実験報告書様式（一般利用課題・成果公開利用）

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CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2017/11/7 承認者 Approver Takenao Shinohara 提出日 Date of Report 2017/11/7
課題番号 Project No. 2017A0048 実験課題名 Title of experiment In operando study of Thermoelectric generators utilizing novel imaging techniques 実験責任者名 Name of principal investigator Søren Schmidt 所属 Affiliation Technical University of Denmark	装置責任者 Name of Instrument scientist Dr. Takenao Shinohara 装置名 Name of Instrument/(BL No.) BL22 (RADEN) 実施日 Date of Experiment May 10th – May 18th 2017

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）

Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.
Two types of thermoelectric devices were imaged, a reference sample of $Bi_{0.5}Sb_{1.5}Te_3$ (n-type) and $Bi_2Sb_{1.5}Te_{1.5}$ (p-type), and a so-called high-performance sample of $DD_y(Fe_{1-x}Co_x)_4Sb_{12}$ (p-type) and $(Mm,Sm)_zCo_4Sb_{12}$ (n-type) with x=0.25 to 0.35, y=0.6 to 0.66 and z= 0.13 to 0.17. The samples were approximate of a size of 10mmx5mmx5mm. Lastly, 4 $Co_{38}Ni_{33}Al_{29}$ samples of approximate size 5mmx5mmx5mm were briefly measured as pre-study for later investigations.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。） Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

All samples were measured using 3D polarimetric neutron imaging/tomography, where Larmor precession of polarized neutrons is used to measure internal magnetic fields.

The experiments on the thermoelectric devices were unsuccessful due to problems with electrical contacts in the in situ setup and to the samples. For both sample types, it was possible to create a temperature gradient as written in the proposal, but only a very small (micro Amps) current was measured, which affected the polarimetric neutron imaging. The neutron images recorded at a series of angles and temperatures up to 400 degrees C showed the expected transmission images and Bragg edges as in the case of no (or very small, i.e. less than a few 100 mA) current. Therefore, the experiments were inconclusive. After shipping the samples and the in situ setup back to our DTU laboratory, we have carefully measured the thermoelectric devices again, and they show the expected build-up of temperature gradient, but the measured current remains very low supporting the hypothesis of problems with the electrical contacts. This is now being investigated further to find a solution as the polarimetric neutron imaging experiment seems very promising.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

When it became evident that the thermoelectric experiments were unsuccessful, we chose to instead do a pre-study investigation of the magnitude and orientation of magnetic domains within two polycrystalline samples of $Co_{38}Ni_{33}Al_{29}$. Alloys consisting of the same elements with slightly different concentrations have shown soft ferromagnetic properties [1] [2], thus making it possible study the magnetic domains by probing with cold polarised neutrons. The two most promising samples were annealed for an hour at 1350 °C and 1250 °C respectively. Annealing temperature will affect the crystallization process and cause different distribution of domain sizes. Previous study by J. Kopecek have shown that the majority of the domains have a diameter in the range of 900 – 1400 μm.

The two crystals where mounted on a sample holder and held apart by a custom made aluminium spacer to avoid the magnetic fields to interfere with each other.

Three angles were chosen to be investigated; 0°, 45° and 90°. In this experiment, the direction of polarisation as well analysis was chosen to be the vertical y-axis in order to measure $P^{Y,Y}$. For each projection angle, both spin up and spin down components were measured each with an acquisition time of 1800. This setting was run twice, in total 2x3x2 measurements. A summed and cropped version of the raw data collected from the experiment is shown in Figure 1. From the three detector images on Figure 1 labelled 'down', the two blue squares indicate the two crystal positions. Throughout this report the two crystals will be referred to as the *top*- and *bottom* crystals. An open beam measurement of $P^{Y,Y}$ was performed at an earlier stage of the beam time. The polarization was calculated from the measured intensities as $P^{Y,Y} = (I^{Y,Y}-I^{-Y,Y})/\ (I^{Y,Y}+I^{-Y,Y})$, and is a function of neutron wavelength. For better statistics, the 119 time frames where binned into 59 frames with a total span of neutron wavelength of {1.56Å, 6.34Å}. Furthermore, each pixel was binned from 1x1 to 2x2 for better statistics. The polarization signal for 3Å neutrons at 0° projection angle can be seen in Figure 2. When the polarization is 1, it can be interpreted as no precession has been observed or that a 2π precession has, and if P=−1 is measured it can be interpreted as a π-precession. The two squares are the effect of the magnetic domains within each crystal and from this the polarization signal can be extrapolated and then the magnetic fields can be found. For the magnetic domain investigations, the crystals have been treated as one single magnetic crystal, as well as divided into 2x2x2 and 3x3x3 domains. In Figure 3 the nomenclature for the areas of investigation is shown. From Figure 4 there is a significant difference in the polarisation signal from the two samples. This can be due to the magnitude of the magnetic field, the orientation, or that the number of

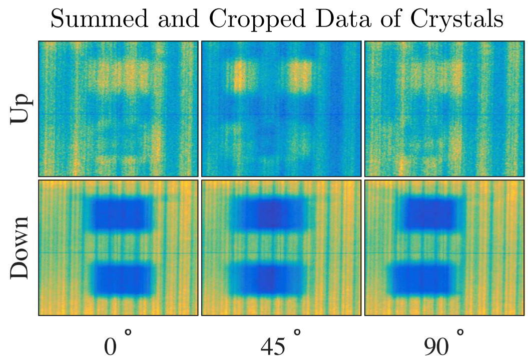

Figure 1: Summed and cropped data for up and down measurements in all three rotations.

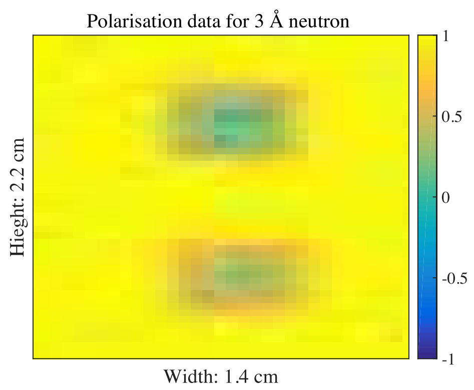

Figure 2: Polarization data for the cropped and binned detector area probed by neutrons with a wavelength of 3Å.

domains are not analysed fully yet. The polarisation signal of the top crystal are the same for 0°, 45°, and 90° rotation for short wavelength and starts to separate as the wavelength increases. For the bottom crystal 0° and 45° rotation show the same polarisation behaviour, which suggest a symmetry of the magnetic field around 45° of rotation.

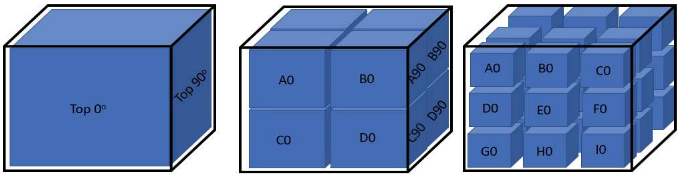

Figure 3: Nomenclature for the crystal investigation. From left to right it is shown how the crystal is divided into 1x1x1, 2x2x2 and 3x3x3 domains.

It is known that the soft ferromagnetic $Co_{38}Ni_{33}Al_{29}$ samples consist of multiple domains and the first approach was to treat all the magnetic contribution from each domain as one total magnetic field. In order to do so, an analytical expression from a single depolarisation matrix have been fitted to the data. In case of a single domain, the neutron only experience one magnetic field but from two different angels. For 0° rotation the neutron experience a magnetic field $B = (B_x,B_y,B_z)$ and the neutron for 90° rotation experience $B = (-B_z,B_y,B_x)$. This constrain was built in the analytical expression. In Figure 5 the best single domain fit is shown together with data for top crystal 0° and 90° rotation. From the fit in Figure 5 it is shown that this is inadequate to describe the magnetic configuration of the polycrystalline sample. From previous studies, it was shown that the average domain diameter is in the range of approximately 0.1 cm and both samples are $(0.5\ \text{cm})^3$ cubes. Based on the fact that the crystals consist of multiple domains a model consisting of multiple domains was made. The two crystals were divided into 8 equal sized domains as shown in Figure 3. Since the data only was treated from two angles in the xz-plane, signals from (path) A0, B0, A90 and B90 contains information from the same four magnetic domains. In Figure 6 the polarisation signal for the four paths is shown together with their respective fit. This was done for all domains in top and bottom crystal with a satisfying result. The magnitudes of the magnetic field varied but they all stayed within the limits that was documented on similar alloys by [1] [2]. The two crystals were then divided into 27 equal sized domains as shown in Figure 3. The data was treated from two angles in the xz-plane, signals form area/path A0, B0, C0, A90, B90 and C90 contains information from the same nine magnetic domains. In Figure 7 the polarisation signal for the 6 paths is shown together with their respective fit. This was done for all domains in top and bottom crystal with a satisfying fit. The error on the polarisation signal increases with increasing number of domains chosen,

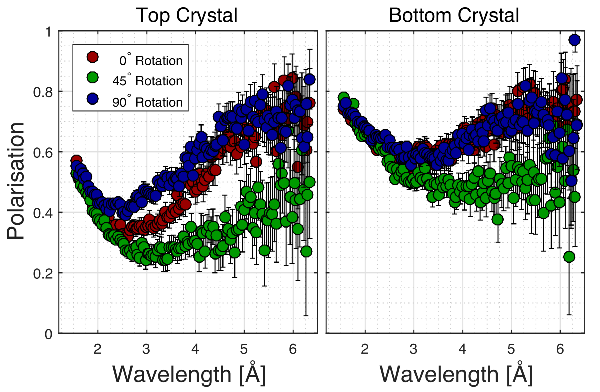

Figure 4: Polarisation data for the full crystal area as function of neutron wavelength for both crystals.

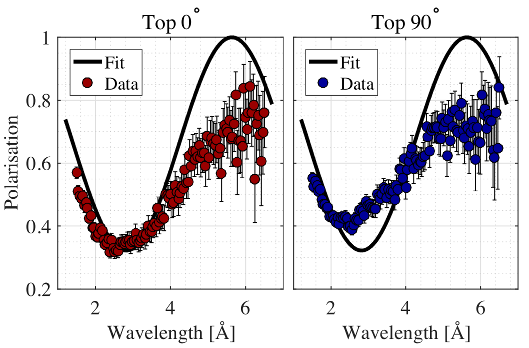

Figure 5: Data and fit for the top crystal under the

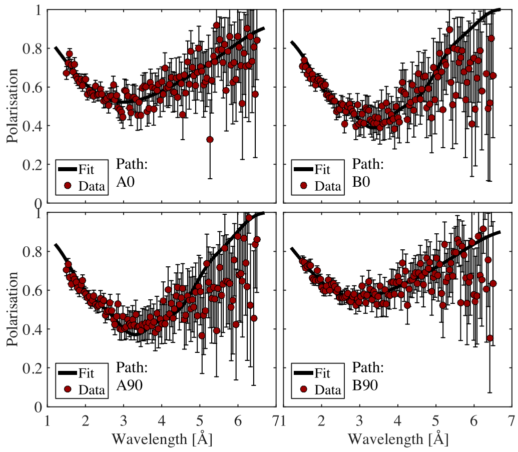

Figure 6: Polarisation signal as function of wavelength for top crystal for 0◦ and 90◦ rotation divided into 4 tiles: A0, B0, A90 and B90.

A significant difference in magnetic orientation and magnitude has been documented. From a 2x2x2 and 3x3x3 investigation it can be shown that the crystals consist of multiple domains.

This successful pre-study experiment probing two poly-crystalline soft ferromagnetic samples of $Co_{38}Ni_{33}Al_{29}$ showed promising results that needs to be further investigated. Therefore, we will be applying for beam time at RADEN in order to fully measure the $Co_{38}Ni_{33}Al_{29}$ poly-domain samples, thereby for the first time reconstruct three dimensional magnetic domains.

which is solely a statistics issue. This constraint sets an upper limit of the number of domains which can be thoroughly investigated. The increasing error can easily be seen by a visual comparison of the errorbars on Figures 4 and 6. The domain model showed very promising results but the resolution of the polarisation data suffers heavily when the number of domains increases. Furthermore, only the YY of the 9 elements in the polarisation matrix was measured. To perform a thorough investigation of the domains within $Co_{38}Ni_{33}Al_{29}$ all 9 combinations of P{x,y,z} must be measured to lower the number free parameters, together with a much larger acquisition time to improve the resolution.

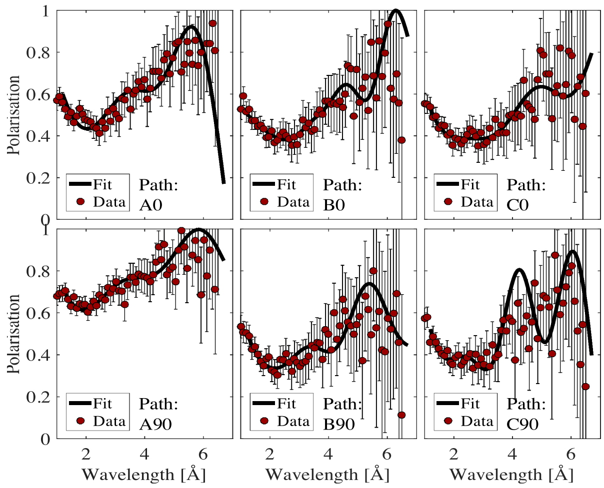

Figure 7: Polarisation signal as function of wavelength for top crystal for 0◦ and 90◦ rotation divided into 9 tiles: A0, B0, C0, A90, B90 and C90.

[1] B. Rajini Kanth and P. K. Mukhopadhyay. Magnetic field and stress Induced strain in CoNiAl Ferromagnetic Shapememory Alloy. Materials Today: Proceedings, 3(10):3960–3965, 2016.

[2] Fethi Dagdelen, Türkan Malkoc, Mediha Kök, and Ercan Ercan. Comparison of the transformation temperature, microstructure and magnetic properties of Co-Ni-Al and Co-Ni-Al-Cr shape memory alloys. 131(6):1–6, 2016.