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Electronic structure and optical spectra of the semimetal ScAs and of the indirect-band-gap semiconductors ScN and GdN

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Local (spin) density functional calculations for ScN and GdN are complemented with estimated quasiparticle corrections and calculations of the optical response to evaluate whether these materials are semimetals as suggested by some transport measurements or semiconductors as suggested by optical measurements. The quasiparticle corrections are estimated by assuming that gap corrections are inversely proportional to the dielectric constant and using experimentally known results on the quasiparticle d-band shift in $\mathrm{Er}_x\mathrm{Sc}_{1-x}\mathrm{As}$. Results for the optical response functions and band structures are presented for ScAs, ScN, and GdN. The conclusion is that whereas ScAs is a semimetal, ScN and GdN are both narrow gap (0.9 and 0.7–0.85 eV, respectively) indirect gap $(\Gamma-X)$ semiconductors, with first direct gap at X at 2.0 and 1.1–1.2 eV, respectively. Due to the strong exchange interaction of $4f$ electrons with the d bands, GdN is predicted to have a magnetic-field-induced redshift of both the indirect and direct absorption edges of about 0.3 eV.

I. INTRODUCTION

While most rare-earth (RE) pnictides have been clearly established to be semimetallic, there still exists some controversy whether RE nitrides and scandium nitride are semimetals or semiconductors.[1,2] Transport measurements in these materials give typical carrier concentrations in the range $n=10^{19}$–$10^{21}\ \mathrm{cm}^{-3}$ which are compatible with a semimetal, but may also indicate a highly degenerate n-type semiconductor. The latter could be due to imperfect stoichiometry, i.e., due to N vacancies, or, to some residual impurity such as oxygen. Recently, ScN samples with carrier concentrations as low as $10^{17}\ \mathrm{cm}^{-3}$ were reported by Moustakas *et al.*,[3] and Bai and Kordesh,[4–6] which strongly suggests that ScN is a semiconductor. Kaldis and Zürcher[7] suggested that GdN could be a semiconductor because it showed a decreasing specific resistivity with increasing temperature but could not extract a definite band gap because of the presence of oxygen contaminations and/or imperfect stoichiometry. Wachter and Kaldis[8] determined that even their best stoichiometric GdN (determined to be $\mathrm{GdN}_{0.99}$) had a carrier concentration of $n/\mathrm{Gd}=0.06$ or $n=1.9\times10^{21}\ \mathrm{cm}^{-3}$. Although they did not completely exclude the possibility of even lower n semiconducting GdN, they concluded that any GdN obtained until then was a semimetal.

Optical absorption studies on the other hand show an onset of absorption at 0.98 eV for GdN (Refs. 9 and 10) and 2.1 eV for ScN.[3,11,4] Values for other RE-nitride gaps are also in the range 1–2 eV.[1,2] While these absorption edges appeared to correspond to a direct gap, it is not clear from presently available optical data whether or not there is a lower energy and weaker indirect absorption edge. Travaglini *et al.*[12] have studied the optical reflectivity in ScN and came to the conclusion that it is a compensated semimetal.

Local density-functional calculations indicate an almost zero indirect gap or slight overlap.[13–15] Most interestingly, Monnier *et al.*[14] suggested that ScN may have an electron-hole liquid as the true ground state: in other words if the gap were really very small, the excitation of electron-hole pairs could be offset by the energy gain in forming a correlated electron-hole liquid as the ground state. This state would be similar to that in laser-induced electron-hole droplets in semiconductors except that here it would be a ground state of the system.

There are several reasons why this question of the existence of a band gap in these materials is of practical interest. ScN is closely lattice matched to GaN, a wide-band-gap semiconductor material which is currently attracting great attention for optoelectronic, high-temperature, and high-power electronic applications. Combining a wide band-gap material with a narrow-gap material is of considerable interest for heterostructure based devices. Second, GdN and other rare-earth nitrides have interesting magnetic properties due to the open shell $4f$ states.

While most Gd pnictides have been found to be antiferromagnetic, GdN has been claimed by some to be a antiferromagnet and by others to be a ferromagnet. Wachter and Kaldis[8] concluded that pure semiconducting GdN with $n/\mathrm{Gd}\ll10^{-3}$, ‘‘if it exists’’ (sic), would be an antiferromagnet but that GdN with the typical carrier concentrations becomes a ferromagnet due to the Ruderman-Kittel-Kasuya-Yoshida-type interaction. Recently, however GdN, claimed to be stoichiometric, has been found to be ferromagnetic with a Curie temperature of 58 K (Ref. 16) and a theory was offered by Kasuya and Li[17] to explain why GdN can be a strong ferromagnet even without ferromagnetic coupling via free carriers. While the question of the ferro- or antiferromagnetic nature of GdN is extremely interesting, it will not be addressed in the present paper. We believe the small energy difference involved in this question requires a very careful treatment of the $4f$ electrons beyond our present computational capabilities. Instead our paper focuses on the question of whether or not GdN is a semiconductor. In any case, application of a moderately strong field (0.35 T) (Ref. 8) is found to align Gd magnetic moments at low temperature. Thus for studying the behavior of GdN in a magnetic field above the Curie (or Néel) temperature (if it were antiferromagnetic), a spin-polarized description, as if it were ferromagnetic, is appropriate. In conclusion, if GdN is found to be a semiconductor, it would be a rather interesting magnetic semiconductor, with possibly also interesting magneto-optic properties.

Unfortunately, the theoretical studies so far have had great difficulty in establishing clearly whether or not these materials are semiconductors or semimetals because the Kohn-Sham eigenvalues obtained in the local-density approximation are known not to represent true quasiparticle energies and hence to underestimate band gaps in semiconductors. Thus, for borderline cases as considered here, it is difficult to establish whether or not a material is a semimetal or a semiconductor. While a quasiparticle calculation in the GW approximation[18] is probably the most desirable approach, it is rather difficult for a material such as GdN or ScN because most GW implementations, with the exception of Ref. 19, are based on pseudopotential plane-wave approaches for which the d bands present a serious difficulty. The $4f$ bands in the RE case present an even more difficult problem.

In the present study we attempt to estimate the quasiparticle gap correction by means of a somewhat semiempirical approach, and combine it with studies of the optical response in ScN. The essential assumption behind the present approach is that gap corrections scale inversely with the dielectric constant ε. This is an obvious fact in the GW approximation because the latter contains the screened Coulomb interaction $W=\varepsilon^{-1}v$. Of course, it is a serious simplification to simply use a scalar macroscopic dielectric constant ε. The reason why we expect this gross oversimplification to be reasonable is that here ε is only used to establish the ratio of the gap correction in one material to that in another. In fact, we use prior empirical knowledge of the quasiparticle correction in related RE arsenides, in particular $\mathrm{Er}_{0.6}\mathrm{Sc}_{0.4}\mathrm{As}$, obtained from a comparison of our LDA band structures to Shubnikov–de Haas measurements.[20,21] We then calculate the dielectric constant ε ''self-consistently'' from the band structure with the estimated gap correction (which in turn depends on ε) included. Using this approach, we obtain a corrected band structure for ScN. The end result is that ScN is indeed a semiconductor but not with a direct gap of 2.1 eV as suggested by Dismukes *et al.*[11] but with an indirect gap of only about 0.9 eV. That the band gap needs to be indirect is very clear from even the simplest tight-binding picture.

In view of the above remarks, this makes ScN a quite attractive material because among the nitrides it has a significantly lower gap than GaN (3.6 eV) or even InN (1.9 eV). This would allow for a much wider band-gap difference in nitride heterostructures than is currently possible, which is beneficial for certain device applications.

Next, a similar approach is used to correct the band structure in GdN. In the latter case, we also need to deal with the $4f$ electrons and with the spin polarization. We do this essentially via a simplified version of the ''LDA+U'' approach.[22] Among the RE nitrides we choose GdN because it has exactly a half-filled $4f$ shell. Thus the orbital dependence of the Coulomb interaction plays no significant role and we can simply shift the occupied states of one spin down and the unoccupied ones up by appropriate U shifts. The spin-polarization effects on the d bands, which form the conduction band minimum, are included within the local-spin-density approximation but with the $4f$ spin occupations fixed by the above U shifts and with gap corrections included in the above described semiempirical manner. Our basic model for GdN is that above the Curie temperature the localized $4f$ derived magnetic moments are randomly oriented and lead to a net zero-spin polarization which we approximate by a non-spin-polarized local-density calculation. Below the Curie temperature or in a saturating magnetic field, we assume that the ferromagnetic state is described by our spin-polarized calculations. The end result of our calculations is the prediction that GdN remains a semiconductor even in the ferromagnetic state but has a sizably lower band gap.

II. THEORETICAL APPROACH

The basic band-structure approach used for our calculations is the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA).[23] The crystal structure of the materials under consideration is the rocksalt structure. As usual, we introduce empty spheres to obtain a better filling of space with slightly overlapping atomic Wigner-Seitz spheres. The ASA has been previously shown to provide accurate band structures for rare-earth monopnictides in this manner.[15]

The main problem addressed in this paper is to estimate the gap corrections beyond the local-density approximation (LDA). As is well known, the GW correction in semiconductors consists primarily in an upward shift of the conduction bands. While there is some variation from k point to k point and state to state due to changes in the wave-function character, these are at most of the order of a few 0.1 eV. In previous work[20] on ErAs and $\mathrm{Er}_{0.6}\mathrm{Sc}_{0.4}\mathrm{As}$, it was found that the volume enclosed by the Fermi surface of these semimetals is overestimated in the LDA by almost a factor of 3. This could, however, be corrected for simply by shifting the metal d band up by a rigid shift of about 0.4 eV. In fact, it was shown that this not only corrects the overall size of the Fermi surface, but also brings the areas of the various extremal orbits in good agreement with Shubnikov–de Haas measurements.[21] So, at least for the region of the band structure in the immediate vicinity of the band gap, a rigid shift appears to be a reasonable approximation because only states with a similar wave-function character (metal $3d$) are involved. In addition, it was shown that this magnitude of the shift could be accounted for by a simplified extreme tight-binding approximation to the GW method, suggested by Bechstedt and Del Sole.[24] In Ref. 15, the dielectric constant used in this approach was estimated from the Penn model.[25] In the present paper, instead of the Penn model, explicit calculations of the dielectric function from the band structure are employed. In any case, the Bechstedt–Del Sole model was only used to justify approximately the size of the gap correction. The important point to note is that the gap correction in the RE-arsenide or Sc-As system can be considered to be known from experiment. In fact, there is no notable difference between Sc, or other IIIb elements and the RE elements in this context because their metal d bands across this family of materials are to a very good approximation the same. Of course, a similar approximation of materials independence would not apply in general but only in this favorable circumstance of considering a family of compounds with very similar band structures.

As already mentioned in the introduction, the second general assumption behind our approach to estimate quasiparticle corrections is that the latter should scale inversely with the dielectric constant. A good first approximation to the GW self-energy is the screened exchange operator. Thus, one expects the gap correction ΔE_g to take the form

$$\Delta E_g \approx U_d/\varepsilon, \tag{1}$$

where U_d is some effective exchange integral for the d electrons, or rather its difference from its LDA counterpart. Although we are here dealing with a d-band shift, we should note that these are wide d bands and the U_d here should not arise primarily from a localized atomic interaction—in other words, it is not a ''Hubbard'' U—but rather from long-range Coulomb interactions between electrons in different atomic sites. As in usual semiconductors, the latter is the term which is essentially missing in LDA, because it falls off like $1/r$ with r the distance between the sites and is completely overscreened in LDA because the latter assumes a metallic or electron-gas-type screening of the Coulomb interactions.[26] So, U_d is essentially a Madelung sum of the Coulomb interactions between electrons treated as point charges sitting on each of the metal lattice sites, multiplied by the occupation number of the metal d states, the latter factor coming from the density matrix in the Hartree-Fock exchange term. Because of the similarity in the crystal structure and bonding type of the various RE pnictides and Sc pnictides, (particularly as far as the metal d contribution to the charge density is concerned) it can approximately be considered a constant within this family of materials. One might actually expect it to scale inversely proportional to the lattice constants, but this is an effect of only 10% or so, given the variation in lattice constants, whereas the dielectric constants will be seen to vary more strongly. In any case, it would lead eventually to further increase the gap correction in nitrides versus those in arsenides and reinforce our conclusion of the semiconducting as opposed to semimetallic character of the nitrides. Thus, if U_d is approximately constant, one expects the gap correction to scale inversely with the dielectric constant. While little change in the dielectric constant is expected between RE-P and RE-As systems, the RE-N systems might be expected to have somewhat different dielectric response because of the deeper N levels and therefore somewhat more ionic nature of the bonding. This is clear also from the difference in their LDA band structures which is clearly semimetallic in the RE-As and RE-P cases but already borderline zero-gap in the nitride case.

Thus, in practice, the approach goes as follows: the dielectric constant of ScAs is calculated from the LDA band structure with a known gap correction of 0.4 eV added. From this ε and ΔE_g, the unscreened U_d is obtained. Then the dielectric constant $\varepsilon(\Delta E_g)$ is calculated for ScN from its LDA band structure with a trial gap correction ΔE_g added. From this a new gap correction is obtained as $\Delta E_g' = U_d/\varepsilon(\Delta E_g)$ and this procedure is iterated to self-consistency.

The way in which the gap correction is added is by shifting the LMTO potential parameter C_d of the Sc or RE atoms in the LMTO Hamiltonian in the nearly orthogonal representation.[23] The latter represents the center of gravity of the corresponding partial density of states in the usual decomposition in angular momentum components and corresponds to the diagonal elements of the Hamiltonian matrix. This affects the occupied valence bands only negligibly and shifts all d bands, from which the bottom of the conduction band is primarily derived, up by a constant.

The dielectric constant is calculated in the random-phase approximation without local field corrections: The imaginary part $\varepsilon_2(\omega)$ is calculated first and the real part is obtained by a Kramers-Kronig transformation. The matrix elements are calculated from the muffin-tin orbitals in the manner described in Refs. 27 and 28. Because the screening dielectric constant involved in the GW approximation should reflect the average behavior of the electrons and not that of the few behaving metallically near the Fermi level, only the interband transitions are included in the calculation of $\varepsilon_2(\omega)$ even for the semimetallic ScAs. Clearly, if metallic screening were included, then in the $q \rightarrow 0$ limit, $\varepsilon(q) \rightarrow \infty$, and the whole approach would become meaningless. It is important to emphasize again that the main reason for the band-gap correction in fact is that the screened exchange term has a *long-range* contribution because the screening is not local.[26] Even in a semimetal with 10^{19} carriers per cm^3, the Thomas-Fermi screening length is of order 15 Å . Thus, the presence of free carriers at the density typical of a semimetal does not lead to a short-range (within the atomic sphere, say) screening of the Coulomb (or exchange) integrals responsible for the band-gap shift. Thus the long-range $1/\varepsilon r$ behavior responsible for the dominant contribution to the band-gap shift is still present and is determined by the finite dielectric constant resulting from the interband contributions of the dielectric response.

Of course, the above procedure still constitutes only a rough approximation to the full GW approach. All local field effects and dynamic effects of the self-energy are neglected here. Nevertheless, it may be argued that in the present case, it does capture the essential difference between the nitrides and the arsenides in this same family of materials. Even though the calculated ε may be in error by a factor of the order of 10% and furthermore, a simple scalar macroscopic dielectric constant cannot capture the full physics, the errors made should be systematically the same for the two materials and a reasonable approximation should still be obtained for the ratio of the screening in the two materials, which is all we need.

For GdN, essentially the same approach is followed, but now the calculations are carried out including spin polarization. The treatment of the $4f$ electrons requires some explanation. Unlike previous work where the $4f$ electrons were treated as core states, they are here treated in a rudimentary ''LDA+U'' fashion. In a LSD calculation, including the $4f$ electrons, the occupied $4f_\uparrow$ band of majority spin lie about -3.2 eV below the Fermi level, while the unoccupied minority spin $4f_\downarrow$ band lies about 1.7 eV above it. The band structure near the Fermi energy in that case is rather strongly perturbed from that obtained previously when the $4f$ electrons are treated as core states. X-ray photoemission spectroscopy (XPS) and inverse photoemission or bremsstrahlung isochromat spectroscopy (BIS) in metallic Gd place the

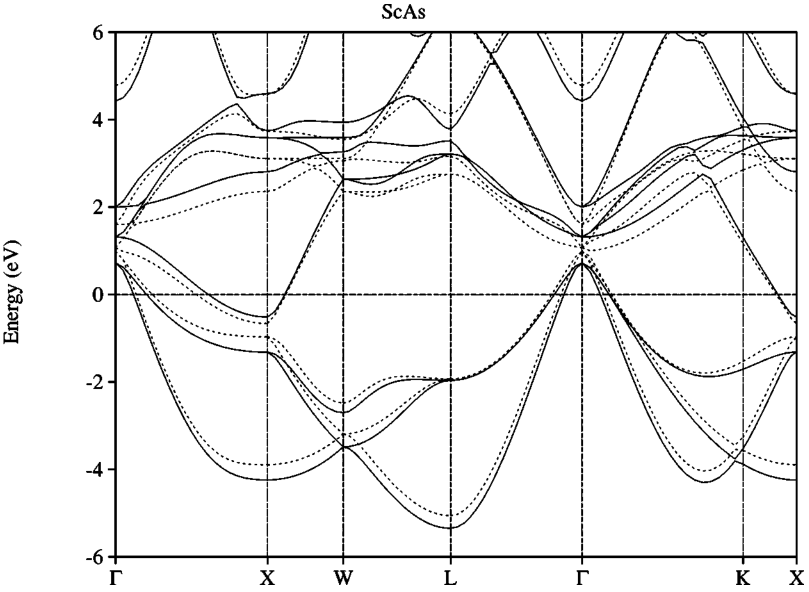

FIG. 1. Band structure of ScAs: dashed lines: LDA, solid lines: including gap correction.

occupied and unoccupied $4f$ bands, respectively, at -8 and 4 eV from the Fermi level.[29] This is a result from the localized character of the $4f$ electrons for which placing an extra electron in the $4f$ shell requires a large Coulomb energy and likewise, removing one reduces the Coulomb energy substantially. The polarization responses of the medium to removal or addition of an electron, which are sometimes referred to as final-state relaxation effects in the context of the experimental spectroscopies, are in principle included in the quasiparticle energies that LDA+U theory approximates and should thus be included in our ''quasiparticle band structure.'' Very similar shifts can be expected in GdN because the $4f$ states essentially behave as localized atomic states. In fact, XPS and BIS on other Gd monopnicitides (P, As, Sb, and Bi) (Ref. 30) indicate a occupied $4f$ level at -9 eV and a unoccupied $4f$ level of 5 eV from the Fermi level. In the present calculation, this effect can simply be included by adding shifts to the $4f$ diagonal elements of the LMTO Hamiltonian in much the same way as they are added for the d band. Below, this treatment will be referred to as LDA+U_f. The resulting band structure approximates rather closely that of the previous treatment[15] in which $4f$ states were treated as core states, except that there still is a larger spin splitting of the valence band maximum. We anticipate that the present calculations somewhat overestimate this splitting because the U_f shifts are not added self-consistently. In other words, all LMTO potential parameters stay frozen as they were in the pure LSDA calculation except for the $C_{4f\uparrow}$ and $C_{4f\downarrow}$ center of the band parameters. Thus, the potential parameters for $N2p\uparrow$ and $N2p\downarrow$, which dominate the valence band maxima for each spin still reflect the spin polarization induced in them when the $4f$ states were closer to the Fermi level as in the LSD. We plan to remove this additional approximation in future work. With some caution in interpreting the results, however, it does not alter the main conclusions of the present work.

The ''standard'' wide band quasiparticle effects on the conduction d band are included in the same way as for ScN. Since the total dielectric response is involved in screening the Coulomb interaction, the corresponding dielectric function is calculated by summing the imaginary part of the dielectric function obtained from transitions between spin-up states and between spin-down states separately. That is $\varepsilon_2(\omega)=\varepsilon_{2\uparrow}(\omega)+\varepsilon_{2\downarrow}(\omega)$ and the real part of the dielectric constant is obtained by the usual Kramers-Kronig transformation.

III. RESULTS

A. Band structure and optical response for ScAs

For ScAs, the dielectric constant obtained from the band structure with a 0.4 eV shift of the Sc 3d band (assumed to be the same as in $Er_{0.6}Sc_{0.4}As$) and including only interband transitions is found to be 9.2 while in the LDA (without shift) it is found to be 11.3. The band structures and dielectric response functions are shown in Figs. 1 and 2 respectively. Thus, we expect $U_d=3.7$ eV. However, in view of the approximations involved in the model and the uncertainty of the gap correction in ScAs in the first place, we round this off to an ''unscreened'' $U_d\approx 4.0$ eV assumed to be valid within the family of RE and Sc pnictides. When we

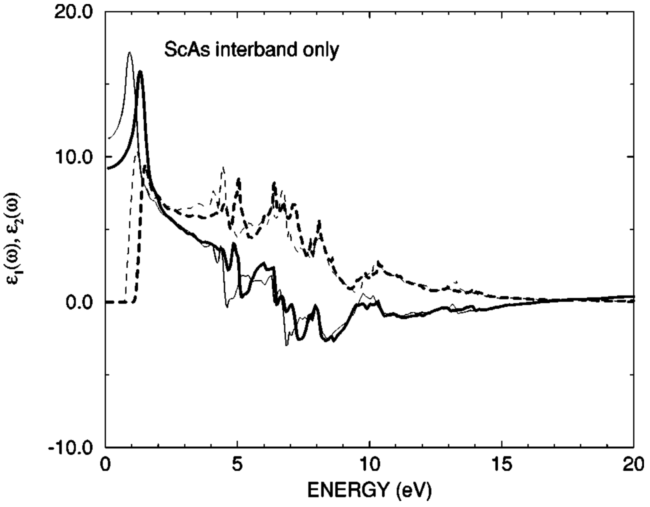

FIG. 2. Real (solid line) and imaginary part (dashed line) of the interband portion of the dielectric function of ScAs; thick lines: LDA + correction, thin lines: LDA only.

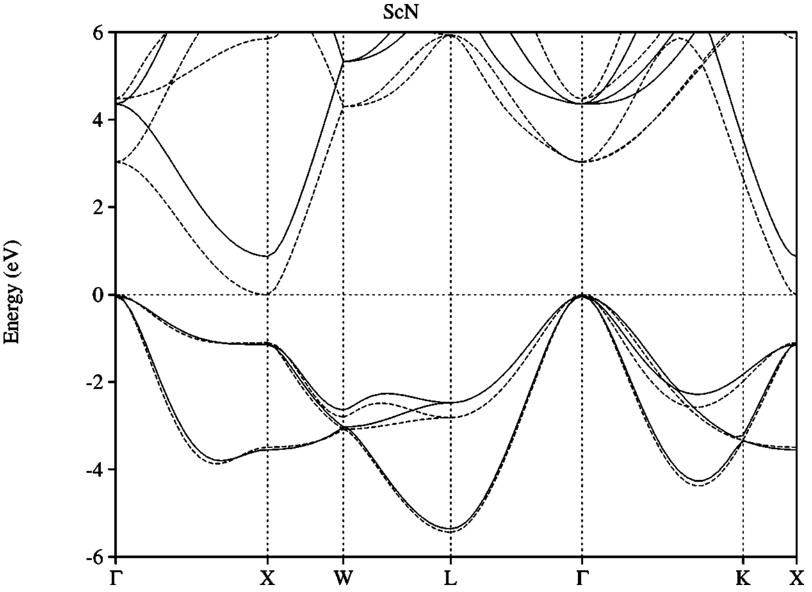

FIG. 3. Band structure of ScN: dashed lines: LDA, solid lines: including gap correction.

use this for nitrides, one may also think of this as approximately including the 10% additional increase due to the smaller lattice constant for nitrides.

B. Band structure and optical response for ScN

The dielectric constant and ΔE_g in ScN were then obtained in the iterative manner described above. The resulting band structure is shown in Fig. 3 compared to the LDA one. A gap correction $\Delta E_g = 0.9$ eV is obtained, leading in fact to an indirect minimum gap of 0.9 eV, since the LDA gap is zero. This corresponds to a dielectric constant of about 4.4. The corresponding dielectric functions are shown in Fig. 4. The dielectric constant is seen to be about half the value of that in ScAs, thus justifying a gap correction which is about twice as large. The main band-gap results are summarized in Table I.

We next check these predictions against experimental data. First of all, we find an onset of direct absorption at *X* at 2.0 eV in good agreement with the results of Dismukes *et al.*[11] for the lowest carrier concentration samples of ScN. Unfortunately, the data of Dismukes *et al.* do not extend below 1.8 eV, although it should be mentioned that their data show a significant amount of absorbance exists in the range 1.8–2.1 eV.

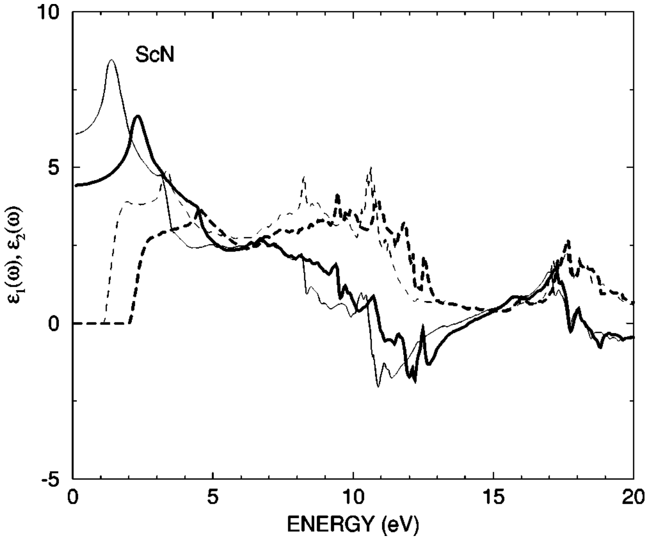

FIG. 4. Real (solid line) and imaginary part (dashed line) of the dielectric function of ScN; thick lines: LDA + correction, thin lines: LDA only.

Very recently, Bai and Kordesh,[4–6] grew ScN films by a variety of methods, including sputtering and molecular-beam epitaxy, and studied their absorption spectra in the range 1.5–3.0 eV. Their data indicate again a direct absorption edge at about 2.1–2.2 eV. Furthermore, however, their data indicate a linear behavior of $\alpha^{1/2}(\omega)$ with photon energy in the range 1.5–2.0 eV. This is indicative of an indirect gap absorption onset. Extrapolating their data linearly, would indicate an indirect gap of about 0.9 eV. The absorption coefficient measured by these authors at 1.5 eV is approximately 1.0×10^4 cm^{-1}, which is consistent with typical values for an indirect gap material about 0.5 eV above the threshold. Confirmation of this result by measurements in the near infrared range is highly desirable and should reveal the different onsets for phonon absorption and emission, which would also provide information on the *X* phonon.

The films are red in appearance, an observation also made by Dismukes *et al.*[11] For the thickness of the films investigated, of order 1–2 μm, this is consistent with the blue-green portion of the spectrum being more strongly absorbed than the red part of the visible spectrum. While the red appearance of the crystals has been very suggestive that the 2

TABLE I. Band gaps and dielectric constant in ScN.

Indirect gap $\Gamma-X$	0.9 eV
Direct gap at X	2.0 eV
Direct gap at Γ	4.3 eV
Experimental ‘‘direct’’ absorption edge[a]	2.0–2.2 eV
Experimental extrapolated ‘‘indirect’’ absorption edge[b]	0.9 eV
Optic dielectric constant	4.4

[a] References 11 and 6.

[b] References 4 and 5.

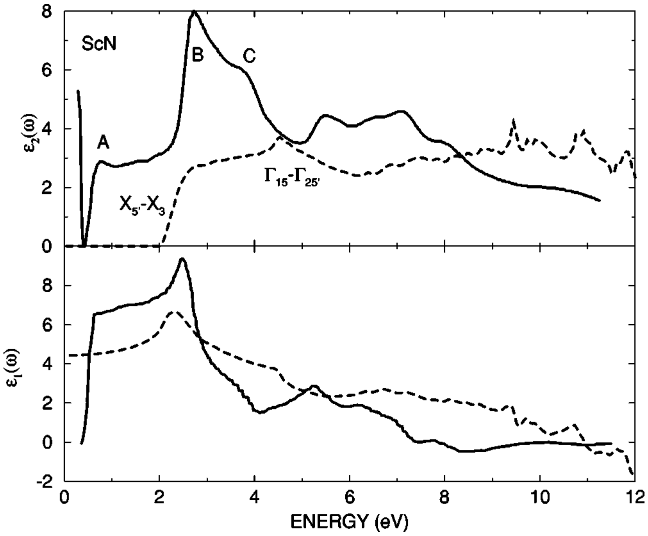

FIG. 5. Real (bottom) and imaginary part (top) of the dielectric function of ScN: solid line experiment from Ref. 12, dashed line present theory including correction.

eV threshold would be the fundamental absorption edge, and has led Dismukes *et al.*[11] to suggest a direct gap material, it is by no means a proof.

In fact, a direct band gap is completely incompatible with the band structure. The fact that the Sc $3d$ bands must bend down from Γ to X is a robust result that would be obtained even in the simplest tight-binding approach. If we consider the X point in the $[001]$ direction, the lowest conduction band is the d_{xy} band. Including only the direct nearest-nearest dd interactions, we need to consider only the fcc sublattice. An explicit expression was given for this band by Harrison and Froyen,[31]

$$\epsilon_{xy}(k_z)=\epsilon_d+3V_{dd\sigma}+V_{dd\delta}+4(V_{dd\pi}+V_{dd\delta})\cos k_z a/2, \tag{2}$$

in terms of the usual Slater-Koster hopping integrals. Since $V_{dd\pi}+V_{dd\delta}>0$, the bands are lower at $k_z=2\pi/a$ than at $k_z=0$.

In conclusion, the optical data on recent films of low carrier concentration are consistent with an indirect gap of about 1 eV, from Γ-X and an onset of direct transitions at about 2 eV at X, as predicted by our calculations, although the indirect onset has not yet been directly observed.

Next, our calculated dielectric function is compared to the one deduced from the reflectivity measurements of Travaglini *et al.*[12] in Fig. 5. These data are in marked disagreement with our calculations and with the other experimental data. According to these authors, the onset of direct absorption, labeled A, occurs at 0.8 eV. They identify it with the first direct transitions at X, which our calculations, however, places at 2.0 eV. Even if we used the LDA band structure, our onset of direct absorption would lie above their value. A downward shift by several 0.1 eV from the LDA is very difficult to explain, unless extremely strong electron-hole or excitonic effects are invoked. This is unlikely in a narrow gap semiconductor or nearly semimetal like ScN. Even if we would allow for an arbitrary shift of our curves versus theirs in energy, there is virtually no correlation in spectral shapes. For example, one might be tempted to identify A with the X transition onset and B with our Γ direct transition, but then the first peak in ϵ_1 would be displaced as well and there is no correlation for the higher energy features. Also, even when strong electron-hole interaction or continuum excitonic effects are invoked, it is hard to explain the discrepancies in overall intensity. One might easily explain a lower intensity in the experiment than the theory by surface roughness scattering, but the experiment has the higher intensity. The electron-hole interaction and local field effects can shift oscillator strength from one peak to another but not increase the overall integrated intensity.

This indicates that the spectra measured by Travaglini *et al.*[12] may be significantly perturbed by extrinsic effects and may not correspond to the bulk ScN band structure at all. Their samples indeed were reported to have carrier concentrations of the order of 10^{20} cm^{-3} and to have about a 1% N deficiency. This accounts for the presence of a strong Drude peak in their data at zero frequency. Even this, however, may be insufficient to explain the discrepancies in the UV reflectivity. We suspect that surface states or a surface layer of scandium oxide or oxynitride may have perturbed the measurements of UV reflectivity because ScN is highly susceptible to oxidation.

We also note that these data are quite different from the other experimental results. The plateau in $\epsilon_2(\omega)$ in the range 0.8–2.0 eV corresponds to an absorption coefficient α of a factor 5–7 stronger than measured by, e.g., Bai and Kordesh.[4–6] Furthermore, Travaglini *et al.*[12] report their crystals to have a green color while the recent works all refer to red colored films. In summary, the UV reflectivity data of Travaglini *et al.*[12] are rather puzzling but appear to be in discrepancy not only with our calculation but also with the data on more recent samples. It would be highly desirable to obtain UV-reflectivity data on the new samples of low carrier concentration.

C. Band structure and optical response for GdN

Figure 6 shows the spin-polarized band structure of GdN including the gap corrections obtained in the same way as for ScN. The corresponding dielectric response functions are shown in Fig. 7. These include a ‘‘self-consistent’’ gap correction ΔE_g of ~ 0.6 eV corresponding to a dielectric constant of 7.0, determined from the calculations in the manner discussed above in detail for ScN. One may note that the spin-up and spin-down Gd $5d$ bands are split by about 0.6 eV, while the valence bands at Γ are split by about 0.5 eV. The minimum indirect gaps at X are thus, respectively, 0.3 and 1.4 eV for majority spin and minority spin. The minimum direct gaps at X are 0.8 and 1.6 eV, respectively. As discussed earlier, the present calculation is expected to overestimate the valence band spin splitting, in particular at the Γ point. The spin-down band is expected to be pushed down less by the interaction with the unoccupied $4f$ band. Comparison to previous calculations[32] treating $4f$ states as core, which provides a lower limit for the spin splitting of the valence band maximum, indicates that this might lower the minority-spin indirect gap by an about 0.3 eV. Unfortunately, no experimental information is presently available on the spin splitting in the valence band of GdN. It should be noted though that the previous work treating $4f$'s as core

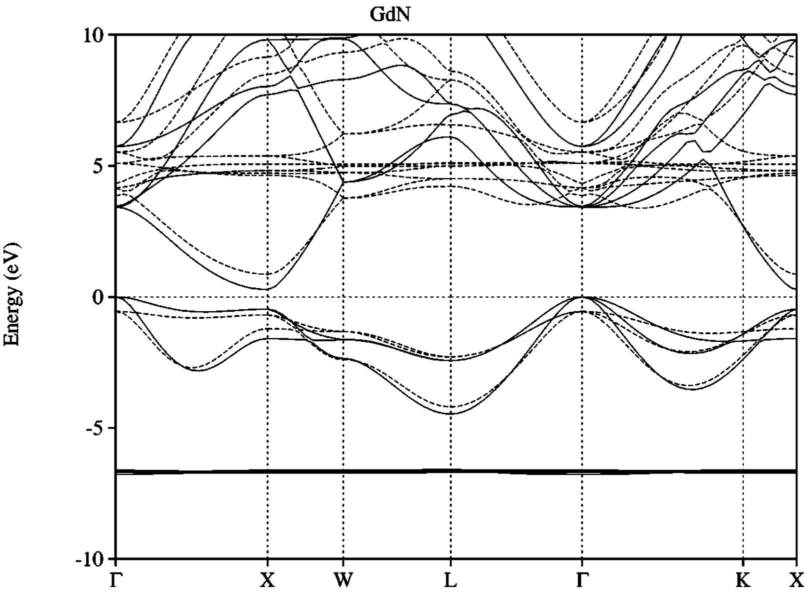

FIG. 6. Spin-polarized band structure of GdN: solid line majority spin, dashed line minority spin, including both U_f shifts of $4f$ states and gap correction.

provided valence band splittings in fair agreement with experimental data obtained from resonant tunneling in ErAs.[33] At the X point the spin splitting is smaller in both cases. Comparison to the $4f$ as core treatment indicates the direct gap for the minority spin might be lowered by 0.1 eV.

In the absence of a magnetic field or at temperatures above the Curie temperature, one may expect that the $4f$ localized moments would still be present but randomly oriented. In the spirit of a virtual crystal approximation, one may model this disordered spin system as having a non-spin-polarized band structure. In other words, the average of the above band gaps would then apply. This would mean a minimum indirect gap of 0.7–0.85 eV and a direct gap of 1.1–1.2 eV. The experimental onset of absorption[9,10] at 0.98 eV is compatible with the latter, given the uncertainties of 0.1 eV at least on our calculated numbers. The results are summarized in Table II. The present calculation indicates that the absorption onset should be lowered by about 0.3 eV in the presence of a magnetic field sufficiently strong to align the Gd $4f$ moments or below the Curie temperature. We note that a similar redshift in a magnetic field has been observed in EuO and EuS, which are well documented to be ferromagnetic semiconductors.[34]

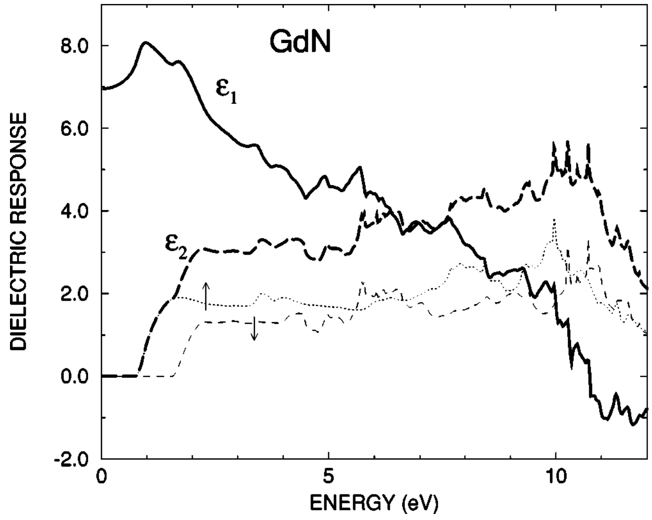

FIG. 7. Real (thick solid line) and imaginary part (thick dashed line) of the dielectric function of GdN; thin lines indicate spin-up and spin-down contributions.

If the gap were slightly lower to start with and the spin splitting remained the same, one might reach the situation where the gap closes in a magnetic field for one of the spin channels. This would change the material from a semiconductor to a ''half-metal,'' which is in some sense a perfect spin filter. Note that a half-metal means a metal for one spin but a semiconductor for the other. Thus in contact with a nonmagnetic metal, such a system would present a Schottky barrier to electrons of minority spin but no barrier at all to electrons of majority spin. From the present results, this situation does not appear to be the case in pure GdN, but in $GdN_{1-x}P_x$, or $GdN_{1-x}As_x$ one might expect the gap to become smaller while the spin splitting would remain the same. Thus at some intermediate composition, this situation should occur. This would also be the ideal system to study the effects of the electron-hole liquid predicted by Monnier *et al.*[14] because one could then in principle tune through the transition by changing the magnetic field. Further work on the band gap bowing in these alloy systems, including the effects of disorder, is required to determine at which composition this cross over is expected.

IV. CONCLUSION

In this paper, the band structures of ScN and GdN were presented including estimated quasiparticle corrections. The latter were obtained semiempirically by using the known quasiparticle correction in the related compound $Er_{0.6}Sc_{0.4}As$, which is required to obtain correct Fermi surface dimensions as determined by Shubnikov–de Haas measurements, and the simple and plausible assumption that gap corrections in this class of materials should scale inversely with the dielectric constant obtained from the interband transitions only. The resulting band structure in ScN was found to provide good agreement for the onset of direct absorption at the X point with optical absorption data, which we argue are also consistent with a indirect gap at about 1 eV, although the latter

TABLE II. Band gaps and dielectric constant in GdN.

	Spin ↑	Spin ↓	Average
Indirect gap $\Gamma-X$	0.3 eV	1.1–1.4[a] eV	0.7–0.85 eV
Direct gap at X	0.8 eV	1.5–1.6 eV	1.1–1.2 eV
Direct gap at Γ	3.3 eV	3.4–3.7 eV	3.3–3.5 eV
Experimental absorption edge[b]			0.98 eV
Optic dielectric constant			7.0

[a] Lower and upper limits depending on $4f$ as core or as LDA$+U_f$ treatment.

[b] References 9 and 10.

remains to be confirmed definitively experimentally. Our results are in disagreement with the UV-reflectivity results of Travaglini *et al.*[12] who claim indirect semimetallic behavior. The lack of agreement of their dielectric functions extracted from UV reflectivity with our calculated ones is worse than one might reasonably blame on local field or excitonic corrections and indicates the possible presence of extrinsic effects in the measurements. The reasons for this discrepancy remain unclear.

Our main result for ScN is a predicted indirect $\Gamma-X$ gap of 0.9 eV, and first direct gap at X at 2.0 eV, making this material of great interest to expand the band-gap range of semiconducting III nitrides. In GdN, our calculations predict indirect gaps of 0.3 and 0.7–0.85 eV and direct gaps of 0.8 and 1.1–1.2 eV in the ferromagnetic and paramagnetic states, respectively. It is predicted that by applying a magnetic field the gaps can be tuned between these values by controlling the degree of alignment of the localized Gd $4f$ magnetic moments which produce this gap variation by the exchange interaction. This material could thus, in principle, be used as a magnetic-field-operated optical switch.

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