Ferromagnetic redshift of the optical gap in GdN

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We report measurements of the optical gap in a GdN film at temperatures from 300 to 6 K, covering both the paramagnetic and ferromagnetic phases. The gap is 1.31 eV in the paramagnetic phase and redshifts to 0.9 eV in the spin-split bands below the Curie temperature. The paramagnetic gap is larger than was suggested by very early experiments, and has permitted us to refine a (LSDA+U)-computed band structure. The band structure was computed in the full translation symmetry of the ferromagnetic ground state, assigning the paramagnetic-state gap as the average of the majority- and minority-spin gaps in the ferromagnetic state. That procedure has been further tested by a band structure in a 32-atom supercell with randomly oriented spins. After fitting only the paramagnetic gap the refined band structure then reproduces our measured gaps in both phases by direct transitions at the X point.

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I. INTRODUCTION

The rare earth nitrides (RE-Ns) have recently attracted attention following theoretical advances that have yielded credible band structures in these strongly correlated materials.[1–10] However, despite their simple rocksalt structure and their strongly localized 4f states there are disagreements among various theoretical treatments regarding the nature of their band structures in either the ambient-temperature paramagnetic state or their magnetic ground states. Interestingly, among the predictions one finds that some may be half metals[6–8] which are of interest for spintronics applications, though their magnetic order is limited to temperatures below 70 K. However, even at ambient temperature the lattice constant varies systematically across the series, leading in turn to a systematically varying band structure and band gap. Thus the RE-N compounds may prove useful in a range of electronic and electro-optic applications.

The ionicity of these materials is manifest in their band structures, so that their valence bands are of N 2p and the conduction bands RE 5d, 6s character. In the presence of partially filled RE 4f levels the exchange interaction shifts the spin-split conduction and valence band edges in the opposite sense, reducing the majority-spin gap while the minority-spin gap opens.[6] Clearly a sufficiently large shift will reduce the majority-spin gap to zero, resulting in a half metal. Besides the strong correlation effects affecting the 4f states, the gap is also affected by the usual underestimate of the gap by the local density approximation (LDA). The latter is primarily due to long-range Coulomb contribution which is overscreened by the electron-gas screening used in LDA. In the present case, the conduction band minimum consists of RE-d_{t2g} states and the underestimated gap can be corrected by shifting the RE-d states upward within the LSDA+U method by introducing a U_d even though the underlying physics is rather different from the Hubbard U_f shifts.[1,6] The calculations require experimental input concerning the gap in order to fix a value for the empirical parameter U_d. In this paper we present transmission data that establish the optical gaps of GdN in both magnetic states, which then allow us to adjust the computed band structure.

The experimental description of RE-Ns is far from clear. Although their NaCl structure is well established,[11] there is remarkably little consensus in the literature concerning their physical properties. Most are known to be magnetically ordered at low temperature,[12] though there remains much uncertainty about transition temperatures, saturation moments, and even in some cases whether there is magnetic order at all and whether it is ferro- or antiferromagnetic.[12–16] There is also a debate about their temperature-dependent conductivity, with specific samples of even nominally the same composition claimed variously as a metal, semimetal, or semiconductor.[13,17–21] Nitrogen vacancies are common, and even in a material that is fundamentally a semiconductor they may dope the material to degenerate carrier densities.[19,20]

Optical transmission experiments have the potential to settle these questions by providing a measurement of the optical (i.e., minimum *direct*) band gap, but here also the few reported measurements have provided ambiguous results. Very early studies of the entire range of rare earth nitrides (except the radioactive Pm) were based on powder samples, which dictated that only diffuse reflection measurements could be made.[19,22] Those data show only a weak dip in their diffuse absorption ($A_{\mathrm{diff}}=1-R_{\mathrm{diff}}$), with enhanced absorption at energies both larger and smaller than the quoted gap, which was interpreted as resulting from competition between interband and free-carrier contributions to the optical conductivity. The gaps, all near 1 eV, were taken as the weak minima between the two competing contributions to the dif-

fuse absorption, rather than by observations of any clear absorption edges. In contrast gaps of 2 to over 4 eV (Refs. 23 and 24) are likely to be associated with severe oxidation; Gd_2O_3 has a 5.2 eV gap.[25] We find that unprotected films become transparent insulators within seconds after exposure to air.[20] The propensity of the RE nitrides to oxidize joins the presence of N vacancies as the phenomena most responsible for ambiguous historical results.

GdN, with its half-filled $4f$ shell, is by far the most thoroughly investigated of the RE-Ns. It has the highest Curie temperature among the RE-Ns,[12,20,21,26–31] with reports as high as 90 K.[27] We and others have recently reported a resistivity showing a magnitude and temperature dependence that is characteristic of a semiconductor above T_C, followed by a rapid fall as the temperature is lowered into the ferromagnetic phase.[20,21] However, below 25 K the resistivity again begins to increase in a form consistent with a reduced-gap semiconducting ferromagnetic state.[20]

We recently reported visible-near IR measurements on GdN demonstrating a clear ambient-temperature absorption edge near 1 eV, but without sufficient data below 1 eV to make a reliable estimate of the gap.[20] In this paper we extend transmission measurements to lower energy, which has permitted an unambiguous determination of the optical gap. More importantly the measurements have been completed at temperatures from ambient down to 6 K and signal clear band structure changes at the Curie temperature.

II. EXPERIMENTAL DETAILS

Thin films of GdN were grown, as described in more detail earlier,[16,20,32] by deposition of Gd from an electron beam heated source in the presence of 10^{-4} mbar of pure nitrogen gas. The 200 nm thick film was capped with ~200 nm GaN, which we have shown to be an effective barrier to reaction with the atmosphere.[20] Note that in GaN the interband edge is 3.4 eV,[33] and there is only a small, approximately energy-independent absorption in the energy range probed in this study.

The GdN in the present study contains crystallites with diameters of about 8 nm and has a resistivity of 0.15 Ω cm at 300 K, rising through a peak of 0.25 Ω cm at a Curie temperature of 66 K and thereafter falling to a minimum of 0.18 Ω cm. A carrier density of 10^{18} cm^{-3} at 300 K has been estimated by noting that the mean free path cannot be larger than the radius of the crystallites.

Spectral measurements in the range of 0.2–2 eV were performed with a Bomem model DA8 Fourier transform spectrometer using films on sapphire substrates. For variable-temperature data the film was mounted in a flow-through cryostat with polyethylene windows. The multilayer system, sapphire-GdN-GaN, shows complex interference. Fringes with a periodicity of about 6 cm^{-1} (~0.1 meV) associated with the substrate have been simply smoothed, leaving weak interference associated with the film and capping layers. Despite the weak fringes the band edges are strikingly clear, permitting an unambiguous determination of the optical gap and its redshift in the ferromagnetic phase.

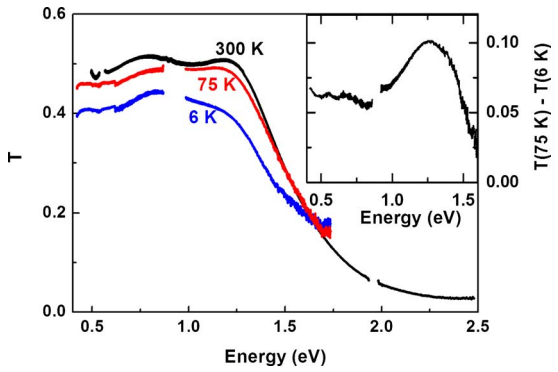

FIG. 1. (Color online) Transmission through a 200 nm GdN/~200 nm GaN film deposited on sapphire. The 300 K data were collected with the sample in vacuum, and for the 6 and 75 K data there were additional four polythene windows in the path which sacrificed intensity above 1.5 eV and across a gap near 0.9 eV. The edge at 1.3 eV is clearly visible in 75 and 300 K data, as is the tail of reduced intensity below that threshold at 6 K. The inset shows the transmission reduction in the ferromagnetic phase, with a clear indication of an interband edge at a lower energy than in the paramagnetic phase.

III. RESULTS

Figure 1 shows the frequency-dependent transmission at temperatures of 6, 75, and 300 K. Turning first to the 300 K data it can be seen that there is a clear onset of absorption just above 1 eV. There is no evidence of subgap absorption at lower energies, with the transmission flat except for interference fringes that modulate the transmission by 3%. The gap of 1.31±0.03 eV is estimated as the intersection of the frequency-independent transmission below the edge and the extrapolation from the inflection point centered on the edge. At 75 K (immediately above T_C) the transmission is little changed from 300 K, showing merely a 1%–2% fall in the low-frequency transmission and a changing interference pattern associated with contraction and with the temperature dependence of the optical constants in the film and substrate. Most importantly there is only a very weakly shifted interband edge as compared to the results at 300 K. In contrast the ferromagnetic phase, at 6 K, shows a very significant change in both the absorption edge and the subgap transmission. A very clear tail extends to a new edge at lower energy, which can be seen much more clearly in a plot of the difference between the transmissions at 75 and 6 K, in the inset of Fig. 1. Using again the intersection of extrapolated data above and below the edge we find a gap of 0.90±0.03 eV in the ferromagnetic state. The lower-energy edge enhances the refractive index below the gap, which then increases the reflectivity and is in turn responsible for the reduced subgap transmission.

In order to estimate the energy-dependent absorption coefficient, η, across the edge note that, with the neglect of interference enhancement within the GdN film, the transmission coefficient T is proportional to $(1-R)e^{-\eta d}$, where d is the thickness and R the reflectivity of the multilayer. Figure 2 shows the absorption coefficient estimated using this equation, replacing the factor $(1-R)$ by the transmission in the

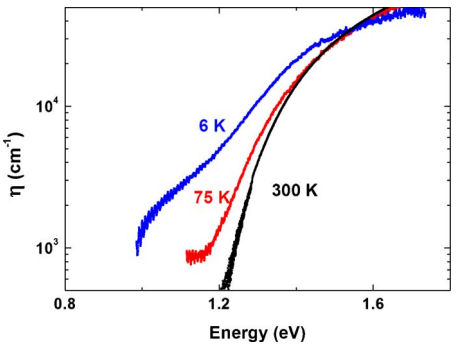

FIG. 2. (Color online) Absorption coefficient (η) implied by the data of Fig. 1 in paramagnetic and ferromagnetic phases.

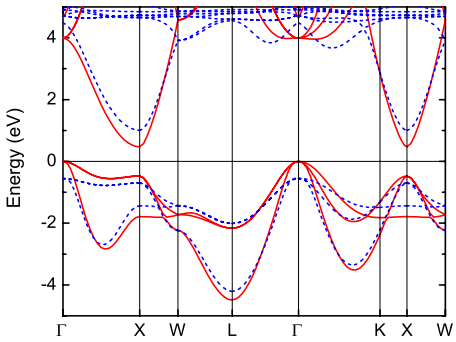

FIG. 3. (Color online) The band structure of GdN calculated with the value of U_d=8.0 eV determined from the paramagnetic and ferromagnetic gaps reported in this paper. The solid lines represent majority-spin bands, and dashed lines minority.

subgap region. It is significant that the absorption coefficient rises steeply to over 10^4 cm^{-1}. Such strong absorption is typical of interband direct transitions, and is orders of magnitude larger than is seen at indirect transitions.

IV. DISCUSSION

As discussed above there exist historical data suggesting that the optical gap in GdN is 0.98 eV.[22] It is interesting that the same paper reported what was regarded as anomalous optical data on one sample of GdN, apparently with a lower-than-typical N deficiency and thus weaker free-carrier absorption, in which the diffuse absorption showed an onset close to that reported here. The paper also made the claim that there was no shift of the edge in the ferromagnetic phase, but that the subgap absorption increased significantly. Although no low temperature data were presented, that description suggests a behavior similar to the present report, except that the data were apparently not extended to the redshifted edge.

More recently there has been a report of band shifts in GdN observed in x-ray magnetic circular dichroism data.[30] The conduction band density of states (CBDOS) at the Gd L_2 edge was seen to redshift by a few hundred meV in the ferromagnetic state. Those data measure the CB maximum relative to the Gd $2p$ core level, so they are not directly comparable to the present interband data. However, it is interesting that the redshift of the Gd $2p$ to CBDOS is of very similar magnitude to the interband edge redshift reported here.

The very clear optical gaps that we report relate directly to the (LSDA+U)-computed band structure of Larson *et al.*,[6] in which the same redshift of 0.4 eV is predicted between the para- and ferromagnetic phases. However, the absolute magnitudes of the gaps are in disagreement with our data. The experimental optical gap of Busch *et al.*[22] was used in that calculation as a means to fine-tune the gap. This is done by choosing a U_d parameter that is applied to the empty Gd $5d$ levels, shifting them up. The gap, 0.98 eV in the paramagnetic state, was assumed to correspond to the average of the majority- and minority-spin gaps in the ground state for which the calculation was made. From this they fix U_d at 6.4 eV. Using the same method and software we have recalculated the GdN band structure to fit the new data. In a remarkable agreement between theory and experiment we find that a choice of U_d=8.0 eV leads to a majority-spin gap of 0.91 eV and an average gap of 1.30 eV, which correspond to our measurements within their uncertainties. Figure 3 shows the band structure calculated with that parameter; note that GdN is an indirect-gap semiconductor with the direct gap at X and an indirect ($\Gamma - X$) gap of 0.43 eV (0.98 eV) in the ferromagnetic (paramagnetic) state.

It is important to explore whether the representation of the gap in the paramagnetic state as the average spin-resolved ferromagnetic gap is realistic. To test the idea we have carried out calculations of both ferromagnetically aligned and noncollinear random-aligned spins in a $2\times2\times1$ supercell of the conventional cubic fcc cell, containing 32 atoms. This calculation was done within the atomic sphere approximation and shifts were simply added to the Gd-$4f$ and Gd-$5d$ bands mimicking the full-fledged LSDA+U ferromagnetic state as closely as possible. With this approach the average gap of spin up (1.12 eV) and spin down (1.58 eV) gaps came out to be 1.35 eV in the ferromagnetically aligned case. The simple shift approach compared to the LSDA+U has as a side effect that the valence band maximum (VBM) at X (of rocksalt) equals the VBM at Γ, making the direct and indirect gap equal. However, the calculation clearly illustrates the relation between the gap of a disordered spin arrangement and the average of spin up and spin down gaps of the ferromagnetic system as a proof of principle. Using the same shifts in the supercell with noncollinear spins, the gap was found to be 1.30 eV, as can be seen in Fig. 4, which is indeed close to but slightly less than the average of the ferromagnetic gaps. The reason for the small discrepancy is that the calculation was performed for only one representative random sample and the size of the cell is still relatively small to represent a random configuration. In fact, it had a net residual magnetic moment of 1.44 μ_B/Gd in the cell. So, one could say it is still 20% magnetized instead of completely demagnetized. Thus it has only 80% of the upward shift in gap from the ferromagnetic case, i.e., 1.30 eV. The bands in Fig. 4 are color coded according to their spin content. Red means 100% majority spin, blue means 100% minority-spin, and bands with mixed spin character have the appropriate mix of

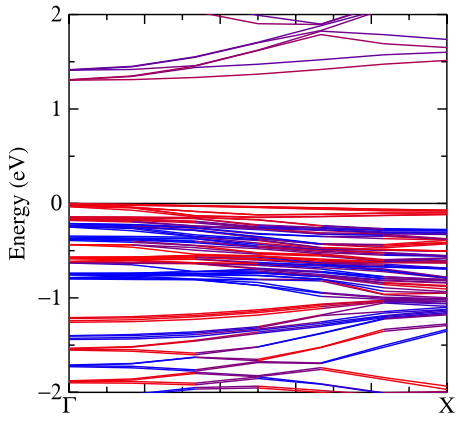

FIG. 4. (Color online) Energy bands of GdN in a $2\times2\times1$ supercell of the cubic fcc cell (containing 32 atoms) from $\Gamma=(0,0,0)$ to $X=\left(\frac{\pi}{2a},0,0\right)$ with randomly chosen spin directions on the Gd sites. The bands are colored according to spin content, with red for majority and blue for minority spin.

blue and red. One may see that the valence band maximum still has 100% majority-spin character but the conduction band minimum has a mixed character, the lower one being slightly more majority and the next one being slightly more minority spin in character. This direct way of simulating the paramagnetic system would require larger cells to be fully converged. Nevertheless, it provides a direct test that the gap is indeed larger for a system with randomly oriented spins compared to the gap for the ferromagnetic system and provides additional support to our procedure of estimating the gap of the paramagnetic system as the average of majority- and minority-spin gaps in the ferromagnetic state.

V. CONCLUSION

We have reported an unambiguous signature of the direct optical gap in a rare earth nitride. The absorption edge is seen as a rapid loss of transmitted intensity as the photon energy rises through the edge, and is accompanied by an energy-independent transmission indicating no significant absorption below the edge. The direct gap is seen at 1.3 eV in the paramagnetic phase at 300 K, and on entering the ferromagnetic phase it falls to 0.9 eV. The redshift of 0.4 eV is in good agreement with recent LSDA+U calculations and a slight fine-tuning of the empirical U_d parameter used in those calculations allows us to reproduce the absolute values of the gaps in the band structure calculation. The procedure of estimating the gap of the paramagnetic state as the average of majority- and minority-spin gaps in the ferromagnetic state was justified by a separate calculation for a system with randomly oriented spins. It is significant that earlier predictions concerning the conducting character of the entire range of RE nitrides were based on the value of U_d in GdN, adjusted so as to reproduce the earlier incorrect optical gap of 0.98 eV in the paramagnetic state. Similar fine-tuning readjustments of band structures will be required also for other RE nitrides.

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[1] W. R. L. Lambrecht, Phys. Rev. B **62**, 13538 (2000).
[2] D. B. Ghosh, M. De, and S. K. De, Phys. Rev. B **72**, 045140 (2005).
[3] M. D. Johannes and W. E. Pickett, Phys. Rev. B **72**, 195116 (2005).
[4] P. Larson and W. R. L. Lambrecht, Phys. Rev. B **74**, 085108 (2006).
[5] S. Bhattacharjee and S. M. Jaya, Eur. Phys. J. B **49**, 305 (2006).
[6] P. Larson, W. R. L. Lambrecht, A. Chantis, and M. van Schilfgaarde, Phys. Rev. B **75**, 045114 (2007).
[7] C. M. Aerts, P. Strange, M. Horne, W. M. Temmerman, Z. Szotek, and A. Svane, Phys. Rev. B **69**, 045115 (2004).
[8] C. Duan, R. F. Sabiryanov, J. Liu, W. N. Mei, P. A. Dowben, and J. R. Hardy, Phys. Rev. Lett. **94**, 237201 (2005).
[9] V. N. Antonov, B. N. Harmon, A. N. Yaresko, and A. P. Shpak, Phys. Rev. B **75**, 184422 (2007).
[10] A. N. Chantis, M. van Schilfgaarde, and T. Kotani, arXiv:cond-mat/0610528 (unpublished).
[11] F. Hullinger, *Handbook on the Physics and Chemistry of Rare Earths* (North-Holland, New York, 1978), Vol. 4, pp. 153–236.
[12] O. Vogt and K. Mattenberger, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier Science, Amsterdam, 1993), Vol. 17, pp. 301–407.
[13] P. Wachter and E. Kaldis, Solid State Commun. **34**, 241 (1980).
[14] R. J. Gambino, T. R. McGuire, H. A. Alperin, and S. J. Pickart, J. Appl. Phys. **41**, 933 (1970).
[15] D. X. Li, K. Sumiyama, K. Suzuki, and T. Suzuki, Phys. Rev. B **55**, 6467 (1997).
[16] A. R. H. Preston *et al.*, arXiv:cond-mat/0703740 (unpublished).
[17] P. Wachter, L. Degiorgi, E. Kaldis, E. Bommeli, P. Burlet, and F. Bourdarot, Solid State Commun. **105**, 675 (1998).
[18] L. Degiorgi, W. Bacsa, and P. Wachter, Phys. Rev. B **42**, 530 (1990).
[19] J. P. Dismukes, W. M. Yim, J. J. Tietjen, and R. E. Novak, RCA Rev. **31**, 680 (1970).
[20] S. Granville *et al.*, Phys. Rev. B **73**, 235335 (2006).
[21] F. Leuenberger, A. Parge, W. Felsch, K. Fauth, and M. Hessler, Phys. Rev. B **72**, 014427 (2005).
[22] G. Busch, E. Kaldis, E. Schaufelberger-Teker, and P. Wachter, in *Coll. Int. CNRS* No. 180, Vol. I (CNRS, Paris-Grenoble, 1970), p. 359.
[23] N. Sclar, J. Appl. Phys. **35**, 1534 (1964).
[24] E. Shalaan and H. Schmitt, Opt. Commun. **260**, 588 (2006).

[25] M. P. Singh, C. S. Thakur, K. Shalini, S. Banerjee, N. Bhat, and S. A. Shivashankar, J. Appl. Phys. **96**, 5631 (2004).
[26] D. P. Schumacher and W. E. Wallace, J. Appl. Phys. **36**, 984 (1965).
[27] R. A. Cutler and A. W. Lawson, J. Appl. Phys. **46**, 2739 (1975).
[28] D. X. Li, Y. Haga, H. Shida, and T. Suzuki, Physica B **199**, 631 (1994).
[29] D. X. Li, Y. Haga, H. Shida, T. Suzuki, Y. S. Kwon, and G. Kido, J. Phys.: Condens. Matter **9**, 10777 (1997).
[30] F. Leuenberger, A. Parge, W. Felsch, F. Baudelet, C. Giorgetti, E. Dartyge, and F. Wilhelm, Phys. Rev. B **73**, 214430 (2006).
[31] K. Khazen, H. J. von Bardeleben, J. L. Cantin, A. Bittar, S. Granville, H. J. Trodahl, and B. J. Ruck, Phys. Rev. B **74**, 245330 (2006).
[32] W. R. McKenzie, P. R. Munroe, F. Budde, B. J. Ruck, S. Granville, and H. J. Trodahl, Curr. Appl. Phys. **6**, 407 (2005).
[33] A. Koo, F. Budde, B. J. Ruck, H. J. Trodahl, A. Bittar, A. R. H. Preston, and A. Zeinert, J. Appl. Phys. **99**, 034312 (2006).