnetic structure with c' = 2 c and all moments parallel c (P-31c, T = 300 K). The honeycomb layers are ferromagnetically ordered while the couplings of the tetrahedra are antiferromagnetic. The substitutions K2-xFe4-yMyO7 (M = Si, Ge, Ti, Mn, Ir, Rh) with preferential site occupation (octahedral site: Mn, Ir, Rh; tetrahedral site: Si, Ge, Ti) show drastic differences in magnetic behaviour. Profound investigation of the magnetic structures will lead to deeper insight into correlations between magnetic behaviour and chemical bonding situation of these wide-bandgap semiconducting compounds with potential high ionic conductivity. Therefore, we propose thermal neutron powder diffraction measurements at 300 K and 5 K.

$K_{2-x}Fe_{4-y}M_yO_7$

We measured thermal neutron powder diffraction of $K_{2-x}Fe_{4-y}M_yO_7$ (M = Fe, Ir, Ge, Mn) samples at room temperature and 5 K using instrument D2B with a wavelength of 1.594 Å and the 10" collimator. Diffraction data was collected in 25 steps with a step width of 0.05° and a monitor value of 200000 counts. 10 repetitions were used to obtain data with good counting statistics within six hours for each sample and temperature. LAMP [1] with macros "straight_2D" and "total" was used to reduce the 2D data to 1D diffraction patterns (Figure 2).

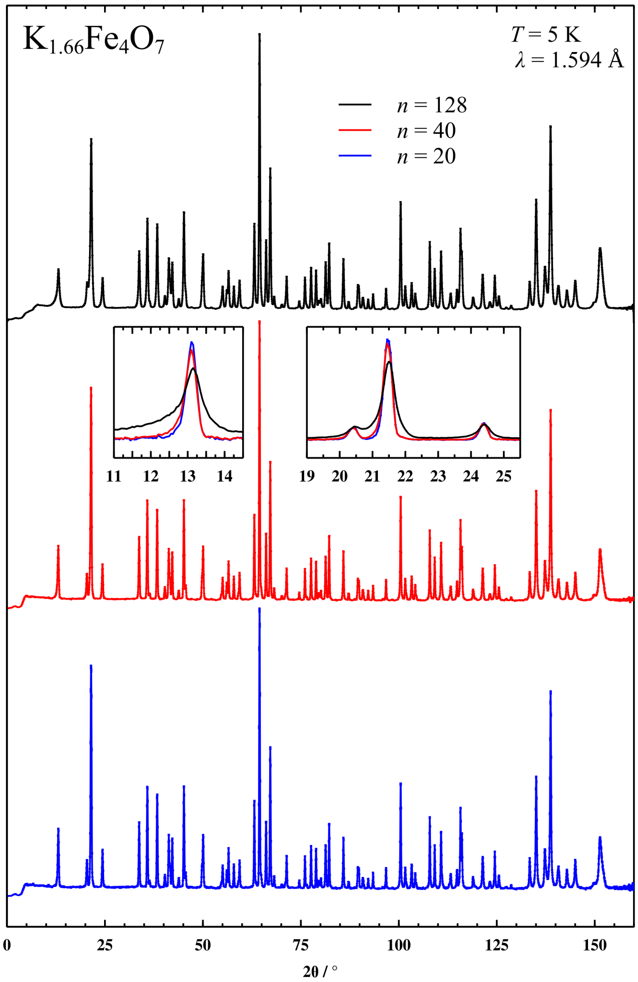

Figure 1: $K_{1.66}Fe_4O_7$ – comparison of processed data obtained using different detector heights.

Reduced data obtained from only 40 channels around the vertical centre of the detector leads to significant reduction of asymmetry at low scattering angles and increase of resolution without relevant decrease of signal-to-noise ratio compared to reduced data obtained from all detector channels (128). Use of only 20 channels around the vertical centre of the detector yields no relevant improvement or even worsening. As an example, reduced data of $K_{1.66}Fe_4O_7$ obtained using different number of detector channels is compared in figure 1.

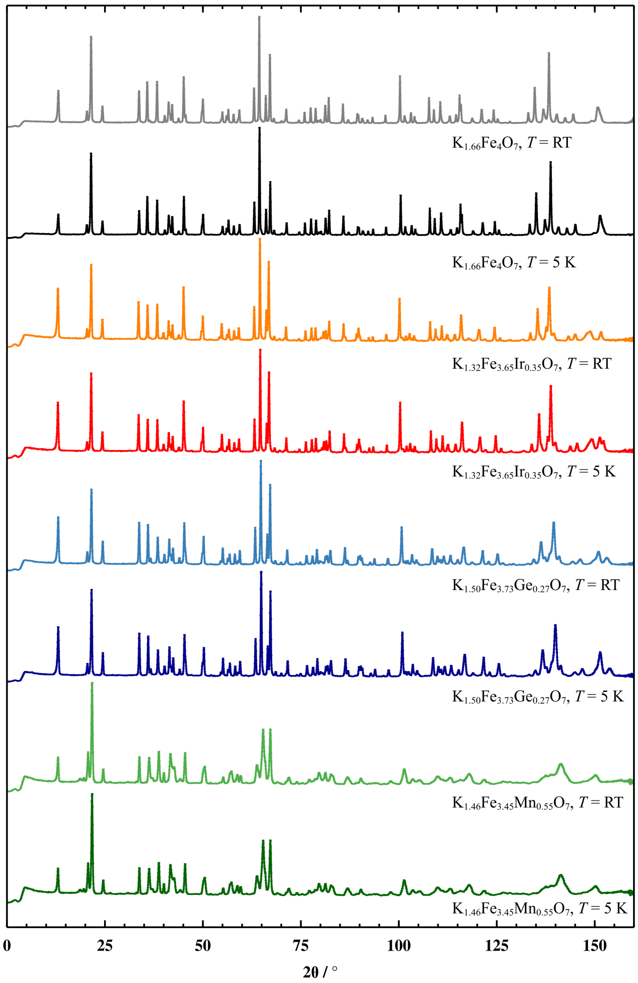

Figure 2: $K_{2-x}Fe_{4-y}M_yO_7$ – processed neutron powder diffraction data from 40 channels around the vertical centre of the detector.

Rietveld refinements with the data from the unsubstituted $K_{1.66}Fe_4O_7$ and the Fe/Ir substituted sample were possible with the conventional structural model [2] in satisfying quality (Figure 3). In case of the Fe/Ge and Fe/Mn substituted samples, acceptable refinement results with that model could not be achieved up to now. Therefore, refinements with more sophisticated models concerning modeling of the potassium ion disorder and local distortions on the framework metal ion site introduced by substitution of Fe by Ge and Mn, respectively, are necessary and still in progress. Furthermore, we try to optimize these models in combination with X-ray powder and single crystal diffraction data.

However, with the current state of refinements some general trends are already extractable. As

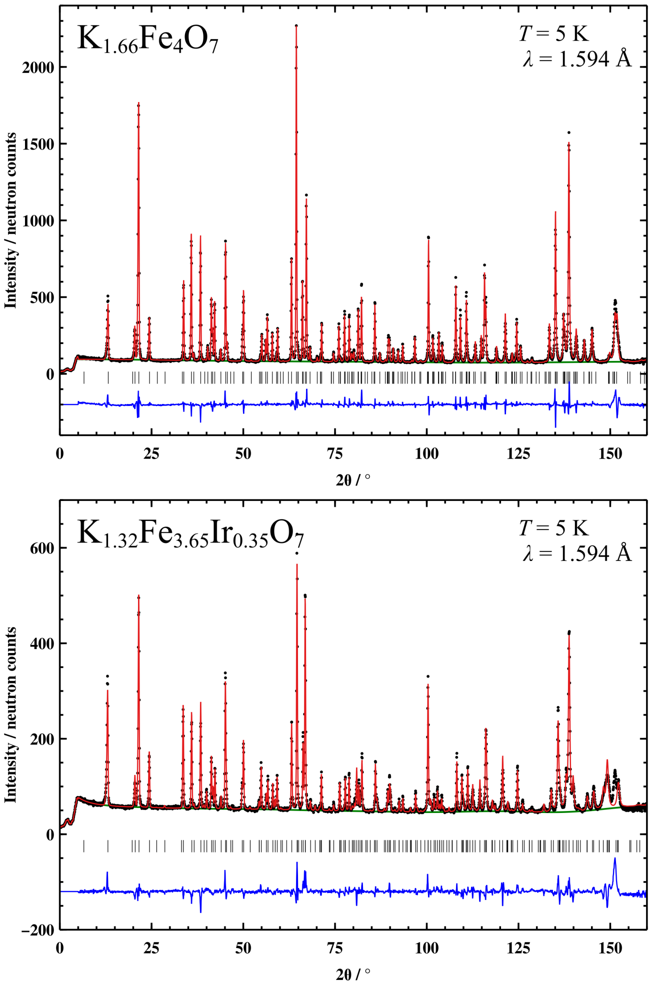

Figure 3: $K_{2-x}Fe_{4-y}M_yO_7$ – Rietveld refinements of the low temperature neutron powder diffraction data of the unsubstituted and Fe/Ir substituted sample.

expected, unit cells of the Fe/Ge and Fe/Mn substituted structures are significantly smaller compared to the unsubstituted structure (Table 1), which is mainly due to shorter a and b axes. In case of the Fe/Ir substituted structure, this shortening is overcompensated by elongation in stacking direction c.

The refined magnetic moments on the framework cation sites (Table 2) show different variations depending on the type of the substituent. The general trends are independent of temperature. The magnetic moment on the octahedrally coordinated site is considerably increased by substitution with Ge or Mn, whereas it is only slightly decreased by substitution with Ir. On the tetrahedrally coordinated site, slight decrease of magnetic moment in case of Ir or Ge substitution and distinct decrease in case of Mn substitution is observed, respectively.

$TbTe_{1.8}$

We recently reported on the structure of three different rare earth metal polytellurides $RETe_{1.8}$ (RE = Gd, Tb, Dy) with a layered structure, closely related to the ZrSSi structure type [3]. The structure consists of puckered layers of $[RETe]^+$ which are separated by planar $[Te]^-$ layers, which are built up of linear Te_2^{2-} and Te_3^{4-} anions. In contrast to $GdTe_{1.8}$, which is paramagnetic down to T = 2 K, $TbTe_{1.8}$ and $DyTe_{1.8}$ are antiferromagnetically ordered below T_N = 12 K ($TbTe_{1.8}$) and T_N = 10 K ($DyTe_{1.8}$), respectively. Because of the commensurate layered structure, the antiferromagnetic ordering attracted our interest and we intend to study this system in more detail. The magnetically active Tb^{3+} ions are only present in the puckered $[RETe]^+$ layers and the $[Te]^-$ layers could be seen as diamagnetic spacers. In the simplest case, an antiferromagnetic ordering should only occur either perpendicular or orthogonal to the c axis within the $[RETe]^+$ layers. However, the origin

Table 1: $K_{2-x}Fe_{4-y}M_yO_7$: Lattice parameters from Rietveld refinements in space group $P\bar{3}1c$.

Compound	T	a / Å	c / Å	V / Å^3
$K_{1.66}Fe_{4.00}O_7$	5 K	5.17598(4)	13.8678(12)	321.75(6)
	RT	5.18265(3)	13.88525(14)	322.990(4)
$K_{1.32}Fe_{3.65}Ir_{0.35}O_7$	5 K	5.1618(3)	13.9641(11)	322.22(4)
	RT	5.16890(17)	13.9813(6)	323.50(2)
$K_{1.50}Fe_{3.73}Ge_{0.27}O_7$	5 K	5.1452(2)	13.8903(8)	318.46(2)
	RT	5.1530(3)	13.9055(9)	319.77(3)
$K_{1.46}Fe_{3.45}Mn_{0.55}O_7$	5 K	5.0981(10)	13.921(5)	313.33(12)
	RT	5.1047(10)	13.932(6)	314.39(13)

Table 2: $K_{2-x}Fe_{4-y}M_yO_7$: Magnetic moments $\parallel c$ from Rietveld refinements in space group $P\bar{3}1c$.

Compound	T	$(\mathrm{Fe}/M)_1^{oct.}$		$(\mathrm{Fe}/M)_2^{tet.}$	
		M / μ_B	Δ/μ_B	M / μ_B	Δ/μ_B
$K_{1.66}Fe_{4.00}O_7$	5 K	−4.18(12)	0	3.81(10)	0
	RT	−4.02(4)	0	3.68(4)	0
$K_{1.32}Fe_{3.65}Ir_{0.35}O_7$	5 K	−3.91(37)	−0.27	3.60(30)	−0.21
	RT	−3.68(19)	−0.34	3.39(15)	−0.29
$K_{1.50}Fe_{3.73}Ge_{0.27}O_7$	5 K	−4.86(16)	0.68	3.76(16)	−0.05
	RT	−4.53(17)	0.51	3.50(16)	−0.18
$K_{1.46}Fe_{3.45}Mn_{0.55}O_7$	5 K	−4.87(26)	0.69	3.25(21)	−0.56
	RT	−4.57(24)	0.55	2.96(19)	−0.72

of the antiferromagnetic ordering might be more complex with interactions between the $[RE\mathrm{Te}]^+$ layers.

To obtain first insights, we collected neutron powder diffraction data of $TbTe_{1.8}$ at room temperature and T = 4 K (Fig. 4). As expected, no magnetic contribution to Bragg scattering is observed at room temperature and the data of the paramagnetic phase could be fitted with the nuclear structure model ($P4/n$, a = 9.60580(9) Å, c = 17.8526(3) Å, V = 1647.29(3) Å^3) out of the box. Refinements with complex models for the low temperature antiferromagnetic phase are still under progress since it was not possible to explain the observed huge magnetic scattering contribution with simple models obtained from representation analysis of the parent structure.

References

[1] D. Richard, M. Ferrand, and G. J. Kearley, *Journal of Neutron Research* **4**, 33 (1996).

[2] R. Albrecht, J. Hunger, T. Block, R. Pöttgen, A. Senyshyn, T. Doert, and M. Ruck, *ChemistryOpen* **8**, 74 (2019).

[3] H. Poddig, T. Donath, P. Gebauer, K. Finzel, M. Kohout, Y. Wu, P. Schmidt, and T. Doert, *Zeitschrift für anorganische und allgemeine Chemie* **644**, 1886 (2018).

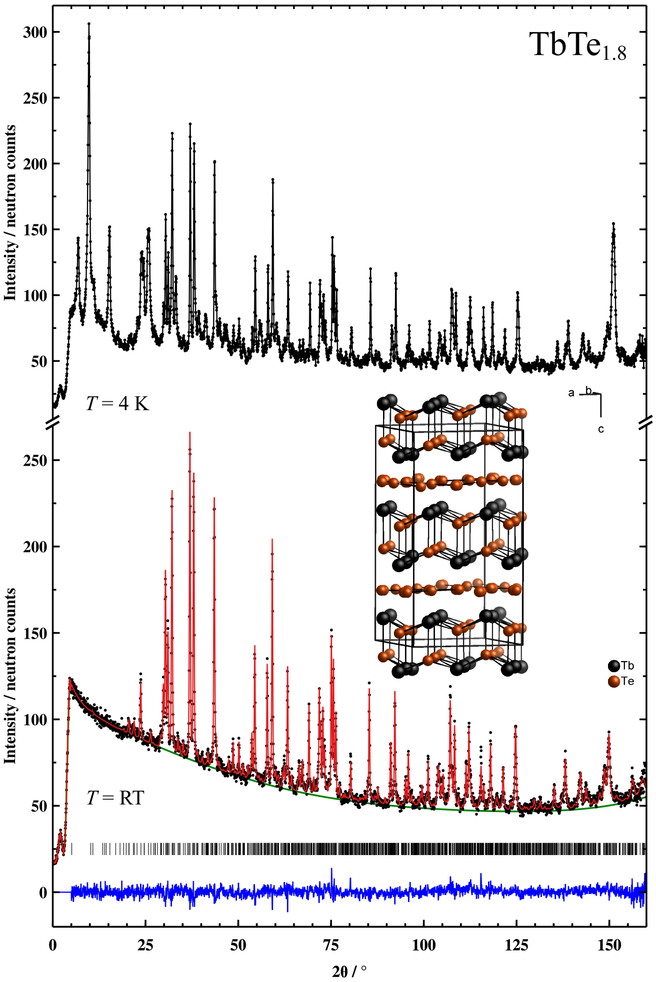

Figure 4: $TbTe_{1.8}$ – Rietveld refinement of the paramagnetic structure (T = RT) and low temperature data (T = 4 K).