Experimental report

21/06/2016

Proposal: 5-31-2430 **Council:** 4/2015

Title: Inducing magnetic order by rare-earth-doping in (Sr,La)Co2As2

Research area: Physics

This proposal is a resubmission of 5-31-2370

Main proposer: Marein RAHN

Experimental team: Marein RAHN

Local contacts: Thomas HANSEN

Samples: Sr0.5 La0.5 Co2 As2
Sr0.2 La0.8 Co2 As2
La Co2 As2

Instrument	Requested days	Allocated days	From	To
D20	2	2	15/09/2015	17/09/2015

Abstract:

By contrast with the closely related iron based superconductors (FeSC), research into isostructural cobalt arsenide compounds aims to isolate the key properties and interactions enabling high temperature superconductivity. The magnetic fluctuation spectrum of SrCo2As2 has recently been found to be a carbon copy of that found in 122-type FeSC [4]. If spin excitations are expected to mediate superconducting pairing in materials such as SrFe2As2, it is relevant to determine what property prevents superconductivity in SrCo2As2.

In the present study, we dope La into the Sr site to destabilise the paramagnetic (possibly spin liquid) state in SrCo2As2. Unexpectedly, this abruptly induces robust ferromagnetic order of the Co3+ ions, with an unusual non-monotonic doping dependence. We select three compounds in the (Sr,La)Co2As2 doping range for magnetic structure determination by neutron powder diffraction. Given their magnetic moments of 0.35 to 0.53 Bohr magnetons, we expect an appreciable magnetic signal on D20.

Summary: Experiment #5-31-2431
$(La,Sr)Co_2As_2$ on D20, ILL
31.10./1.11.2015

We have performed a neutron powder diffraction (NPD) study on $(La,Sr)Co_2As_2$. It was the goal of this experiment to gather evidence on the magnetic order in this system, with a special interest in qualitative differences between the La-rich and -poor compounds. One day of beam time each was spent to investigate the materials with 30 % and 100 % lanthanum substitution. We were not able to observe magnetic Bragg peaks of the main phase of either sample. This fact may be interpreted as evidence for collinear magnetic order with the magnetic moment directed along the c-axis.

The samples had been thoroughly characterised by lab XRD and magnetometry (cf. Fig.1). The key results are:

- Ferromagnetic characteristics of the magnetisation, with ordering temperatures $T_{30\%}$=45 K and T_{100}=202 K.
- Saturating magnetic moments of $\mu_{30} \sim 0.1\ \mu_B$ and $\mu_{100} \sim 0.45\ \mu_B$
- Both samples contain impurities of CoAs and LaOCoAs.

The system crystallises in the tetragonal $ThCr_2Si_2$ structure (I4/mmm). Only few reports on the magnetic properties of cobalt arsenides are available in the literature. Some notable findings are:

- [1] Reehuis *et al.*, 1994: NPD study on the closely related compound $LaCo_2P_2$. Magnetic properties are qualitatively similar to the present materials of interest. Using instruments D1A and D1B (theoretically less suited than the presently used D20), the authors found evidence of ferromagnetically ordered moments of 0.4 μ_B . The study went on to confirm the moment direction by polarised neutron powder diffraction.
- [2] Jin *et al.*, 2009: Magnetometry, indicating that the impurity compound LaOCoAs is a ferromagnet with $\mu = 0.5\ \mu_B$.

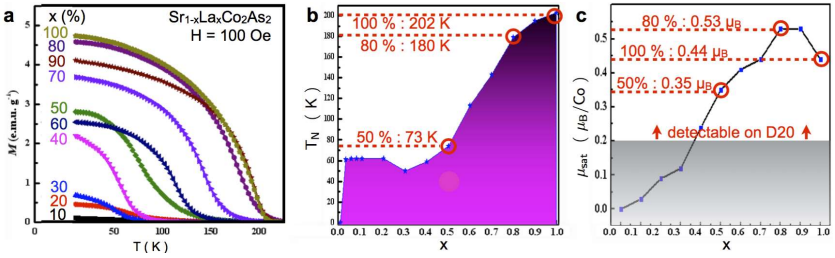

Figure 1: Preliminary sample characterisation, adopted from the beam time proposal.

The samples weighed (m_{30} = 5.99 g, m_{100} = 5.19 g) and filled into standard cylindrical vanadium cans of 7 mm diameter. The resulting sample height compared well to the vertical dimension of the neutron beam (~4 cm). The instrument was optimised to detect magnetic Bragg peaks using a low take-off angle and the (002) graphite monochromator at λ=2.41 Å. The neutron flux of the instrument could have been increased by a factor of two by using the λ=1.3 Å Cu (200) setup. However, the most relevant regime of low momentum transfer would then not have been accessible. The sample was cooled in a standard orange ILL He cryostat. The available beam time for the two compounds was each split equally between 250 K (>> T_c) and 1.8 K (base temperature).

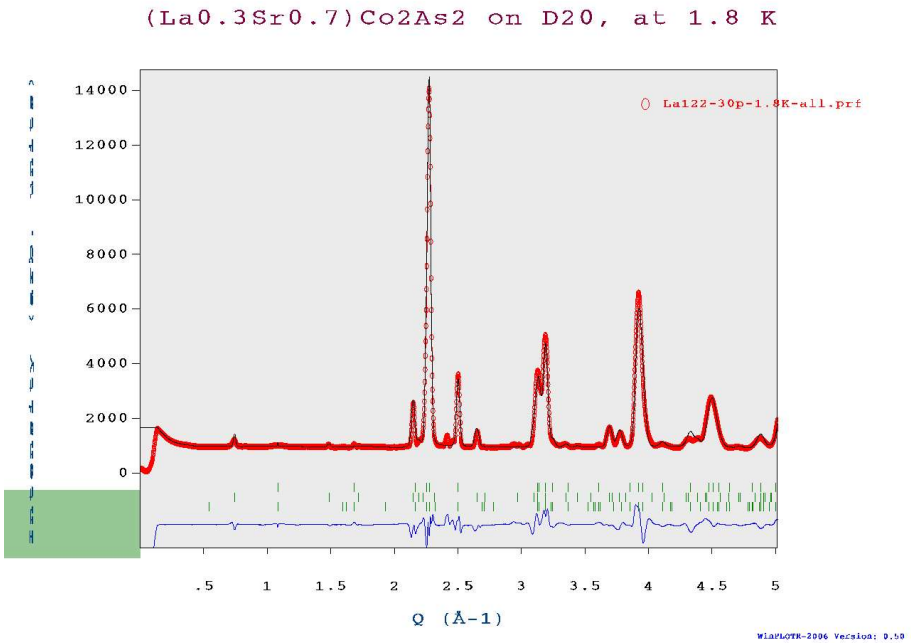

Figure 2: Preliminary Rietveld refinement of the $Sr_{0.7}La_{0.3}Co_2As_2$ 1.8 K dataset, including a 13.4 % LaOCoAs impurity.

All powder diffraction histograms obtained in this experiment can be Rietveld Refined (FullProf suite) using the main $(La,Sr)Co_2As_2$ phase and a large (~13%) LaOCoAs impurity. However, given that only the low-Q regime (up to 5 $Å^{-1}$ / with optimal resolution around 2.5 $Å^{-1}$) was measured, laboratory x-ray diffraction results will produce a superior refinement of structural parameters.

For the 30 % ($Sr_{0.7}La_{0.3}Co_2As_2$) sample, the data obtained at 1.8 K was indexed in the cell [3.94 3.94 11.61 90. 90 90]. The difference pattern of the two datasets (' 2 K – 250 K ' cf. Fig. 3) reveals two very weak candidates for magnetic peaks, at Q_1 = 0.15 $Å^{-1}$ and Q_2 = 0.30 $Å^{-1}$. Notably, neither of these peaks coincide with Bragg positions of the main phase. It is not possible to index these peaks with finite (fractional) propagation vectors (also, the observed magnetisation characteristics would contradict antiferromagnetic order, cf. Fig.1 a). Further, a refinement of the peak at Q_2 = 0.30 $Å^{-1}$ as the (001) ferromagnetic peak of the LaCoAsO impurity was attempted (cf. Fig.). A satisfactory fit can be achieved, with a magnetic moment of ~ 3.5 μ_B, which surpasses by far the expected value of 0.5 μ_B [2].

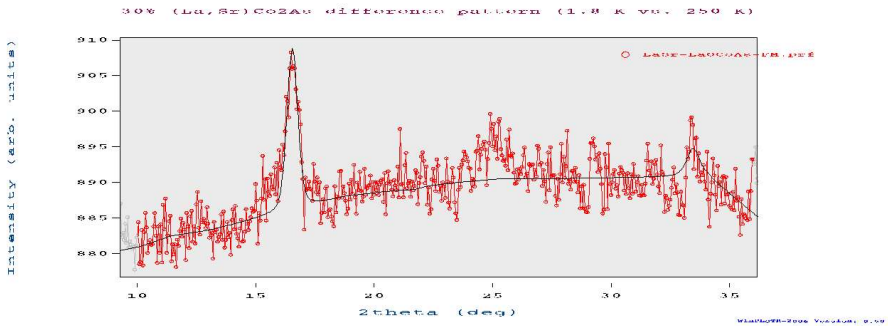

Figure 3: Fit of a ferromagnetic phase in the LaOCoAs cell to the difference pattern of $Sr_{0.7}La_{0.3}Co_2As_2$. The fitted (001) peak (16.5 deg.) appears only if the magnetic moment lies in the a-b plane. The fit of the very weak (002) peak (34 deg) would be consistent with this model but is hardly statistically significant. The refined magnetic moment of ~3.5 μ_B does not agree with published magnetometry [2].

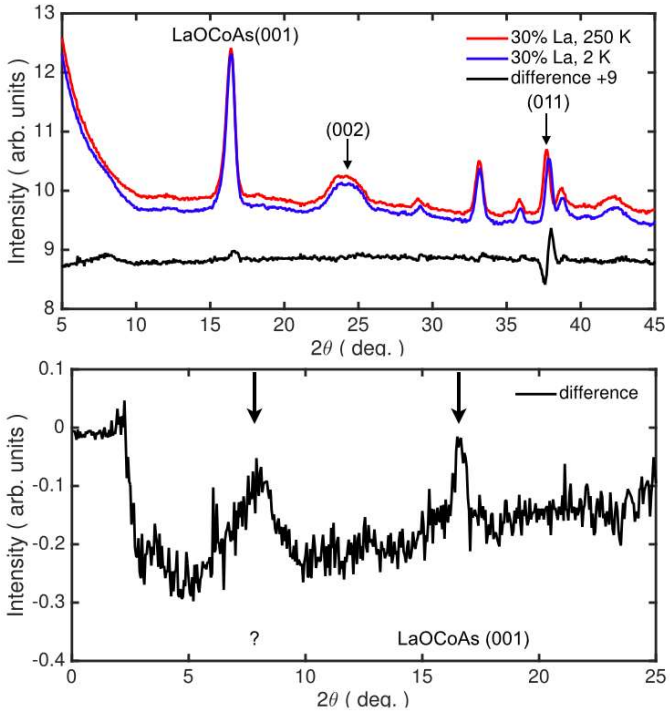

Figure 4: Top: Detail of the $Sr_{0.7}La_{0.3}Co_2As_2$ powder histograms, at 250 (red) and 1.8 K (blue); as well as their (offset) difference pattern. Two weak peaks of possibly magnetic origin become visible; at 2θ ~ 8 deg., Q = 0.15 Å^{-1} and 2θ ~ 16.5 deg, Q = 0.30 Å^{-1}. We were not able to index these peaks in the main phase. One peak may be attributed to ferromagnetic order in the 13.4 % LaOCoAs impurity.

Although a larger (compared to the 30% compound) magnetic moment of ~ 0.45 μ_B was expected from magnetometry, t**he 100%, $LaCo_2As_2$, sample** shows very similar characteristics to the 30 % sample (cell at 1.8 K: [4.05 4.05 10.37 90 90 09]). In particular, the difference pattern (1.8 vs 250 K) reveals only one candidate magnetic peak, close to the (001) reflection of the 13.0 % LaOCoAs impurity phase. A ~10% Co vacancy in the main phase was reproduced by the refinement (preliminary refined actual stoichiometry: $LaCo_{1.79}As_2$).

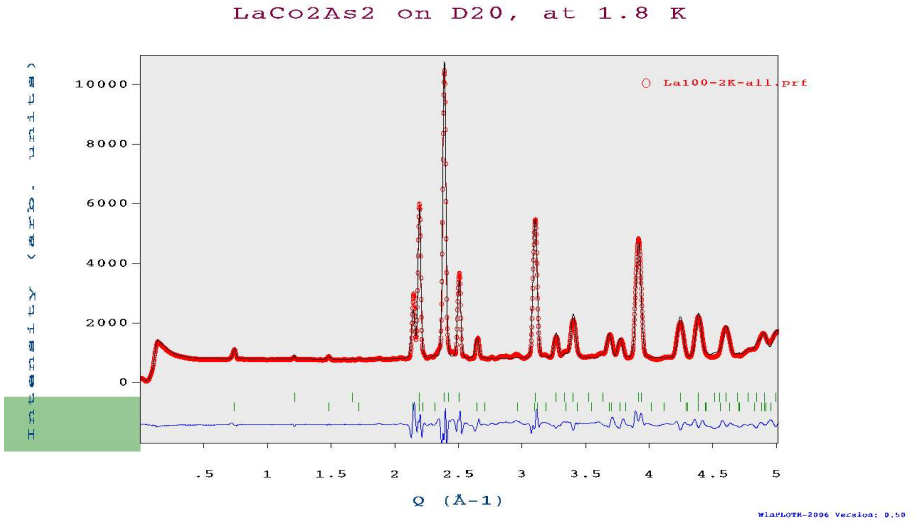

Figure 5: Preliminary refinement of $LaCo_2As_2$ sample at 1.8 K, including a 13.0 % LaOCoAs impurity phase.

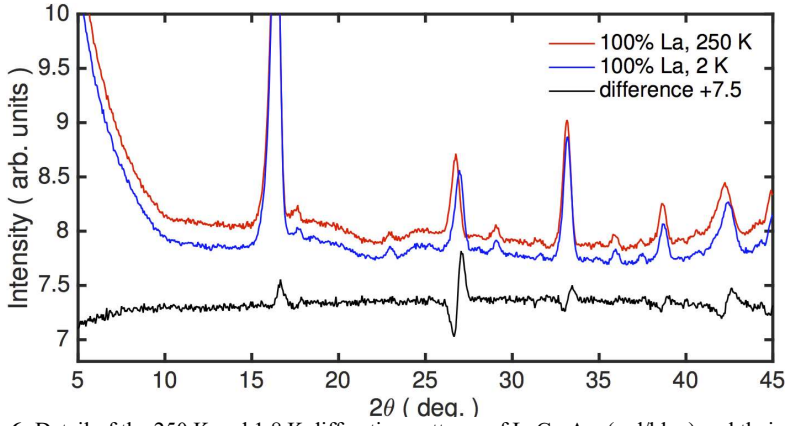

Figure 6: Detail of the 250 K and 1.8 K diffraction patterns of $LaCo_2As_2$ (red/blue) and their difference pattern (black, with offset). One candidate magnetic peak becomes evident on the shoulder of the LaOCoAs (001) Bragg reflection (~16.5 deg.). By shifting the patterns in 2th to correct for thermal expansion, we confirmed that no ferromagnetic contributions are associated with any Bragg peaks of the main phase.

Lastly, we simulated the scattering pattern for a ferromagnetic order in $LaCo_2As_2$ (cf. Fig. 7). The results indicate that under the conditions of the experiment, a small but measurable magnetic intensity would be expected at the (002) position (26.8 deg.), if the magnetic moments we directed in the a-b plane. This situation has been evidenced in a magnetically very similar system $LaCo_2P_2$ [1]. The absence of this peak in the present data may be interpreted as due to the momentum transfer being parallel to the magnetic moment direction (thus not fulfilling the magnetic neutron scattering condition, cf. Fig. 7, bottom panel). This implies c-axis parallel ferromagnetism.

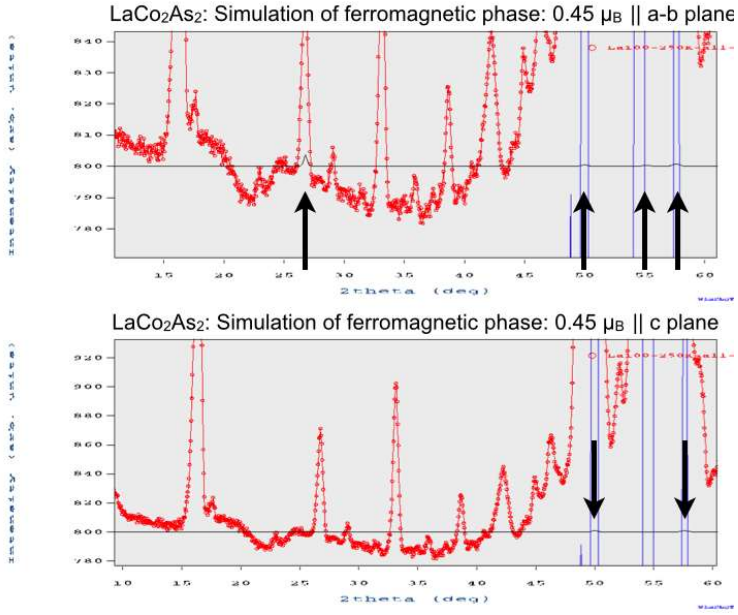

Figure 7: Simulated diffraction pattern (black line) for a purely ferromagnetic phase in the $LaCo_2As_2$ cell (superimposed on measured data, red). Top panel: Magnetic moments of 0.45 μ_B (as inferred from the saturating magnetisation) oriented in the a-b plane. A measurable peak (not observed in experiment) appears at the (002) position. Bottom panel: Corresponding plot with the magnetic moments parallel to the c-axis. This may portray the present experimental observation.

[1] Reehuis, M. *et al.*, Ferromagnetism in the ThCr& type phosphide $LaCo_2P_2$
JMMM 138 (1994) 85-93

[2] Jin, X. *et al.*, Electrical and Magnetic Properties of Layered Oxypnictide LaOCoPn (Pn = P, As)
Journal of Physics: Conference Series **150** (2009) 052085
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