Evaluation of Ce and Gd valences in $Ce_xGd_{1-x}N$ estimated by rare earth L_{III} XANES and magnetic susceptibility measurements

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Introduction

Cerium is a typical multi-valence rare earth element, and its valence of Ce in CeN varies from +4 to +3 with increasing temperature(1). Such valence fluctuation is understood as a result of a change in occupancy of 4*f* orbital. Gadolinium possesses seven unpaired electrons on 4*f* orbitals which give rise to a large magnetic moment and a small magnetic anisotropy. Gadolinium mononitride, GdN, is a ferromagnet with the highest Curie temperature of the rare earth nitrides (Ln-N)(2). The magnetic moment of a rare earth atom originates in angular momentum and consequently reflects a state of the 4*f* electrons usually localized to atoms. However, when we study a compound containing two or more rare earth elements, it is practically difficult to estimate the 4*f* state of the respective elements with the magnetic methods in which only their total contributions can be measured. Therefore, we employed XAFS technique to estimate the valences of rare earth elements in $Ce_xGd_{1-x}N$ because this technique is element specific and free from interference of coexistence of other elements.

Experimental

$Ce_xGd_{1-x}N$ with various *x* were synthesized by the carbothermic reduction of oxide mixture followed by ammonia nitridation.

Ce and Gd L_3-edge X-ray absorption measurements of $Ce_xGd_{1-x}N$ at room temperature were carried out at the beamline BL7C and 9A in a transmission mode with Si (111) plane of the inclined double-crystal monochrometer. X-ray energy was carefully calibrated at times by measuring *K*-edge energy of Cu metal foil. Energy resolution was 0.3 eV for both Ce and Gd L_3-edges. The incident and transmitted X-ray intensities were monitored by ionization chambers.

Magnetization of the binary nitrides was measured with a superconducting quantum interference device magneto-meter in a temperature range of 5 – 200 K under magnetic fields from 0 to 5 T.

Results and Discussions

Figure 1(a) shows Ce L_3-edge XANES of the $Ce_xGd_{1-x}N$ together with that of CeF_3 as a reference material of a trivalent Ce, while Fig. 1(b) shows Gd L_3-edge XANES of our samples and GdF_3 as a trivalent Gd. The spectrum was normalized to each edge jump height after subtracting a background from the raw spectrum. As for Ce L_3-edge XANES, a significant *x*-dependence was observed as shown in Fig. 1(a). A clear single peak at 5727 eV was seen in the spectrum of CeF_3, while another significant peak at 5738 eV was noticed in that of CeN which may be assigned to tetravalent. This double peak feature is clear when Ce-content $x \geq 0.7$, but the peak at 5727eV is predominant when $x \leq 0.5$. Similar double peak feature, though different peak energies, has been indeed reported for CeO_2, in which Ce has +4 valence(3). Figure 1(b) clearly shows that Gd L_3-edge XANES of $Ce_xGd_{1-x}N$ is insensitive to *x* and substantially coincides with that of GdF_3, in which Gd has +3 valence.

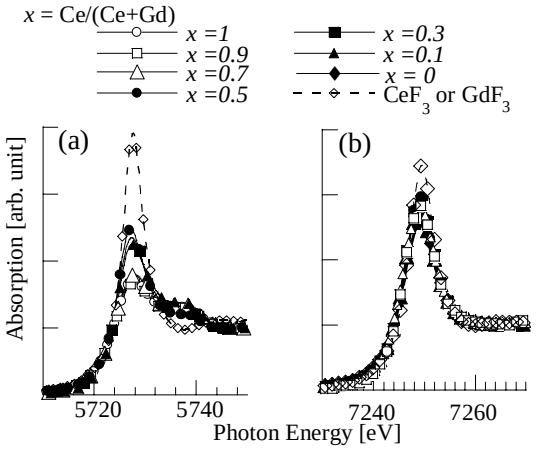

Fig.1(a) CeL_3 XANES spectra of $Ce_xGd_{1-x}N$ and CeF_3
(b) GdL_3XANES spectra of $Ce_xGd_{1-x}N$ and GdF_3

The effective magnetic moments of $Ce_xGd_{1-x}N$ theoretically estimated in terms of Landè *g*-factors calculated from these results (Ce has +4 valence above x = 0.7 and +3 valence below x = 0.5; Gd is trivalent in any mixing ratio) well agree with those obtained by magnetic susceptibility measurements.

References

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