XAFS understanding of “repeated” magnetic compensation in Nd$_{0.8}$Tb$_{0.2}$Al$_2$

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Abstract. Magnetic compensation (zero-moment) has important advantage in spintronics as it does not generate any self stray magnetic field. The physics of magnetic compensation (at a well defined temperature $T_{\text{comp}}$) is well understood in terms of competition and compensation between antiferromagnetically coupled magnetic moments of two rare earth ions. The different thermal evolution of the dissimilar rare earth moments can compensate each other at a particular temperature determined by the concentration of the dopant. We have observed, for the first ever time, “repeated” magnetic compensation in both polycrystalline and single crystals of Nd$_{0.8}$Tb$_{0.2}$Al$_2$ ($T_{\text{f1}} \sim 86$ K and $T_{\text{f2}} \sim 34$ K). A possible reason could be the non-random distribution of magnetic rare earth ions on different crystallographic sites, presenting deviation from mean field like situation. The motivation for XAFS derives from detection of these circumstances. XAFS at Nd, Tb L$_3$ edges reveals that 25% (Nd,Al) anti-site defect exists in Nd$_{0.8}$Tb$_{0.2}$Al$_2$. This implies that Nd atoms occupy two different sites. In contrast, Tb preferentially substitutes only one of the Nd sites. The implication of these results upon magnetic compensation is discussed.

1. Introduction

The phenomenon of magnetic compensation (zero-moment) in mixed rare-earth compounds [1] is well known. The concurrent condition of finite spin and zero net-moment is ideal for spintronics [2] as it inhibits the generation of stray magnetic field. The physics of magnetic compensation, at single temperature $T_{\text{comp}}$, is well understood. In an admixed alloy viz. $R_{1-x}R'_{x}$, with anti-ferromagnetically coupled magnetic moments $\mu_{R}$ and $\mu_{R'}$, magnetic compensation (between $R$ and $R'$) could result if $(1-x)\mu_{R} = x\mu_{R'}$. The thermal evolution of $\mu$ is monotonic over practical temperature range and solving the equation for particular $x$, results in single
compensation temperature \( T_{\text{comp}} \). We have observed, for the first ever time, “repeated” magnetic compensation \( (T_{f1} \approx 86 \text{ K and } T_{f2} \approx 34 \text{ K}) \) in both polycrystalline and single crystals of \( \text{Nd}_{0.8}\text{Tb}_{0.2}\text{Al}_2 [3] \). [In this case, R=Nd, R’=Tb]. This is curious since it directly challenges the basis of the above equation viz. monotonic thermal evolution of moments. Additionally, the phenomenon is encouraging since it raises \( T_{\text{comp}} \) towards practical temperature range (e.g. \( T_{f1} > T_{f2} \)). Heat capacity, resistivity, ac-susceptibility and XMCD show fingerprints at both these temperatures [3], indicating the involvement of two magnetic sub-lattices. [Fingerprints at \( T_{f1} \) are more prominent compared to \( T_{f2} \)]. These observations suggest (i) co-existence of different phases; (ii) one phase (corresponding to \( T_{f1} \)) more dominant than the other (corresponding to \( T_{f2} \)). Although XRD has detected single phase for these compounds, defects on nano-scale (beyond the detection limits of XRD) cannot be ruled out. The motivation for our Nd and Tb L3-edge XAFS experiments derived from detection of these phases. Since the coupling between Nd and Tb is responsible for compensation, XAFS at Tb L3 edge is intended to characterize this coupling in terms of Tb-Nd bond-length and coordination.

2. Experimental

Polycrystalline samples of \( \text{Nd}_{0.8}\text{Tb}_{0.2}\text{Al}_2 \) were prepared by melting together stoichiometric amounts of the end members \( (x=0 \text{ and } x=1) \) in an arc furnace. They were characterized by element-analyzer, XRD and magnetization (SQUID-VSM) prior to XAFS measurements. For XAFS measurements, the polycrystalline samples were further ground to \( \approx 5 \mu \text{m} \) particle size and pasted on scotch tape. XAFS data at Nd L3- edge (6.208 keV) and Tb L3-edge (7.514 keV) were collected in transmission-mode at the bending magnet beamline 10-BM of MRCAT (Materials Research Collaborative Access Team) [4], Advanced Photon Source, USA. During XAFS measurement, reference compounds / foils were measured in parallel at respective edges to calibrate the monochromator [Si (111)]. The latter was detuned to remove higher harmonics. For the incident and transmitted ion chambers, [He:N2=1:4] and [N2:Argon=4:1] were used respectively. The data were processed using ATHENA [5] and the structural parameters (bond-length, coordination and DWF) were fit using the programs FEFF8 and FEFFIT [5].

![Graph](image1.png)

3. Results and Discussions

XANES and EXAFS spectra are shown in Figures 1a-b. Nd L3-XANES whiteline is significantly more suppressed (than Tb L3), despite lower DWF \( i.e. \) better order for Nd bonds (observed from EXAFS analysis). This could be consistent with co-existing different structural phases for Nd site. The oscillations from these phases interfere destructively and reduce Nd L3 XANES whiteline. EXAFS signal shows noise and scan-to-scan irreproducibility beyond 8 \( \text{Å}^{-1} \) due to large absorption in air (etc.) at these low edges. For
fitting, $k^{1,2,3}$-weighted data were transformed over 3-8 Å$^{-1}$. Due to limited spline range, the Fourier transforms of the data showed relatively large background peak at < 2 Å (Figures 2a-c). However, since the structural peaks of interest are farther away (2.5-4 Å), the contribution of background peak could be ignored during fitting. NdAl$_2$ crystallizes in $d$-$3$ $m$ group. The bond lengths for the pure NdAl$_2$ phase were generated using the crystallographic structural parameters in the ATOMS program. Simulation generated for the pure phase, using the NOFIT option in feffit.inp, is compared with the Nd L$_3$ XAFS data in Figure 2a. $S_0^2$ and DWF were constrained to be 0.9 [6] and 0.01 Å$^2$ respectively. Figure 2a suggests marked deviation between the simulated and experimental data over 2-2.8 Å. We attempted to correct for this deviation by actually fitting (i.e. not using NOFIT) the data. During fitting, coordination was constrained to crystallographic values while bond-lengths and DWF were varied. The fit resulted in corrections to crystallographic $R_{Nd-Al}$ and $R_{Nd-Nd}$ by 0.23 Å and 0.14 Å respectively, with DWF ~ 0.02 Å$^2$ each. [It may be noted that Nd and Tb neighbors are indistinguishable by XAFS]. Even including these corrections, the structure of pure NdAl$_2$ phase failed to fit the experimental data (the peak shape) well, as is clear from Figure 2a and poor fit quality (R-factor = 0.03). Even including coordination vacancy could not improve the fit. These results consolidated our speculation that single structural model may not be sufficient to fit the data and co-existing second structural phase (Phase 2) needs to be considered. “Pure” phase will henceforth be referred to as Phase 1.

For Phase 2, we considered several models and generated the corresponding transforms. Out of these, Nd-Al anti-site defect appeared to be the most plausible model. Bond lengths, corresponding to the site exchanged phase, were generated by interchanging the Nd and Al sites in the ATOMS file. XAFS simulation, for site-exchanged phase (Phase 2), is shown in Figure 2b. Subsequent simulations, combining different proportions of pure and site-exchanged phases, show considerable improvement in the peak shape between 2-2.8 Å. To quantify the fraction ($x$) of anti-site defect, the fit strategy included linear combination of the ordered and site-exchanged phases. Scattering paths, for the two phases, included: (i) $R_{Nd-Al} = 3.31$ Å (N = 12) and $R_{Nd-Nd} = 3.46$ Å (N = 4) for Phase 1 and (ii) $R_{Nd-Al} = 2.82$ Å (N = 6) and $R_{Nd-Al} = 3.31$ Å (N = 6) for Phase 2. The fraction of each phase was duly included in feffit.inp through multiplicative factor “degeneracy”: viz. (1-$x$) for Phase 1 paths and $x$ for Phase 2 paths. Best fit was obtained for $x = 0.25 \pm 0.03$ i.e. 75% Nd atoms occupy Phase 1 site while 25% Nd atoms occupy Phase 2. The refined bond-lengths are determined to be $R_{Nd-Al} =$
3.28 Å, \( R_{\text{Nd-Nd}} = 3.39 \) Å and \( R_{\text{Nd-Nd}} = 2.94 \) Å. Good fit quality is ensured by low R-factor (= 0.007) and demonstrated in Figure 2b.

Tb L\(_3\) dataset was fit, following the same procedure as Nd L\(_3\). Interestingly, the best fit is obtained for Tb preferentially substituting only the Nd sites in Phase 1 (with increased DWF: \( \sigma^2_{\text{Tb-Al}} = 0.01 \) Å\(^2\) and \( \sigma^2_{\text{Tb-Nd}} = 0.03 \) Å\(^2\). [Constraining Tb to occupy both the sites degrades fit quality considerably.] This is clear from Figure 2c, where the Tb edge transform, rather than Nd edge, resembles the structure of Phase 1. \( R_{\text{Tb-Nd}} = 3.46 \) Å implies that Tb bonds preferentially with the Nd atoms in Phase 1 site.

These structural results suggest that Nd-Tb magnetic compensation (at least partial) occurs only at one Nd site viz. Phase 1. Nd atoms in Phase 2 remain magnetically uncompensated due to absence of Tb neighbor. Phases 1 and 2 result in different \( \mu - T \) curves. Their weight-averaged \( \mu_{\text{net}} - T \) curve crosses zero magnetization line twice, at \( T_1 \) and \( T_2 \). Thus, repeated compensation is result of structural inhomogeneity, with the latter acting like two magnetic sub-lattices. Detailed theoretical modeling is underway to account for the observed repeated compensation more quantitatively.

4. Conclusion

In summary, we have studied the structure around Nd and Tb sites in Nd\(_{0.8}\)Tb\(_{0.8}\)Al\(_2\), using XAFS. The system is determined to be structurally inhomogeneous, with Nd atoms occupying ideal crystallographic and site-exchanged (with Al) sites in 3:1 ratio. In contrast, Tb dopants preferentially substitute only the ideal Nd sites. This causes inhomogeneity in Nd-Tb coupling (or magnetic cancellation) since only the Nd atoms in ideal sites find Tb neighbors. Nd atoms, in site-exchanged site, remain magnetically uncompensated due to absence of Tb neighbors. The two structural phases resemble two magnetic sub-lattices, resulting in different magnetic moments (and their thermal evolution) and subsequently, double compensation of the weighted averaged magnetic moment.

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