Electronic band structure information of GdN extracted from x-ray absorption and emission spectroscopy

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The electronic structure of GdN films grown by pulsed laser deposition has been investigated by soft x-ray absorption (XAS) and x-ray emission spectroscopy (XES) at the N K-edge. Density functional calculations within the local spin density approximation with Hubbard-U corrections of the N p weighted bands and density of states are used to extract band information from the spectra. Gd $M_{4,5}$ XAS and XES spectra are also presented. The XES-XAS separation is shown to give information on the f-band spin splitting and the XAS line shapes are shown to reflect atomic multiplet effects. © 2010 American Institute of Physics. [doi:10.1063/1.3291057]

The rare-earth nitrides (ReNs) exhibit highly interesting magnetic and electronic properties. In particular, most of them appear to be intrinsic (as opposed to dilute) magnetic semiconductors. The most studied ReN is GdN. It has been shown that GdN is semiconducting at ambient temperature and that spin splitting caused by the onset of ferromagnetism at 68 K significantly narrows the direct band gap.[1] A strong negative magnetoresistance is also seen close to its Curie temperature.[2] As a result, it has potential for future magnetic sensor and spintronic applications.[3]

The correlated electronic and magnetic properties of GdN are due to the presence of the half-filled Gd $4f$ band. This band is highly localized, complicating electronic structure calculations, so experimental electronic structure probes on high quality samples are essential. We recently reported the growth of epitaxial thin films of GdN by pulsed laser deposition.[4] Here we use a synchrotron-based x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) at the N K-edge and Gd M-edges to provide the first detailed information confirming the accuracy of specific features in the computed band structure, including the Gd $4f$ splitting, and the evolution of conduction band (CB) states across the ReN series.

Epitaxial GdN films with well-oriented crystallites of up to 30 nm were grown on yttria-stabilized zirconia (YSZ) substrates by pulsed laser deposition in a plasma-activated nitrogen atmosphere. In Ref. 4 we reported the effects of substrate temperature, nitrogen pressure, and plasma power on film quality. The GdN film in this study has a ferromagnetic transition temperature of 70 K and is heavily doped with nitrogen vacancies; carrier concentrations, extracted from Hall effect measurements, are about 4×10^{20} cm^{-3}. Since GdN oxidizes rapidly in ambient atmospheric conditions the highest quality films from that study were capped with YSZ to allow transport to beamlines 511 at MAXlab in Lund, Sweden and X1B at the NSLS, Brookhaven National Laboratory.

At the N K-edge the total experimental resolution was estimated to be 0.2 eV (0.4 eV) for the XAS (XES). The XAS was measured in total fluorescent yield mode in order to penetrate the insulating capping layer. The Gd M-edge was measured in total electron yield mode at a resolution was 0.5 eV (1.0 eV) for the XAS (XES).[5] All experiments were performed at room temperature.

The electronic band structure was calculated using the full-potential linearized muffin-tin orbital method within the local spin density approximation (LSDA+U). Hubbard-U corrections were applied to the Gd $4f$ bands to correct for their localized nature, and to the largely unoccupied $5d$ bands to tune the optical band gap to agree with experiment.[6,7] For comparing theory to XAS measurements, it is important to consider the core-hole that is present in the final state. A calculation was performed for a simple cubic superlattice containing four GdN units in which one N atom contained a core-hole. Selecting the p-like partial density of states (PDOS) reflects the most important effect of the core-state to valence or conduction state matrix elements of the dipole operator. The additional energy dependence of the matrix elements was verified to be negligible.

Figure 1 shows the GdN N K-edge XES and XAS. The XES signal is largely due to N $2p$ bands that form the valence band (VB). A shoulder on the low energy side of the peak is clearer here than in the SmN and DyN XES (Ref. 8) because of the superior crystalline quality of the present GdN sample. In GdN the occupied Gd $4f$ bands are calculated to lie 8 eV below the VB maximum (VBM). The occupied Zn $3d$ bands in ZnO are in a similar position; we recently reported evidence for the observation of O $2p-$Zn $3d$ hybridization in XES (Ref. 9) but see no evidence for a similar effect here. The Gd $4f$ levels do not interact strongly with the N. This is in agreement with the M-edge XAS (see measurements below).

The unoccupied states, measured by the K-edge XAS, are largely Gd $5d$ and $6s$ like in nature. The N K-edge signal is due to the p-like character of these orbitals' tails when expanded in spherical harmonics about the N site. The XAS

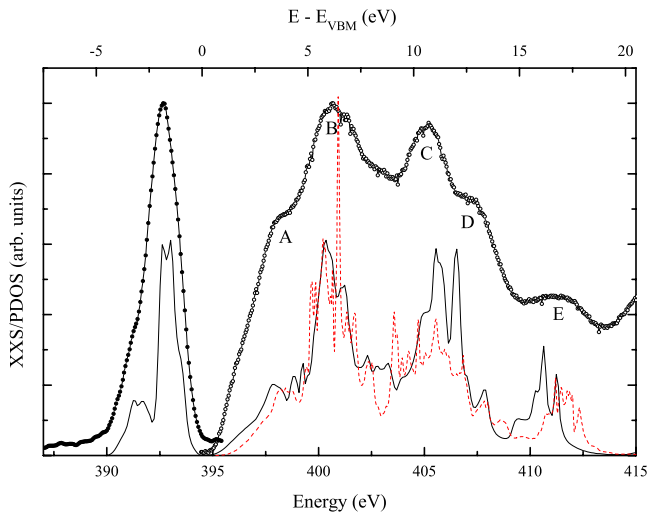a)Electronic mail: andrew.preston@gmail.com.

FIG. 1. (Color online) GdN N K-edge XES (solid circles) and XAS (empty circles). Also shown is the calculated PDOS. Both the standard PDOS (black line) and a core-hole calculation (dashed red line) are shown.

FIG. 3. (Color online) Left: calculated spin resolved GdN band structure. Vertical bars indicate the *p*-like character of the band. When viewed in color the majority- (black) and minority-spins (red) can be distinguished; right: spin resolved PDOS and XAS (from Fig. 1). Horizontal lines indicate points of interest labeled in Fig. 1.

shows two main peaks (labeled B and C) at 400 and 405 eV. Band structure calculations and symmetry considerations suggest that these peaks represent the Gd $5d$ orbital crystal field split into t_{2g} and e_g states, respectively. The e_g states in the CB are σ-antibonding with N p. Further confirmation of this interpretation is provided by examining the trend of this peak in the series SmN, GdN, DyN, and LuN, shown in Fig. 2.[10] A clear upward shift of the C-peak with increasing atomic number is seen, reflecting the increase in bond strength and decrease in lattice constant across the series. Evidence for the increase in bond strength across the series was also noted in Raman spectra.[11] In contrast, the lower peak (B) is constant across the ReN series indicating that it arises from the much weaker (π-bonding) t_{2g} orbitals.

The experimental spectra are compared with PDOS extracted from the LSDA+U calculation. For comparison to the room temperature experimental data (well above the ferromagnetic transition temperature) the PDOS shown is an average of the contributions from both spins. The PDOS have been rigidly shifted so that the main VB peak matches with experiment. This yields excellent agreement with the XES, accurately locating the main peak and the lower energy shoulder.
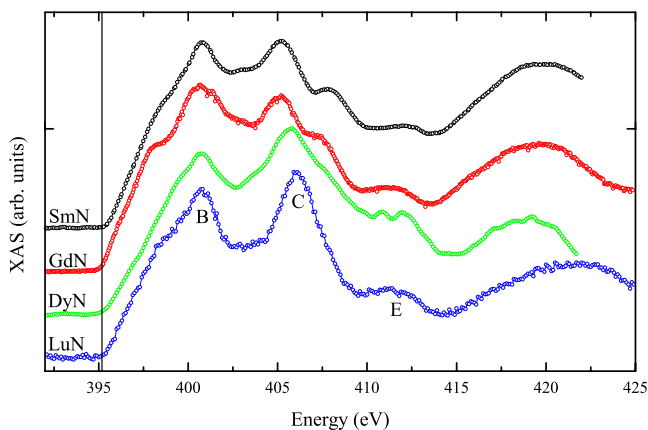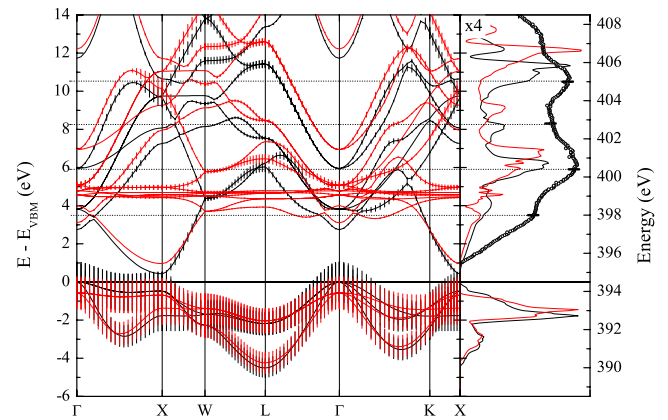
For the XAS, the final state rule[12] stipulates that the PDOS be calculated in the presence of the core-hole. Both PDOS with and without core-hole are shown in Fig. 1. Two effects are noticeable as follows: (1) the higher energy (e_g like) peak is reduced in intensity relative to the lower energy (t_{2g} like) peak; (2) the higher energy [e_g like (spin-split) peaks] broaden and shift to lower energy, consistent with an attractive core-hole potential. The lower energy peak agrees about equally well in position (and shape) with the experiment with and without core hole, indicating that the t_{2g} like states are little affected by the N p core-hole because of their weak hybridization. The upper experimental peak C appears to be located in between the peak position with and without core-hole, which could indicate partial screening of the core-hole. Differences in how strongly the core-hole final state affects different states in the CB were also observed for GaN.[13]

The peaks in PDOS are related to regions of the band structure with flat bands and to van-Hove singularities in the bands. We, therefore, show the band structure weighted by the N p-character of the bands in Fig. 3 together with the PDOS. The vertical bars on the band structure indicate the relative strength of the N p character along each band. Red and black indicate minority and majority spin, respectively. Peak B is split in two in the theory because of spin-splitting and is related to a van-Hove singularity along the Γ–K direction, (onset of the peak) and L (at the peak maximum). Peak C is related to a van-Hove type singularity at ~10.5 eV corresponding to a maximum of the highest band shown along Γ–X (of symmetry Δ_2). See Ref. 14 for a symmetry labeled band structure. The shoulder A is stronger in GdN than the other ReN and is clearly seen to be related to the minority spin PDOS and the lowest band along W–L–Γ–K, which (except near Γ) are f-like hybridized with N p.

Figure 4 shows the $M_{4,5}$ XAS and XES for GdN. The XAS is in agreement with that reported by Leuenberger *et al.*[2] The XAS probes dipole allowed transitions from the $3d^{10}4f^7$ ground state multiplets to the $3d^94f^8$ excited state multiplets, and the XES probes transitions from the $3d^94f^7$ excited state to the $3d^{10}4f^6$ relaxed state multiplets. Thus the $4f$ final states are the same as in x-ray photoemission spectroscopy (XPS)/bremsstrahlung isochromat spectroscopy.[15] A

FIG. 2. (Color online) Comparison of N K-edge XAS spectra of SmN, GdN, DyN, and LuN. Note the shift of the higher energy (c) peak.
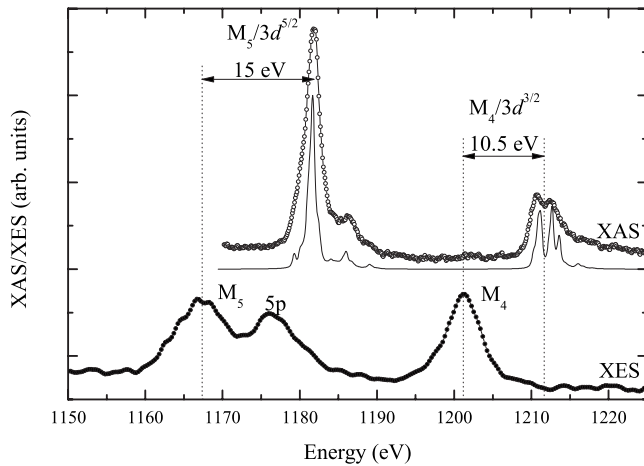
FIG. 4. GdN Gd M-edge XAS (empty circles) and XES (solid circles), and an atomic Gd^{3+} multiplet calculation (solid line).

multiplet calculation, following Thole *et al.*,[16] is also shown in Fig. 4. The line shapes of the XAS M-edge spectra and atomic calculation are in good agreement, indicating the atomiclike nature of the Gd $4f$ states. This is reinforced by the similarity to Gd metal M-edge XAS also reported in Ref. 16.

The combination with XES gives additional information. First, the average of the splittings between the M_4 (and M_5) XAS and XES gives approximately the splitting between empty (minority spin) f- and occupied (majority spin) f-states. This assumes that the center of gravity of each multiplet split set of states gives the corresponding f-level as would occur in a band calculation. The ($M_{4,5}$-averaged) splitting of 12.5 ± 0.5 eV is in good agreement with the LSDA $+U$ calculated $4f$ bands at about -8 eV in agreement with XPS (Ref. 2) so we now can also be confident about the position of the empty states at 4–5 eV above the CB minimum. Second, we can in the XES spectrum see a second peak just above the M_5 main peak which corresponds to the Gd $5p$ to $3d_{3/2}$ semicore states. The position of these semicore states is thus at about 23 eV below the f states or 31 ± 1 eV below the VBM.

In summary, detailed information on the GdN electronic band structure was extracted from a combination of XAS and XES of the N K-edge and the Gd M-edge. The two peak structure of the XAS is related to Gd t_{2g} and e_g $5d$-bands

which show a different sensitivity to the presence of the N $1s$ core-hole because of their different degree of hybridization with the N $2p$ states. The M_4 XAS-XES splitting gave information on the $4f$ spin splitting and the $5p$ semicore to $4f$ energy splitting.

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