Experimental Report

Proposal: **INTER-274** **Council:** 10/2012

Title: Internal time on D9

This proposal is a new proposal

Researh Area:

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Samples: Gd(HCOO)3

Instrument	Req. Days	All. Days	From	To
D9	8	8	31/07/2013	08/08/2013

Abstract:

EXPERIMENTAL REPORT FOR EXPERIMENT INTER-274

(Instrument D9, 31/07/2013-08/08/2013)

This was an extremely difficult experiment which brings the D9 instrument to its limits with success, in our opinion. The interest does not lie merely on scientific problem but also on checking the experimental capabilities of D9. The experimental problem is to determine the magnetic structure of gadolinium formate, $Gd(HCOO)_3$, below the ordering temperature T_N/T_C = 0.73 K and below a second anomaly in C_P occurring at 0.4 K.

The scientific interest is that $Gd(HCOO)_3$ is the strongest magnetocaloric compound ever found (Lorusso *et al*. 2013), useful for the refrigeration technology in the range of liquid helium temperatures. This behaviour is due to a frustrating crystal structure, producing a very low ordering temperature in spite of its high magnetic density. The crystal structure is rhombohedral s.g. *R3m* in which Gd^{3+} ions form chains along the *c* axis, with a Gd-Gd intra chain distance of 3.98 Å. Other chains are well apart, the shorter Gd-Gd inter chain distance being 6.19 A. Moreover the inter chain exchange interaction cancels by symmetry.

Natural gadolinium is a strong absorber for thermal neutrons, but diffraction can be performed with hot neutrons, i.e. in the instrument D9 with λ = 0.5 Å. This wavelength is not the best choice for magnetic structure determination, since many low angle reflections cannot be separated from the direct beam but still allows an acceptable neutron flux and accessing to many significant magnetic reflections.

In addition to the problem with gadolinium, experiments below 0.4 K need ^{3}He/^{4}He dilution refrigeration device. That imposes the normal beam Weissenberg geometry in which the sample rotates only along the vertical axis, while the detector can move along the vertical and horizontal axes.

The crystal was small perfect hexagonal prism, with diameter of *d* = 0.1 mm and 1.3 mm long (crystal *c* axis). It was mounted along the cryostat vertical rotation axis, in order to minimize the absorption and making easier to correct it. The normal beam geometry imposes another drawback. The unit cell parameters (hexagonal setting, *a* = 10.466 Å, *c* = 3.984 Å) has a small *c* parameter and the limited motion of the detector along the horizontal axis allow to access only to *hkl* reflections with *l* = 0, ±1, ±2. Finally the crystal diameter was quite smaller than the ideal size for λ = 0.5 A, when the mean free path of the neutron is near 0.6 mm. Using λ = 0.8 A increases the absorption by a factor of 10, but also the neutron flux increases. Moreover *d* = 0.2 mm is the ideal diameter. That allows to access to lower angle reflections but limits *l* = 0, ±1. For this reason we did the experiments with λ = 0.5 Å and with λ = 0.8 Å.

Nuclear structure at 10 K with λ = 0.512 Å

The crystal was aligned an oriented using the four-circles configuration at RT. The crystal was transferred to a conventional insert cooled in an orange cryostat. Reflections were very weak but perfectly distinguishable, with long scanning times. A set of 65 nuclear *hkl* reflections were scanned with with *l* = 0, ±1, ±2, 53 unique, 36 of them observed with intensity > 4 × sigma.

The nuclear structure was refined using FULLPROF in the single crystal mode, giving a fair (for the extreme conditions of this experiment) RF2 = 17.5%, considering all reflections, being the maximum disagreement , among the observed reflections, for (6,4,-1) with Dif/sigma = 5.1 . Absorption was corrected using data for cylinders in table 6.3.3.2 in International Tables for Crystallography. The scattering factor for Gd b(Gd) = (1.5 – 0.042 i)$\times 10^{-12}$ cm was interpolated from the data in table 1 of (Abell et al 1983)

The refined nuclear structure is consistent with that reported at 298 K (Pabst 1943) and determined by powder X-ray diffraction. The refined parameters are listed in Table 1

TABLE 1: refined parameters for $Gd(HCOO)_3$ at 60 mK (atomic positions at 10 K). The *z*-coordinate was fixed for Gd

atom	x/a	y/b	z/c
Gd	0	0	0.8
O1	0.2485(11)	0.497(2)	0.947(11)
O2	0.1331(11)	0.266(2)	0.779(9)
C	0.1801(9)	0.3603(17)	0.008(10)
H	0.1567(15)	0.313(3)	0.268(18)
cell(Å) *a,b,c*	10.375	10.375	3.990

Magnetic structure at 60 mK.

Reflections were scanned with λ = 0.512 Å and λ = 0.84 Å (shortly referred as 0.5 and 0.8 Å throughout this report) . The absorption is 10 times stronger for 0.8 Å than for 0.5 Å but given the small crystal size, and the higher neutron flux for 0.8 Å the intensity of reflections was approximately equal. The larger wavelength allows to access to lower angle magnetic reflections (hidden by the direct beam for 0.5 Å) and the shorter one to scan a wider *q* space. This detail is important because for 0.8 Å *hkl* reflections could be scanned only for *l* = 0,±1, due to the small cell parameter *c* (*i.e.* only 23 unique reflections could be scanned). *q*-scans gave no other observed reflections other than those observed at 10 K. Especial attention was devoted for *l* = ±0.5 and for *h* = 0.5 and *k* = 0.5. No new reflections was found concluding that the propagation vector should be ***k*** = 0. All reflections with integer *h,k,l* (even those not allowed by the obverse rhombohedral centering condition –*h*+*k*+*l* = 3*n*) but all observed reflections were also observed at 10 K, concluding that magnetic structure must be ferromagnetic.

Some of the observed reflections were more intense at 60 mK than at 10 K. The magnetic moment is strongly correlated with the nuclear part. Morever the theoretical value μ = 7 μ_B for Gd^{3+} agrees very well with experiment in this type of ionic compounds, particularly with the macroscopic magnetization data. Therefore the value of the moment was fixed and the

orientation refined in spherical coordinates, giving the best refinement for the moment along the z axis (Fig. 1). We conclude that the magnetic structure is ferromagnetic Fz with the moments along the crystal *c* axis. This configuration makes minimum the dipolar energy for a chain $U_{dip}/particle$ = -1.4977 K × $\mu(\mu_B)^2/a(Å)^3$ = -1.16 K near of the ordering temperature. A Monte-Carlo simulation shows that this chain orders at 0.75 K , as experimentally observed. Therefore the observed magnetic structure corresponds with that expected for a system with dipolar interaction only, where the exchange can be neglected.

A second collection of reflections at 600 mK dis not show any difference with respect to resultas at 60 mK. Then, contrarily to the expected from heat capacity or susceptibility data, no other intermediate magnetic structure between 400 mK and 0.74 K.

Finally the strongest accessible magnetic reflection (-1 -1 0), with $\boldsymbol{\mu}$ perpendicular to the scattering vector ***q***) was scanned at T = 1.0, 0.8, 0.6, 0.4, 0.2, 0.1 and 0.05 K. Results (Fig. 2) show an intensity increase of 30% at 0.6 K, consistent with the ordering temperature T_C = 0.74 K observed in C_P data.

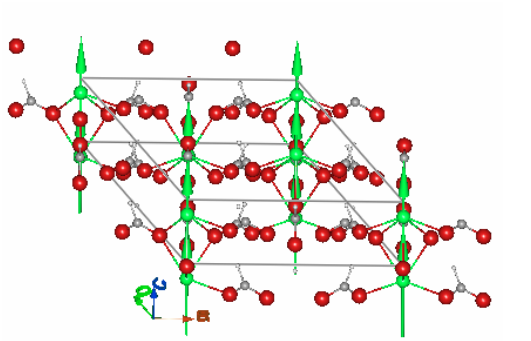

FIGURE 1: Nuclear and magnetic structure of $Gd(HCOO)_3$ at 60 mK

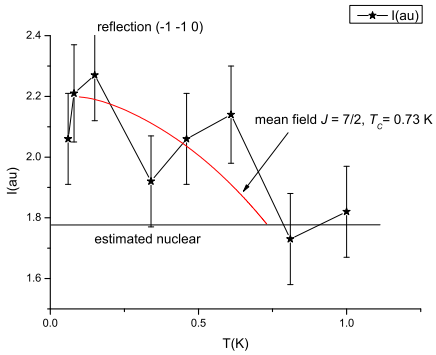

FIGURE 2: Thermal evolution of the intensity of the (-1,-1,0) reflection.

1) JS. Abell, JX. Boucherle, R. Osborn, BD. Rainford, and J. Schweizer, *J. Mag. Magn. Mater.* 31-34, 247-248 (1983).

2) G. Lorusso, J. W. Sharples , E. Palacios , O. Roubeau , E. K. Brechin , R.Sessoli , A. Rossin , F. Tuna , . J. L. McInnes , D. Collison , and Marco Evangelisti, *Adv. Mater.* ,25, 4653-4656 (2013). DOI: 10.1002/adma.201301997

3) A. Pabst, *J. Chem. Phys.* 11, 145 (1943); doi: 10.1063/1.1723815