ESRF	**Experiment title:** The crystal structure of magnetoresistant pnictides LnMnAsO (Ln = La, Nd)	**Experiment number**: HS-4268
Beamline:	**Date of experiment**: from: 08/09/2010 to: 10/09/2010	**Date of report**: 28/02/2011
Shifts: 6	**Local contact(s)**: Andy Fitch	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Abbie C. Mclaughlin
*Eve. J. Wildman
Nicolas Emery

Report:

We have recently synthesised manganese pnictides LaMnAsO and NdMnAsO. A sizeable magnetoresistance is detected for both samples (MR_{5T} (200 K) = -12 and -20 % for Nd and La respectively) [1]. -MR is observed below 380 K and 360 K for NdMnAsO and LaMnAsO respectively and decreases slowly upon cooling reaching a maximum –MR of -24 % and -11 % at 200 K. At 150 K (T_e) the –MR for NdMnAsO increases rapidly to zero; at the same time a subtle electronic transition is observed as a result of a crossover between two 3-dimensional variable range hopping (VRH) states. The electronic transition is thought to arise due to a change in hopping with hopping via multiple sites occurring at high temperature and hopping via two sites below 150 K. If tunnelling of the electrons occurs via more than 2 sites, then quantum destructive interference (QDI) is possible. Upon application of a magnetic field the QDI is diminished resulting in the –MR observed between 150 – 380 K for NdMnAsO. A weak ferromagnetic transition is observed for both materials at 320 and 335 K respectively. SQUID magnetometry measurements also evidence the Nd^{3+} spin transition at 25 K for NdMnAsO.

In order to ascertain if there is a change in crystal structure with temperature (as observed in other pnictides) we performed a variable temperature synchrotron x-ray diffraction study on both NdMnAsO and LaMnAsO between 290 – 5 K. Data were recorded for both samples at 5, 15, 30, 70, 100, 115, 130, 150, 200 and 290 K with a data aquisition time of two hours per temperature.

The synchrotron X-ray powder diffraction patterns of LnMnAsO (Ln = La, Nd) were fitted by the Rietveld method using the GSAS program. The backgrounds were fitted using linear interpolation and the peak shapes were modelled using a pseudo–Voigt function. Our data confirmed that LnMnAsO (Ln = La, Nd) crystallize in the ZrCuSiAs type-structure as previously reported [1] (S.G. *P4/nmm* a = 4.11398(1) and 4.043959(7); c = 9.03044(2) and 8.87868(3) for Ln = La and Nd respectively). Unlike LnMAsO (M = Fe, Co), no orthorhombic distortion is observed down to 5 K. Excellent fits were obtained at all temperatures for both compounds as shown in Figure 1. The refinement results show that both compounds are anion stoichiometric

and there is no evidence of cation or anion disorder. Non-stoichiometry on the Ln site is observed for both samples so that the La and Nd occupancies refine to 0.966(2) and 0.970(2) respectively.

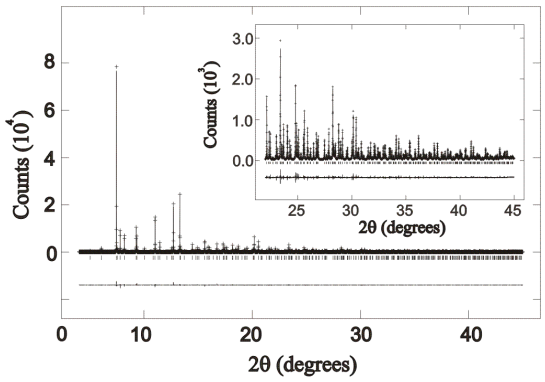

Figure 1: Rietveld refinement fit to the 290 K synchrotron X-ray data for NdMnAsO.

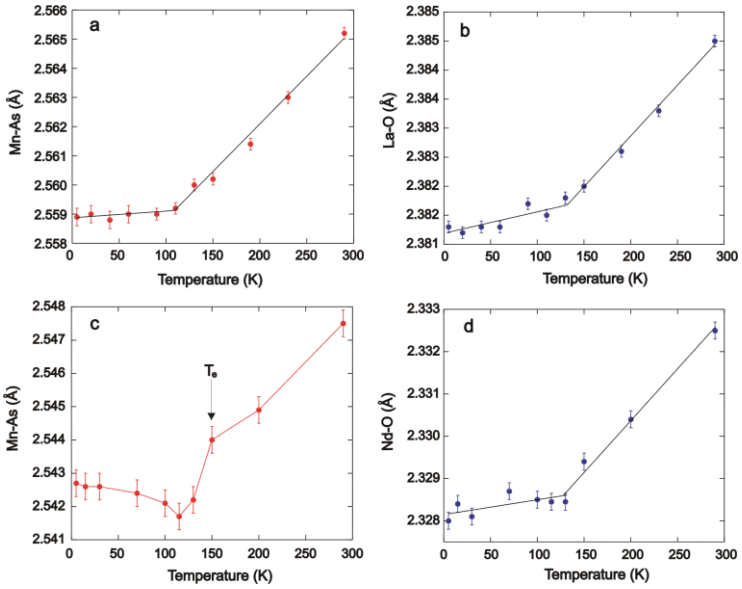

Figure 2: Temperature variation of a) Mn-As bond length in LaMnAsO; b) La-O bond distance; c) Mn-As bond length in NdMnAsO and d) Nd-As bond distance.

The results show that at T_e a clear discontinuity is evidenced in the variation of cell volume with temperature for both LaMnAsO and NdMnAsO [2]. Figure 2 shows the variation of the Mn-As and Ln-O bond lengths with temperature and it's clear that the discontinuity in the cell volume is due to changes in these bond lengths at ~T_e [2]. The results show that a reduction in the tetrahedral bond angle La-O-La α_1 is observed with decreasing temperature whilst α_2 increases so that at 5 K the angles are 119.49(1) ° and 104.706(5) ° for α_1 and α_2 respectively [2]. In contrast both the Nd-O-Nd tetrahedral bond lengths are almost constant with temperature (α_1 =120.58(1) ° and α_2 = 104.219(4) ° at 5 K). The greater distortion in the Nd-O-Nd tetrahedral can be attributed to the larger bond mismatch between Mn-As and Nd-O in this material (Mn-As = 2.5427(3) Å and Nd-O = 2.3280(1) Å for NdMnAsO at 5 K compared to Mn-As = 2.5589(3) Å and La-O = 2.3813(1) Å). For both compounds the α_2 As-Mn-As bond angles are almost temperature invariant whereas the electronic transition T_e is manifest in the α_1 As-Mn-As tetrahedral bond angle. Electronic transitions such as the one reported for LnMnAsO [1] are well known in disordered semiconductors, for example a crossover between two 3D VRH states has previously been reported for $SrFeO_{3-\delta}$ [3]. The synchrotron X-ray refinement results demonstrate that the structural parameters are sensitive to subtle changes in the electronic state in LnMnAsO so that the electronic transition at 150 K is coupled to the crystal lattice.

References

1. N. Emery, E. J. Wildman, J. M. S. Skakle, G. Giriat, R. I. Smith and A. C. Mclaughlin, Chem. Comm. **46**, 6777 (2010).
2. N. Emery, E. J. Wildman, J. M. S. Skakle, R. I. Smith, A. N. Fitch and A. C. Mclaughlin, *Phys. Rev. B* (accepted).
3. S. Srinath, M. M. Kumar, M. L. Post and H. Srikanth, Phys. Rev. B **72**, 054425 (2005).