Experimental report

29/08/2019

Proposal:	**DIR-164**	**Council:**	4/2018
Title:	Revealing the magnetic structure ofGd0.35Dy0.65(Co,Fe)2with unusual zero thermalexpansion property		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: $Gd_{0.35}Dy_{0.65}(Co,Fe)_2$

Instrument	Requested days	Allocated days	From	To
D4	2	2	07/10/2018	09/10/2018

Abstract:

Proposal: DIR-164

Title: Revealing the magnetic structure of $Gd_{0.35}Dy_{0.65}(Co,Fe)_2$ with unusual zero thermal expansion property.

Metallic materials that exhibit negligible thermal expansion or zero thermal expansion (ZTE) have great merit for practical applications, but these materials are rare and their thermal expansions are difficult to control. Here, we successfully tailored the thermal expansion behaviors from strongly but abruptly negative to zero over wide temperature ranges in a series of (Gd,*R*)$(Co,Fe)_2$ (*R*= Dy, Ho) intermetallic compounds by tuning composition to bring the first-order magnetic phase transition to second-order. The short-wavelength neutron powder diffraction, synchrotron X-ray diffraction, and magnetic measurement studies evidence this ZTE behavior was ascribed to the rare-earth-moment-dominated spontaneous volume magnetostriction, which can be controlled by adjustable magnetic phase transition.

How does the magnetic phase transition tune the thermal expansions in (Gd,Dy)$(Co,Fe)_2$? It is known that the abnormal thermal expansion in magnetic materials were induced by MVE. To extract the contribution from atomic magnetic moment to MVE and give insight into its mechanism, we determined the magnetic structures by neutron powder diffraction (NPD) experiment. Given the extremely high neutron absorption cross section of Gd, NPD data were recorded with a two-axis diffractometer using short-wavelength neutrons (λ=0.4952) at D4 of ILL,[i] see Figure 1a.

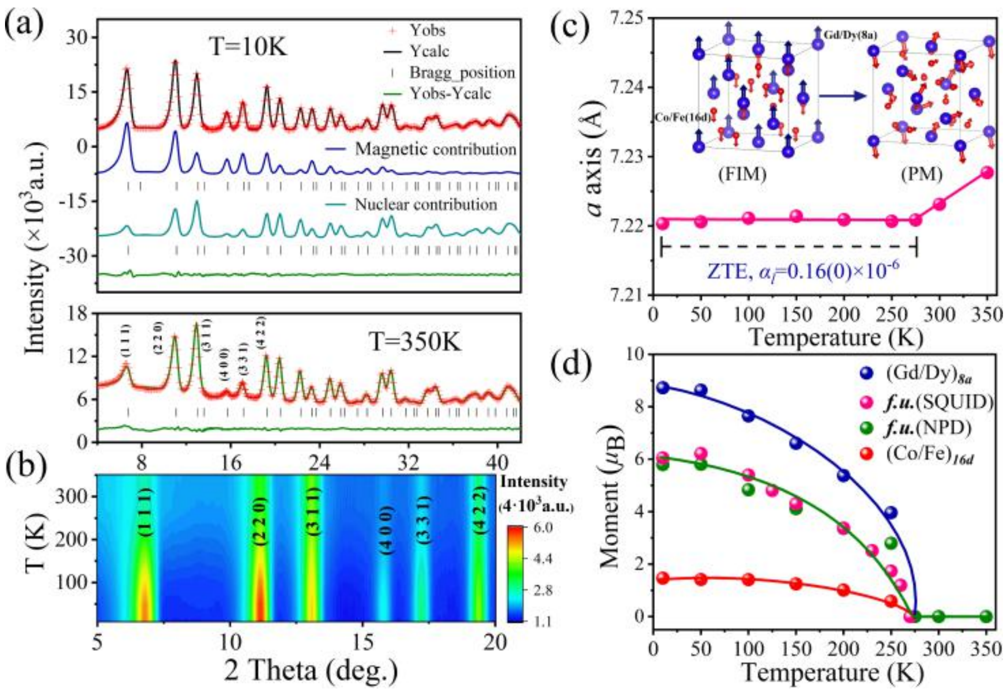

Figure 1. (a) NPD patterns of *GDCF* at 10 K and 350 K (b) Contour plots of the NPD profile intensity for *GDCF* (c) Temperature dependence of lattice parameter *a* of *GDCF* measured by NPD, insert shows its crystal and magnetic structure above and below T_C. (d) A comparison of total and partial moments for *GDCF*. The total magnetic moment for a chemical formula unit

$M_{f.u.}$ (calculated by $M_{Gd/Dy}$ - $2M_{Co/Fe}$ from NPD), agrees well with the macroscopic measurement by a superconducting quantum interference device (SQUID) magnetometer.

Below T_C, the magnetic moments of Gd/Dy and Co/Fe in *GDCF* are antiparallel arranged and form a ferrimagnetic (FIM) structure. While above T_C, they are randomly distributed without long-range ordering (Figure 3c Inset). Figure 3c shows the temperature dependence of lattice parameter *a* of *GDCF* in the temperature range of 10 - 350 K determined by the NPD. In addition to the dilatometer and X-ray results, it shows *GDCF* displays a ZTE property down to 10 K with α_l = 0.16(0)×10^{-6} K^{-1} (10 - 275 K). Figure 3d shows the magnetic moments of Gd/Dy and Co/Fe sites plotted as a function of temperature for *GDCF* sample. The magnetic moment of Co/Fe atoms (1.47 μ_B at 10 K) are much smaller than that of Gd/Dy atoms (8.72 μ_B at 10 K) at all temperatures due to the strong spin-orbit coupling of 4*f* rare earth Gd/Dy and the quenched orbital magnetic moments of 3*d* transition metals Co/Fe.[ii]

The data has been published or submitted to:

1. Hu, J. *et al.* Adjustable Magnetic Phase Transition Inducing Unusual Zero Thermal Expansion in Cubic RCo_2-Based Intermetallic Compounds (R = Rare Earth). *Inorg Chem* **58**, 5401-5405 (2019).
2. Hu, J. *et al.* A case of multifunctional intermetallic compound: negative thermal expansion coupling with magnetocaloric effect in (Gd,Ho)$(Co,Fe)_2$, Submitted to *Inorg. Chem. Front.*

(i) (a) Fischer, H. E.; Cuello, G. J.; Palleau, P.; Feltin, D.; Barnes, A. C.; Badyal, Y. S.; Simonson, J. M., D4c: A very high precision diffractometer for disordered materials. *Appl. Phys. A-Mater.* **2002**, *74* (0), s160-s162. (b) Lin Kun; Henry E. Fischer; Hu Jinyu, Revealing the magnetic structure of $Gd_{0.35}Dy_{0.65}(Co,Fe)_2$ with unusual zero thermal expansion property. *Institut Laue-Langevin (ILL)* **2018**, doi: 10.5291/ILL-DATA.DIR-164.

(ii) (a) Nesbitt, E. A.; Williams, H. J.; Wernick, J. H.; Sherwood, R. C., Magnetic Moments of Intermetallic Compounds of Transition and Rare‐Earth Elements. *J. Appl. Phys.* **1962**, *33* (5), 1674-1678. (b) Guirado-Lopez, R. A.; Dorantes-Davila, J.; Pastor, G. M., Orbital magnetism in transition-metal clusters: from Hund's rules to bulk quenching. *Phys. Rev. Lett.* **2003**, *90* (22), 226402.