ESRF	**Experiment title:** Crystal structures of zinc-doped magnetites	**Experiment number**: HC2308
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Names and affiliations of applicants (* indicates experimentalists):

Prof J. Paul Attfield, Centre for Science at Extreme Conditions, University of Edinburgh

*Dr. Elise Pachoud, Centre for Science at Extreme Conditions, University of Edinburgh

Dr. James Cumby, Centre for Science at Extreme Conditions, University of Edinburgh

*Giuditta Perversi, Centre for Science at Extreme Conditions, University of Edinburgh

Report:

This experiment investigated the structural transition of Zn-doped magnetite $Fe_{3-x}Zn_xO_4$, which undergoes the so-called Verwey transition upon cooling below ~ 125 K [1]. Honig et al. [2] reported a remarkable variability of this transition temperature and correlated it with iron deficiency and chemical doping: increasing the doping level lowers the transition temperature as low as 81 K for 3.5% of doping; additionally, they state that above 1.5% of doping the phase transition changes from first to second order and, though discontinuity in magnetization and resistivity are mantained, the structural transition is suppressed.
The aim of our current work is to provide structural insights on this complex phase transition, following the successful results on stoichiometric magnetite (HE3133 and [3]), mineral magnetite (HC1452 and [4]) and off-stoichiometric magnetite (HC1452).

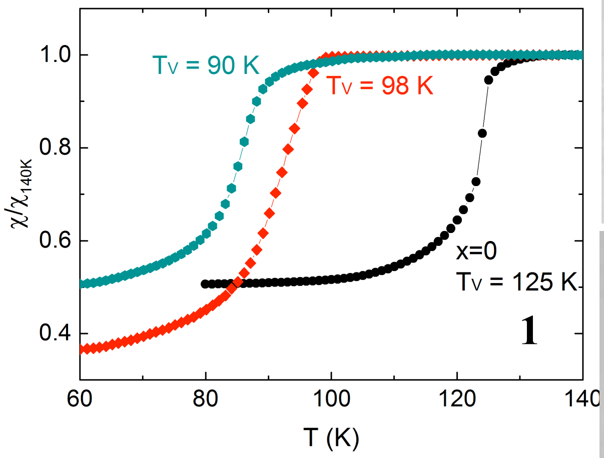
In order to acquire high-quality data for the Zn-doped samples, a precise process of preliminary screening was necessary: several microcystals with dimensions spanning from 40 μm to 80 μm were mounted and analysed in the cubic phase and after cooling through the transition. The scope of the work was to identify high quality crystals, since Zn-doping seems to stabilize domain walls and even on the small scale of crystals under investigation it was common to find multiple crystals in the same grain.
The efforts were concentrated on microcrystals coming from a batch with T_V = 98 K and 93 K, as measured through SQUID magnetometer data (Fig. 1).
The most promising crystals were cooled through the transition while collecting wide-angle diffraction images. This process was paramount for the scope of the experiment: we managed to identify good quality crystals with a clear structural transition below 100 K and a good accord with

the susceptibility values (Fig. 2).
Highly redundant datasets where subsequently collected on microcrystal $Fe_{3-x}Zn_xO_4$ with experimental T_V = 99 K and 92 K.

Most of the efforts were concentrated on the sample with T_V = 92 K, which had the best crystal quality and the lowest transition temperature.
The data collection required long exposure time and several datasets at different angular range to capture both the faint superstructure reflections and the strong crystal reflections, especially because the sample proved to be composed of more than one grain.

The data are currently under analysis. Accurate integration procedures were implemented to deal with the mosaicity and the twinning at the same time. The aim is to achieve an unrestrained refinements of the crystal structure at low temperature.
Preliminary results suggest that the monoclinic model of the low temperature phase still stand, but the specific variations in the structure are yet to be determined.

The experiment was overall successful and the preliminary results are conclusive on the presence of a structural transition in the so-called “second order regime”, contrary to the previous findings of Honig et al. [1]. The complete refinement will provide insights on the possible change of order of the transition and on the influence of doping on the specifics of the monoclinic superstructure.



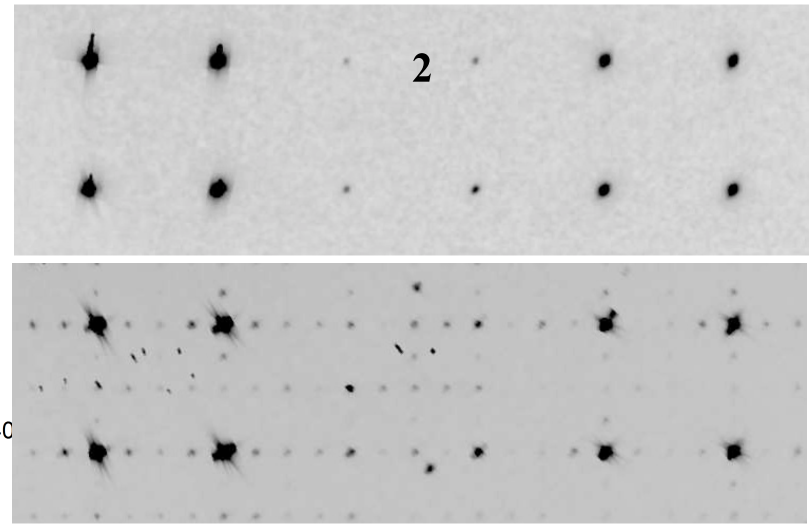


Figure 1: Susceptibility measurements of the samples under investigation and their transition temperature (green and red) compared with the transition temperature of a perfectly stoichiometric sample (black).
Figure 2: Reciprocal space reconstructions for $Fe_{3-x}Zn_xO_4$ with nominal T_V = 90 K, above (top) and below (bottom) the transition. The structural transition is remarkably evident from this high quality data.

References

[1] E. J. W. Verwey, Nature, 1939, **144**, 327-328.
[2] J. M. Honig, J. Alloys Compds. 1995, **229**, 24-39.
[3] M. S. Senn, J. P. Wright, and J. P. Attfield, Nature, 2012, **481**, 173-176.
[4] G. Perversi, J. Cumby, E. Pachoud, J.P. Wright and J. P. Attfield, Chem. Comm., 2016, **52**, 4864-4867.