Experimental report

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Proposal: 5-41-793 **Council:** 10/2014

Title: Determination of the Magnetic Structure of GdVO4 below 2.5 K

Research area: Physics

This proposal is a new proposal

Main proposer: Elias PALACIOS LATASA

Experimental team: Elias PALACIOS LATASA

Local contacts: Jose Alberto RODRIGUEZ VELAMAZAN
Oscar Ramon FABELO ROSA

Samples: GdVO4

Instrument	Requested days	Allocated days	From	To
D9	5	5	23/07/2015	28/07/2015

Abstract:

The zircon-type GdVO4 is an interesting compound for magnetic refrigeration at low temperature, similarly to the previously studied monazite-type GdPO4. For the phosphate, neutron diffraction shows that long-range magnetic ordering at TN = 0.77 K is a delicate balance between dipolar andexchange interactions in a frustrated lattice. The magnetic structure, as obtained by minimizing the dipolar energy, is characterized by a negligible exchange energy difference with respect to the disordered state. For the vanadate, the much higher TN = 2.5 K makes us believe that magnetic frustration is not so determining and ordering should proceed differently. Therefore, GdVO4 is an interesting study case, not only in an application perspective but also from the fundamental point of view. We ask for 5 days in the D9 instrument to determine the magnetic structure at 1.8 K. Short wavelength is necessary to avoid the huge absorption of Gd for thermal neutrons but acceptable for lambda = 0.5 A.

EXPERIMENTAL REPORT FOR EXPERIMENT 5-41-793

(Instrument D9, 23/07/2015-28/07/2015)

Title: **Determination of the Magnetic Structure of $GdVO_4$ below 2.5 K**

The GdMO_4 (M = P, As, V) family has interest in the technology of magnetic refrigeration due to the large magnetic density, low anisotropy and low ordering temperature. As a consequence $GdPO_4$ has the largest entropy decrement ever observed for a given isothermal magnetic field increase, ΔS_T = -62.1 J/kg.K at 2.1 K for a field B = 7 T. That is possible due to a weak exchange in the ionic compound and frustrating monazite-type structure. Consequently this compound, in spite of the very high magnetic density (saturation magnetization: $\mu_0 M$ = 1.18 T) orders only at T_N = 0.77 K in a non-collinear arrangement labeled as $C_xA_yC_z$, in the Bertaut's notation. This type or ordering is produced by a competition of the dipolar interaction and the weak anisotropy, being the exchange (exchange energy estimated as 0.1 K) much weaker [1].

$GdVO_4$ has the zircon structure and orders at T_N = 2.5 K (more than three times higher than $GdPO_4$) with similar magnetic density. The ordering mechanism cannot be dipolar at such relatively high temperature, therefore the exchange energy must be about 25 times larger than in $GdPO_4$, being so similar in other physical features. $GdVO_4$ has intrinsic interest as complementary to other compounds in the series, but also to study the Gd-Gd interactions in the zircon polymorphs. Other zircon-type compounds with M = Cr are very interesting in magnetic refrigeration since order ferromagnetically due to the Cr-Cr exchange [2]. The Gd-Gd exchange has been assumed ferromagnetic but then the peak in heat capacity (C_p) at 4.9 K is difficult to explain. $GdVO_4$, where M is a non-magnetic atom, offers the possibility of studying the Gd-Gd interactions.

The neutron diffraction experiments for the determination of the magnetic structure of $GdVO_4$ were performed at the ILL institute, instrument D-9 with a needle-shaped crystal of diameter 0.2 mm and 2 mm long. Wavelengths of λ = 0.509 Å and 0.8 Å were used. In the first case the strong absorption of natural Gd is much reduced. The longer λ allows accessing to some intense low angle reflections which merge in the direct beam for shorter λ. The nuclear structure was tested at 298 K with the 4-circle configuration. Collections for the magnetic structure determination were taken with a ^{3}He/^{4}He dilution cryostat in the Weissenberg normal beam configuration, with the crystal axis (crystallographic c-axis of the tetragonal zircon unit cell) vertical.

At 298 K, the nuclear structure agreed with data in literature [3], zircon-type structure, $I4_1/amd$, $Z = 4$, a = 7.2137 Å c = 6.3709 Å. In this structure type Gd atoms are at the special positions Gd1 (0,0,0), Gd2 (0/1/2,1/4), Gd3 (1/2,1/2,1/2), and Gd4 (1/2,0,3/4). At 2 K (slightly below T_N = 2.5 K) the unit cell has reduced to a = 7.193, c = 6.339, with the same structure. Some pure magnetic reflections are already visible, but for a better analysis we will consider first the data at 90 mK, taken in the normal beam configuration with λ = 0.8 Å. Finally a new collection was taken at 5 K, with the normal beam configuration to make the difference with the 90 mK data and establish the pure magnetic diffracted intensities.

At 60 mK, 113 *(h,k,l)* accessible reflections were scanned with l = 0, -1, -2, 69 of them observed with $I > 3\sigma$. Among them 26 purely magnetic (not allowed by the nuclear structure). The q-scans between pairs of observed reflections showed no intensity and consequently all magnetic reflections can be indexed with integer indices. The most intense ones are, in decreasing order (±1,±1,0), (±1,±3,0),(±3,±1,0), (±5,±1,0), and (±1,±5,0). These ones are forbidden by the nuclear zircon structure. Their existence unambiguously breaks the diamond plane in the nuclear structure, but preserves the I centering of the lattice. The most intense reflections have all $\boldsymbol{q}$ in the *ab* plane and the reflections (310) and (130) and (510) and (150). That suggest moments in the c direction, the intensity decreasing due to the form factor. The z components of the 4 Gd spins transforms among themselves (without mixing with x,y components) under the symmetry operations and form a reducible representation that reduces (using the Bertaut's notation) to the $F_z = S_{1z}+S_{2z}+S_{3z}+S_{4z}$, $G_z = S_{1z}-S_{2z}+S_{3z}-S_{4z}$, $A_z = S_{1z}+S_{2z}-S_{3z}-S_{4z}$, $C_z = S_{1z}-S_{2z}-S_{3z}+S_{4z}$. Reflections with $\boldsymbol{q}$ in the c direction (when the scattering factor cancels for the z components) could not be accessed in the normal beam configuration to check if weak x or y components are

present. Data have to be analyzed in more detail, and parameters refined, but most probably the structure is collinear antiferromagnetic G_z type, with moments in the *c* direction, being the moments of Gd1 and Gd2 up and Gd3 and Gd4 down. Physically the nearest neighbours, at 3.84 Å have opposite moments.

This experiment proves that the in absence of any other magnetic atom, in zircon the Gd-Gd exchange interaction is antiferromagnetic, what gives also physical sense to the peak observed in C_p at 4.8 K in $GdCrO_4$ when the Gd-Cr interaction produces a gradual ordering of Gd in ferromagnetic F_z mode. The weak anisotropy of Gd allows to order the residual component (not polarized by the Cr-Gd interaction) to order in a G_x or G_y mode rather than in the reported F_x mode. The peak in C_p at 4.9 K would be a spin-flop-like transition, acting the Cr-Gd exchange as an external field on the Gd sublattice.

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[4] H. Suzuki, Y. Masuda, and M. Miyamoto, J. Phys. Soc. Jpn. 52, 250-253 (1983).