Experimental report

13/02/2019

Proposal:	**5-41-983**	**Council:**	4/2018
Title:	Structural refinement of the dimerization in NaFe(WO4)2		
Research area:	Physics		

This proposal is a continuation of 5-41-911

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Samples: NaFe(WO4)2

Instrument	Requested days	Allocated days	From	To
D10	8	6	03/10/2018	09/10/2018

Abstract:

During a previous allocated beam time (proposal 5-41-911) it was possible to confirm the presence of a structural dimerization effect in NaFe(WO4)2. This effect is directly related to the strong thermal expansion anomalies upon entering the commensurate phases. After the qualitative confirmation of this dimerization effect, the residual beam time was not sufficient to measure as many reflections as would be necessary for a structural refinement in these commensurate phases. We propose for a continuation of this experiment in order to obtain sufficient data for a structural refinement and hence, for a quantitative determination of the structural distortion and dimerization.

Experimental report 5-41-983

During the experimental course of the prior beamtime 5-41-911, it was possible to verify qualitatively a dimerization effect in the double tungstate system NaFe$(WO_4)_2$. The system exhibits a sequence of different magnetic phase transitions [1], where the transition to a commensurate spin up-up-down-down arrangement is accompanied by a dimerization in form of a variation of Fe-O-Fe bond angles, following the more ferro- or antiferromagnetic exchange. A dimerization implies here a loss of the c-glide plane and hence, the existence of this effect allows for $\mathbf{Q} = (h\ 0\ l = \text{odd})$ superstructure reflections. Unfortunately those superstructure reflections are weak and in addition are sitting on top of the signal that stems from multiple reflection. Thus, only the intensity difference between the commensurate phase of interest and the incommensurate phase yield the absolute intensity of respective superstructure reflections. In order to get into the LF-C phase, an applied magnetic field along b-direction has first to overcome $\mu_0 H \approx 2\,\mathrm{T}$ at $T \approx 2\,\mathrm{K}$ in order to force the system into the commensurate high-field phase HF-C. After decreasing the field again, the system doesn't fall back to its initial incommensurate arrangement but shows a spin flop transition to a canted commensurate structure.

As it has been shown that this low-field commensurate (LF-C) phase exhibits the most pronounced dimerization within the iron chains (see report 5-41-911), omega-scans have been executed in the LF-C, as well as in the LF-IC phase in order to obtain the intensity difference that corresponds to weak superstructure reflections. Figure 1.1 displays exemplary the measured intensity difference for two superstructure reflections.

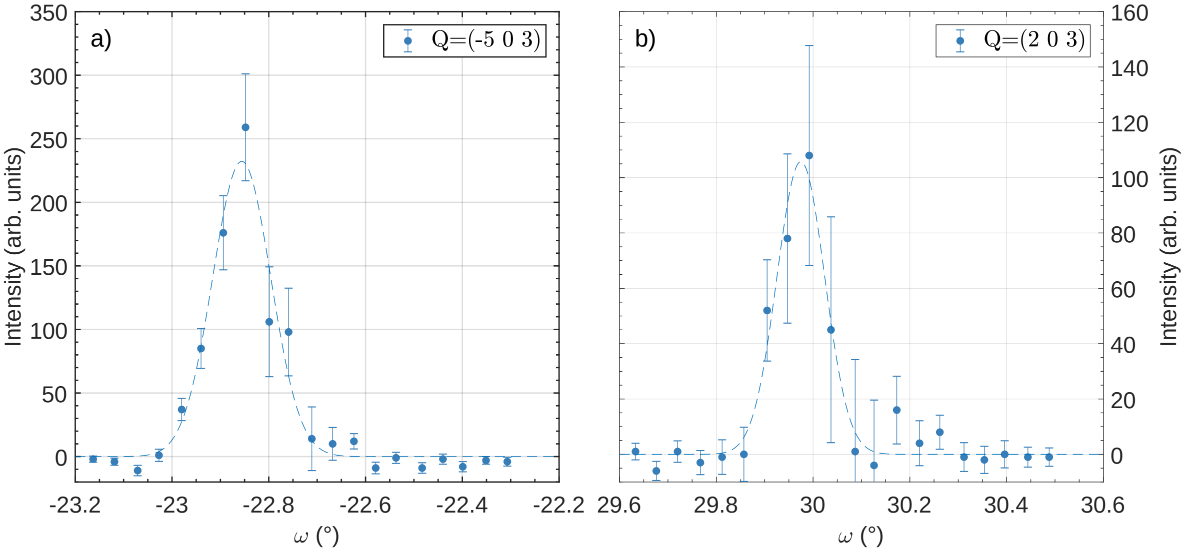

Figure 1.1: Superstructure reflections

Both plots correspond to intensity differences between the LF-C and LF-IC phase. Thus, these shown reflections correspond to $\mathbf{Q} = (h\,0\,l = \text{odd})$ superstructure reflections.

During the first part of the experimental course, we collected 108 unique allowed nuclear reflections in the LF-IC phase for refining the extinction coefficients. After switching from the area detector to the single detector with analyzer setup, the background has been reduced and we collected again 19 unique allowed nuclear reflections in order to refine the scaling parameter for the respective instrument setup.

	Paramagnetic phase (spacegroup $P2/c$)					Paramagnetic phase (spacegroup $P\bar{1}$)			LF-C phase (spacegroup $P\bar{1}$)		
	x	**y**	**z**	$\mathbf{B}_{\text{iso}}$		**x**	**y**	**z**	**x**	**y**	**z**
Fe	0.0	0.67074(19)	0.25	0.04(2)	**Fe**	0.0	0.67074(19)	0.25	0	0.67074	0.2503(7)
Na	0.5	0.6971(6)	0.25	0.35(5)	**Na**	0.5	0.6971(6)	0.25	0.5035(7)	0.6971	0.243(2)
W	0.23704(14)	0.1831(2)	0.2572(3)	0.12(3)	**W1**	0.23704(14)	0.1831(2)	0.2572(3)	0.254(17)	0.1831	0.25(3)
O1	0.35385(12)	0.3813(3)	0.3816(3)	0.25(3)	**W2**	0.76296(14)	0.1831(2)	0.2428(3)	0.746(18)	0.1831	0.25(3)
O2	0.10888(13)	0.6226(3)	0.5923(3)	0.22(2)	**O1_1**	0.35385(12)	0.3813(3)	0.3816(3)	0.3539(3)	0.3813	0.3810(7)
O3	0.33177(13)	0.0897(2)	0.9533(3)	0.22(3)	**O1_2**	0.64615(12)	0.3813(3)	0.1184(3)	0.6462(3)	0.3813	0.1178(7)
O4	0.12606(13)	0.1215(3)	0.5757(3)	0.17(2)	**O2_1**	0.10888(13)	0.6226(3)	0.5923(3)	0.1106(3)	0.6226	0.5945(8)
					O2_2	0.89112(13)	0.6226(3)	0.9077(3)	0.8928(3)	0.6226	0.9099(8)
					O3_1	0.33177(13)	0.0897(2)	0.9533(3)	0.33177	0.0897	0.9533
					O3_2	0.66823(13)	0.0897(2)	0.5467(3)	0.66823	0.0897	0.5467
					O4_1	0.12606(13)	0.1215(3)	0.5757(3)	0.12606	0.1215	0.5757
					O4_2	0.87394(13)	0.1215(3)	0.9243(3)	0.87394	0.1215	0.9243

Table 1.1: The left side of this table displays atomic positions in the paramagnetic phase at $T = 12\,\mathrm{K}$ [1]. In the middle part, all positions have been tranformed to spacegroup $P\bar{1}$, which would allow for a dimerization within the FeO_6 chain along c and a corresponding variation of bond angles of Fe-O-Fe bonds. The refinement has been done by using JANA [2] with $R(\text{obs}) = 19.37$, $wR(\text{obs}) = 21.53$, $R(\text{all}) = 38.55$ and $wR(\text{all}) = 28.36$. The refined parameters are shown on the right side.

During the subsequent experimental course, we didn't change the setup further and were able to collect 26 superstructure reflections of which 24 are independent. The distinct small number of measured reflections originates from the weakness and thus the associated long counting time, while having only limited beamtime.

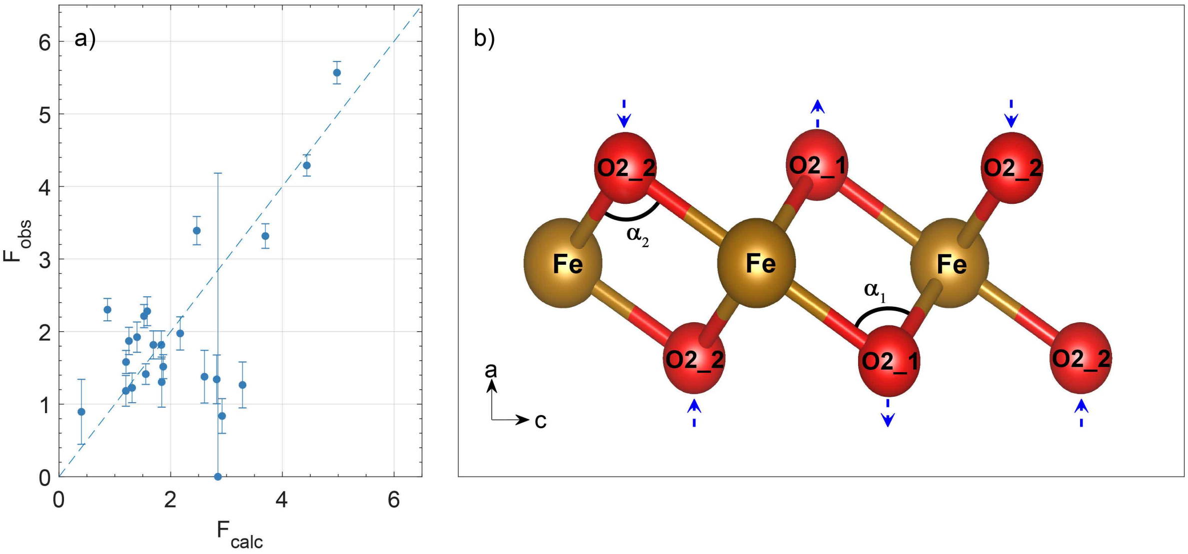

Figure 1.2: Structural refinement of bond angle variation
Figure a) displays the obtained F_{obs} and F_{calc} values for the structural refinement. In b), the respective bond angle variation is illustrated. The blue arrows mark the relevant oxygen shift but it has to be noted that the refinement also yielded a small shift along *c*-direction, which has not been illustrated.

Table 1.1 and figure 1.2 a) summarize the structural refinement. By considering the small number and weakness of all reflections, the obtained *R*-value (see table 1.1) substantiate the validity of the refined parameters. From those, it can be calculated that the Fe-O-Fe bond angles α_1 and α_2 amounts 97.60(15)° and 99.09(15)° in the LF-C phase respectively, whereas in the non-dimerized state, the bond angle is equal to $\alpha = \alpha_1 = \alpha_2 = 98.35(7)°$. Hence, it can be stated that a variation of Fe-O-Fe bond angles of about 0.75° is present and thus, a quantitative investigation of the dimerization effect in $NaFe(WO_4)_2$ was successful. We would like to acknowledge for the allocation of beamtime and especially for the on-site support from our local contact Navid Qureshi.

References

[1] S. Holbein, M. Ackermann, L. Chapon, P. Steffens, A. Gukasov, A. Sazonov, O. Breunig, Y. Sanders, P. Becker, L. Bohatý, T. Lorenz & M. Braden: Strong magnetoelastic coupling at the transition from harmonic to anharmonic order in $NaFe(WO_4)_2$ with $3d^5$ configuration, *Phys. Rev. B* **94** (2016)

[2] V. Petrícek, M. Dušek & L. Palatinus: Crystallographic computing system JANA2006: General features, *Zeitschrift fur Kristallographie* **229**, 345 (2014)