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Half-metallic to insulating behavior of rare-earth nitrides

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The electronic structure of the rare-earth nitrides is studied systematically using the *ab initio* self-interaction corrected local-spin-density approximation. This approach allows both a localized description of the rare-earth *f* electrons and an itinerant description of the valence electrons. Localizing different numbers of *f* electrons on the rare-earth atom corresponds to different valencies, and the total energies can be compared, providing a first-principles description of valence. We show that these materials have a broad range of electronic properties including forming a different class of half-metallic magnets with high magnetic moments, and are strong candidates for applications in spin-filtering devices.

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I. INTRODUCTION

Rare-earth (RE) materials have high magnetic moments and form a wide range of magnetic structures. It is the occupancy of the highly localized $4f$ states that determines the magnetic properties while the other electronic properties are determined principally by the itinerant s-d electrons.[1] The standard method of determining the electronic properties of magnetic materials is density-functional theory with a local-spin-density (LSD) approximation for the exchange-correlation energy.[2] Traditionally this method has been applied to the s-d electrons in rare-earths while the *f* electrons have been treated in an atomic model. Attempts to include the $4f$ electrons within the LSD have had only very limited success because the LSD is insufficient to describe the strong correlations experienced by the rare-earth *f* electrons. In recent years more advanced methods of electronic structure determination such as LSD plus self-interaction corrections[3,4] (SIC) and LDA+U (Ref. 5) methods have sought to remedy this problem and have met with considerable success.

There has been speculation in the literature that rare-earth nitrides may form half-metallic ferromagnets.[6–8] This is surprising because, based on a simple ionic model, trivalent rare-earth nitrides would be expected to be insulators with a similar electronic structure to the divalent rare-earth chalcogenides. However if it is the case that they are half-metallic or narrow gap insulators, then they have potential applications in spin-filtering devices. There are severe technical barriers to the creation of such devices because the highest Curie temperature known for rare-earth nitrides is about 60 K in GdN,[9] well below the boiling point of nitrogen. However devices have been fabricated with other rare-earth compounds with low Curie temperatures such as EuS (Refs. 10 and 11) and EuSe.[12,13] Furthermore, the magnetic structure of the rare-earth nitrides is not always known. Only NdN, GdN, TbN, and DyN definitely order ferromagnetically. SmN is known to be antiferromagnetic, and to our knowledge most of the others have not been investigated in sufficient detail for their magnetic structure to be unambiguously known. We are unaware of any systematic study of the electronic structure of the rare-earth nitrides at all. This is particularly surprising, given that they all crystallize in the simple sodium chloride structure.[14]

It is the purpose of this paper to discuss our calculations of the electronic structure of these materials and thus to gain a deeper understanding of these materials and their potential applications. We have performed SIC-LSD calculations for all the rare-earth nitrides, in the ferromagnetic ordering, in both the divalent and trivalent states. Thus, in this systematic study of rare-earth nitrides we shall be concerned with the nominal valence of the rare-earth ion as we progress through the series. Will these materials turn out to be all trivalent? What is the character of the rare-earth *f* and *d* hybridization with the nitrogen *p* states? Obviously, the position of the empty *f* states will be an important factor in determining this. By performing this systematic study, we will be able to determine the trends.

The remainder of the paper is organized as follows. After a brief summary of our calculational method in Sec. II, in Sec. III we discuss the detailed electronic structure of these materials, and trends in behavior as one proceeds across the periodic table. We conclude the paper in Sec. IV.

II. SIC-LSD

The SIC-LSD approximation[3] is an *ab initio* electronic structure scheme that is capable of describing localization phenomena in solids.[4,15,16] In this scheme the spurious self-interaction of each occupied state, which is inherent in any local approximation to density-functional theory,[17,18] is subtracted from the conventional LSD approximation to the total-energy functional

$$E^{SIC}=E^{LSD}-\sum_{\alpha}\delta_{\alpha}^{SIC}, \tag{1}$$

where α labels the occupied states and δ_{α}^{SIC} is the self-interaction correction for state α. This leads to a greatly improved description of static Coulomb correlation effects over the LSD approximation. Demonstrations of the advantages of the SIC approach have been made in studies of the

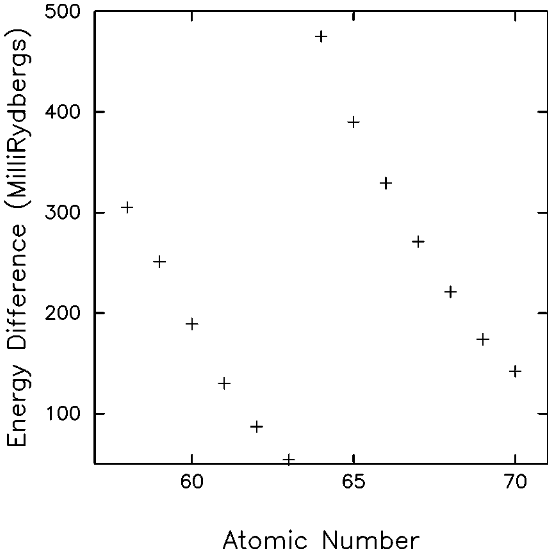

FIG. 1. The difference in total energy between the divalent and trivalent states of the rare-earth nitrides. The differences are all positive, indicating that the trivalent state is preferred over the divalent state in all cases in agreement with the published literature.

Hubbard model,[19,20] in applications to 3*d* oxides such as monoxides,[15,16] high-temperature cuprates,[21–23] magnetite,[24] *f*-electron systems,[25,26] and solid hydrogen.[27]

In the SIC-LSD method it is necessary to minimize the total energy with respect to the number of localized electrons which also leads to a determination of the nominal valence defined as the integer number of electrons available for band formation

$$N_v = Z - N_{core} - N_{SIC},$$

where Z is the atomic number of the rare-earth and N_{core} is the number of atomic core electrons. N_{SIC} is the number of *f* states for which the self-interaction correction has been removed and is determined so that N_v equals 3 for trivalent, and 2 for divalent, systems.

Further details of the SIC-LSD method are discussed elsewhere.[4,28]

III. RESULTS AND DISCUSSION

A. Energetic properties

We have performed calculations for all the rare-earth nitrides in ferromagnetic ordering and both the divalent and trivalent configurations (and for CeN the tetravalent configuration), and hence have determined the ground-state energy and valence from first principles. We have found that the ground state for Ce in CeN is tetravalent while all the other rare-earths are trivalent in the nitrides. In Fig. 1, we show the difference in energy between the divalent and trivalent states of all the rare-earth nitrides. This follows the expected trend of strongly trivalent state at the start of the series in both spin channels, and a decreasing energy difference between the trivalent and divalent state as the filling of the *f* shell occurs. However, none of the nitrides attains the divalent state. Furthermore the number of occupied itinerant *f*-electron states stays well below 0.7 required for the materials to become divalent, as observed by Strange *et al.*,[25] because of the strong hybridization with the nitrogen *p* states. The lattice constants for the *f* configuration that yields the lowest total energy can be evaluated by looking for the minimum in total energy as a function of lattice size and these are shown in Fig. 2 along with the experimental values.[29] The jump in lattice constant between Ce and Pr is due to the valence change from tetravalent to trivalent. For Ce, Pr, and the heavy rare-earths, theory and experiment agree very well both for the absolute values and the trend. For the remaining light rare earths the absolute agreement is still very good but there is a trend apparent in the theory that is not clear in the experimental results. The most probable cause of this is experimental uncertainty which can arise in these materials very easily, particularly as many of these measurements were performed at a time when samples of rare-earth materials were known to have very limited purity.[29]

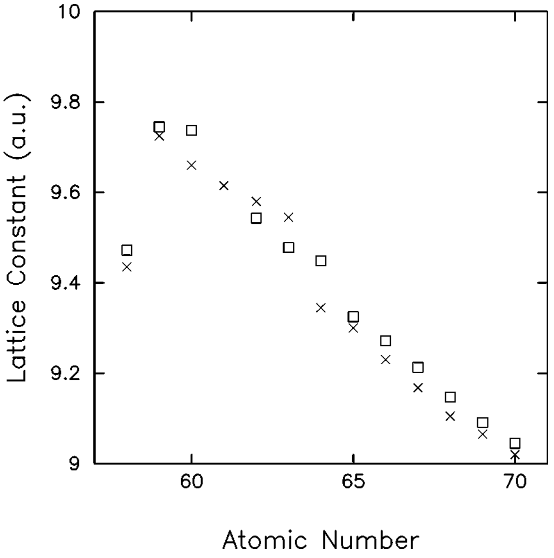

FIG. 2. The lattice constant for the rare-earth nitrides, crosses are the calculated values and the squares are experimentally determined for thin films of the material (Ref. 29).

B. Magnetic properties

Now let us look at how the magnetism varies as we proceed along the rare-earth series. The total and species-decomposed spin magnetic moments are displayed in Table I. There we also present the rare-earth's orbital moments. It should be noted that there is some arbitrariness involved in the values of the spin magnetic moments due to the atomic sphere approximation. However, we found this to be small, and moreover to make comparisons between different systems consistent we kept the ratio of the rare-earth/nitrogen sphere volumes constant.

With the exceptions of ErN, TmN, and YbN, the spin magnetic moments of these materials take on an integer value. This indicates that these systems are either insulating (Tb, Dy, and Ho nitrides) or half metallic (Pr to Gd compounds). CeN is a nonmagnetic metal, and the last three compounds of the series are metallic in both spin channels.

TABLE I. Various components of the spin magnetic moment M_S of the rare-earth nitrides. All values are in Bohr magnetons (μ_B), where the numbers do not quite add up to the total. The remaining spin moment is in the empty spheres used in the calculation. The rare-earth orbital moment M_L assumes that the rare-earth ions obey Hund's rules.

Material		M_S		M_L
	RE	N	Total	RE
CeN	0.0	0.0	0.0	0.0
PrN	2.07	−0.08	2.00	−5.0
NdN	3.10	−0.11	3.00	−6.0
PmN	4.13	−0.14	4.00	−6.0
SmN	5.22	−0.24	5.00	−5.0
EuN	6.30	−0.30	6.00	−3.0
GdN	7.01	−0.04	7.00	−0.0
TbN	5.97	0.01	6.00	3.0
DyN	4.93	0.05	5.00	5.0
HoN	3.91	0.08	4.00	6.0
ErN	2.90	0.09	2.99	6.0
TmN	1.83	0.12	1.96	5.0
YbN	0.79	0.14	0.94	3.0

These results are as one would expect; the spin magnetic moment is dominated by the rare-earth *f* electrons, with some hybridization yielding small contributions from the rare-earth s-d electrons and the nitrogen p states. This indicates that the nitrogen p states occur in the same energy range as the valence rare-earth states, allowing hybridization to occur. It is interesting to note that the contribution from the nitrogen atom changes sign halfway through the series, in which it follows the RE's orbital moment. It appears that the nitrogen moment wants to point antiparallel to the partially occupied *f*-spin channel. An explanation of this hybridization phenomenon will be given in a later section.

C. Density of states

In Fig. 3 we show typical densities of states of RE nitrides to illustrate the main features. Around −1.5 Ry are the rare-earth 5*p* bands. Above these, just above −1.0 Ry, are the nitrogen 2s bands. Just below the Fermi energy E_f, we reach bands which are predominantly nitrogen *p*-like, but with a substantial hybridization with rare-earth s-d and *f* states. There is a small gap or minimum around the Fermi energy. Above E_f are the mainly rare-earth s-d bands. Superimposed on this are the rare-earth *f* bands. The fully occupied majority-spin *f* bands fall below the nitrogen 2s bands and push the rare-earth 5p bands lower in energy. The occupied minority-spin *f* bands sit just above the nitrogen 2s bands and there is essentially a single peak above E_f which are the unoccupied *f* states. Below half filling the occupied majority-spin peak moves to just above the nitrogen 2s bands, and just above E_f there are two *f* peaks, first the unoccupied majority-spin bands and then the completely unoccupied minority-spin *f* bands.

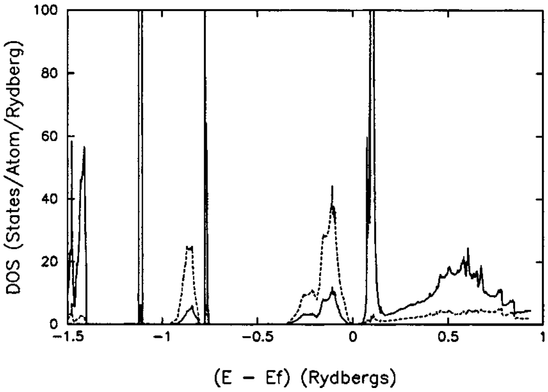

FIG. 3. The density of states for terbium nitride in the trivalent state (Tb site, full line; nitrogen site, dashed line).

Let us look more closely at the electronic properties of the rare-earth nitrides. Table II shows the electronic properties of each material at the Fermi energy. It is clear from the table that most of the light rare-earth nitrides are found to be half metallic. Only CeN is metallic because it exists in the tetravalent state (in fact the trivalent state is also just metallic). TbN, DyN, and HoN are found to be narrow gap insulators and ErN, TmN, and YbN are metallic in both spin channels.

In Table III we show the key spin- and *l*-decomposed densities of states at the Fermi energy. This table shows that the principal character of the electrons at E_f is rare-earth s-d and nitrogen *p*-like in PrN, NdN, and GdN, while it is dominated by the majority-spin rare-earth *f* electrons in PmN, SmN, EuN and the minority-spin rare-earth *f*-electrons in ErN, TmN and YbN. When the *f* contribution is large we also note a relatively large N *p* component, reflecting the strong N *p* rare-earth *f* hybridization. From the results above it is also clear that there is a wide range of electronic properties in the rare-earth nitrides which we discuss in detail in the following section.

To discuss the properties of these materials more fully it is necessary to understand the details of the density of states around E_f. For this reason we show in Fig. 4 the spin-

TABLE II. Spin-resolved band gaps and densities of states (DOS) at the Fermi energy for the rare-earth nitrides. Band gaps are in rydbergs and densities of states are in states/rydberg/formula unit.

Material	Band Spin up	Gap Spin down	DOS Spin up	DOS Spin down
CeN	0	0	15.37	15.37
PrN	0	0.039	0.0001	0
NdN	0	0.065	0.068	0
PmN	0	0.076	31.77	0
SmN	0	0.095	154.56	0
EuN	0	0.107	69.85	0
GdN	0	0.082	0.065	0
TbN	0.008	0.052	0	0
DyN	0.018	0.058	0	0
HoN	0.031	0.004	0	0
ErN	0	0	0.682	69.57
TmN	0	0	1.52	220.78
YbN	0	0	1.72	93.18

TABLE III. The spin-resolved and *l*-decomposed densities of states at the Fermi energy for the rare-earth nitrides in states/rydberg/formula unit.

Material	DOS up			DOS down		
	RE *s-d*	RE *f*	*Np*	RE *s-d*	RE *f*	*Np*
CeN	2.10	11.19	0.13	2.10	11.18	0.13
PrN	0.0001	0	0	0	0	0
NdN	0.020	0.003	0.030	0	0	0
PmN	0.061	31.02	0.40	0	0	0
SmN	0.44	151.42	2.06	0	0	0
EuN	0.64	64.76	3.24	0	0	0
GdN	0.013	0.002	0.040	0	0	0
TbN	0	0	0	0	0	0
DyN	0	0	0	0	0	0
HoN	0	0	0	0	0	0
ErN	0.017	0.037	0.605	0.069	68.45	0.634
TmN	0.029	0.070	1.30	0.28	218.81	1.26
YbN	0.098	0.08	1.46	0.37	89.71	2.10

resolved densities of states on each site for SmN, DyN, and TmN. These materials were chosen as typical examples of the half-metallic, insulating, and metallic rare-earth nitrides, respectively.

D. The light rare-earth nitrides

We now explain how the rare-earth nitrides can exhibit such a wide range of electronic properties in a series of materials that ostensibly have similar outer electronic structures. In previous work,[25,30,31] we have calculated the electronic structure of rare-earth chalcogenides. In agreement with observation for the chalcogenides of Sm, Eu, and Yb, and with the naive ionic model, we found that they are insulators in the divalent state. One might have expected the trivalent nitrides to be similarly insulating, but, as Table II shows, this is not the case. After the SIC-LSD has been applied to the rare-earth nitrides the three valence electrons of the trivalent rare-earth can fill the three holes of the N *p* band and create a full *p* band. This would lead to insulating behavior in a similar manner that the two electrons of the divalent rare-earth in the rare-earth chalcogenides fill the two holes in the chalcogenide *p* band. In the nitrides there are three nitrogen *p* electrons and in the chalcogenides there are four *p* electrons. The difference in the number of *p* electrons means that the *p* bands sit closer to the Fermi energy in the nitrides than in the chalcogenides. In trivalent CeN the nitrogen *p* bands are close enough to E_f to hybridize slightly with the low-energy tail of the rare-earth *s-d* bands, causing the materials to be metallic. As we proceed across the periodic table from CeN to GdN we fill the majority-spin *f* states and create an exchange field that is felt by the other electrons in the material. In the rare-earth chalcogenides this has little effect because the filled bands are well down in the potential well. However, in the nitrides its effect is more pronounced and leads to a significant spin splitting of the nitrogen *p* bands.

The SIC splits the *f*-band manifold into two, localized and bandlike *f* electrons. The SIC *f* bands are completely local-

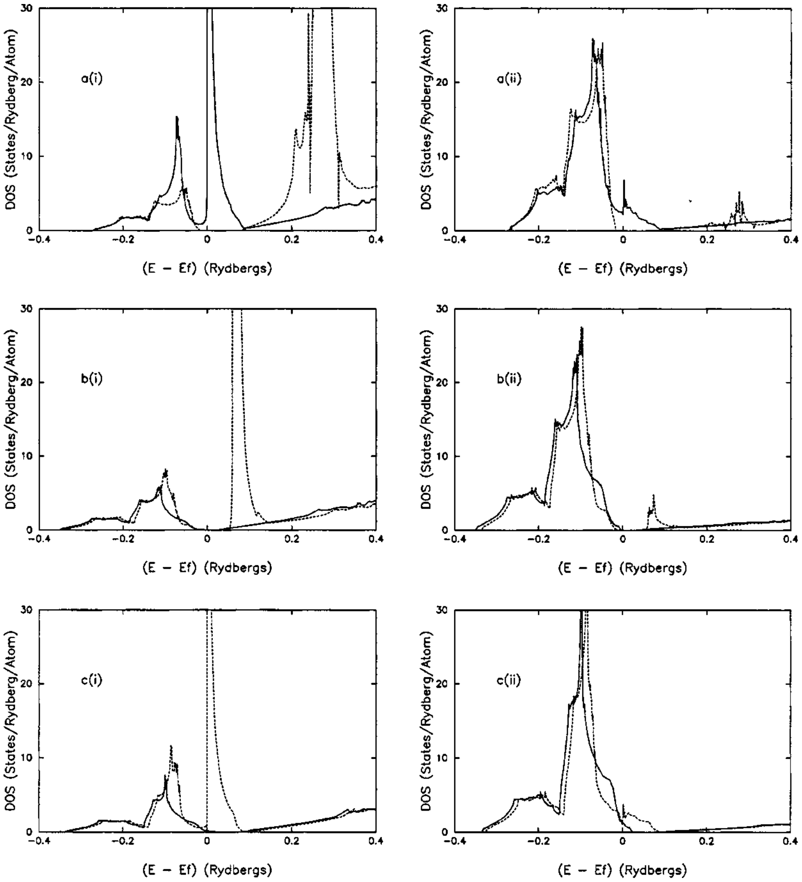

FIG. 4. The density of states around the Fermi energy for (a) SmN, (b) DyN, and (c) TmN. (i) refers to the rare-earth site and the (ii) to the nitrogen site. Full lines represent majority spin and dashed lines are minority spin.

ized and are unable to hybridize significantly. The non-SIC *f* states have a degree of itineracy that allows hybridization. We find that N *p* rare-earth *f* hybridized states play a role in the electronic bonding. This is clear in Fig. 4. In a(ii) panel, for example, the N *p* states, which lie within 0.2 Ry of E_f, lead to structure, in this energy range, in the Sm density of states. This is an energy window where *f* states do not occur, and a *p*-*f* hybridized bonding state has been formed. This occurs to some extent in all the rare-earth nitrides.

Of course, there is also a *p*-*f* antibonding state and it is this that is key to understanding the trends in electronic properties in this series of materials. The upper tail of the majority-spin *p* bands rises to above the Fermi energy and hybridizes with the empty majority-spin bands just above E_f to form the antibonding state. For SmN this can be seen clearly in a(i) and a(ii) in Fig. 4. Just above E_f the majority-spin nitrogen *p* density of states in a(ii) has a small peak that corresponds with the rare-earth *f* bands in a(i).

The exchange field keeps the minority-spin *f* bands well above E_f, and hybridization with the nitrogen *p* bands is very small. In PrN and NdN the empty majority-spin *f* bands are well above E_f and so the electronic properties are dominated by the majority-spin rare-earth *s*-*d* bands. In PmN, SmN, and EuN the empty majority-spin *f* bands have lowered and are very close to the Fermi energy. The density of states at E_f is then dominated by *p*-*f* bands.

In the minority-spin channel there is no significant *p*-*f* hybridization and so the predominantly *p* bands are entirely filled and the *s*-*d* bands are empty. There is an energy gap at the Fermi energy. The minority-spin bands behave much more as expected in the naive ionic model.

A consequence of this behavior is that the nitrogen majority-spin bands are not fully occupied while the minority-spin bands are. This means that the nitrogen moment is antiparallel to the rare-earth moment.

E. The heavy rare-earth nitrides

In the heavy rare-earth nitrides a repeat of the behavior of the light rare earths might be expected with the minority-spin bands replacing the majority-spin ones. This does indeed occur. Inspection of Figs. 4(b) and 4(c) verifies that the comparable features can be seen in the minority-spin densities of states. However, other effects also come into play in the heavy rare-earth nitrides that modify the electronic properties significantly.

In GdN, the majority-spin *f* bands are all filled and the minority-spin bands are well above E_f. The exchange field continues to split the nitrogen *p* band. The majority-spin *p* band hybridizes with the Gd *s*-*d* bands. There is a minimum in the density of states very close to E_f, but it does not quite reach zero. This is very similar to what happens in CeN. Experimentally GdN appears to be a ferromagnetic insulator,[9] and we do find a semiconductor if the calculations are performed at the theoretical, rather than the experimental minimum.

In TbN, the minority-spin *f* bands begin to fill up. This pushes the majority-spin *f* bands closer to the nucleus and so increases the efficiency of the screening of the outer states, so they are less strongly bound to the nucleus. Because of this the rare-earth *s*-*d* states are higher above the Fermi energy in the heavy rare earths than in the light rare earths. In TbN, DyN, and HoN then, there are no bands at the Fermi energy and therefore they are small gap insulators. In ErN, TmN, and YbN the minority-spin *f* peak has come down close to E_f and there is a bonding and an antibonding minority-spin state as in the light rare earths. As the *f* peak comes down the antibonding state gets very close to E_f. The Fermi energy enters the major minority-spin *f* peak. To compensate for this some hybridized majority-spin *p*-*d* character has to rise above E_f creating a nonzero density of states in both spin channels.

The *p*-*f* hybridization pulls some minority-spin character above the Fermi energy and so for the heavy rare earths the nitrogen moment is parallel to the rare-earth moment.

For most rare-earth nitrides very little experimental data appear to be available. However, for YbN several papers have appeared in the literature reporting experiments which can be compared with our work. Trivalency has been established from the magnetic moment.[32] Ott *et al.*, Sakon *et al.*, and Takeda *et al.*[33] reported measurements consistent with heavy-fermion behavior in YbN. However it was shown later by Monnier *et al.*[34] that these results were also consistent with a scenario in which there is interplay between the crystal field and the Kondo effect for an isolated magnetic impurity. The SIC-LDA method does not include the dynamical effects necessary to describe the Kondo effect or heavy-fermion behavior, so we are unable to comment on this point directly. However, we can point out that our results do exhibit the *p*-*f* mixing necessary for the *p*-*f* Kondo effect that explains the low-temperature anomalies in the magnetic susceptibility and specific heat.[35]

The low-temperature magnetic structure of YbN was established to be antiferromagnetic III by Dönni *et al.*[36] Spectroscopic investigations of YbN include core level x-ray photoemission spectroscopy[37] which revealed no evidence of valence mixing, and optical spectroscopy[35] which was able to locate the empty *f* state 0.2 eV above the Fermi energy. They also found the bare occupied *f* states to be around 6.5 eV below the Fermi energy, which is not in good agreement with our results, although there are always considerable uncertainties in locating ground-state bands using spectroscopic techniques. Temmerman *et al.*[38] were able to estimate the relaxation energy for praseodymium and showed that it is around 6 eV. If we assume this does not change much across the rare-earth series, then this estimate would bring our results for YbN into good qualitative agreement with experiment. These experiments also showed that samples exhibiting a small amount of nonstoichiometry can show strongly enhanced Kondo features. The experimental situation for YbN has been well summed up by Wachter[39] who shows that small amounts of doping could raise the Fermi energy to the empty *f* state in YbN and yield intermediate valence or heavy-fermion behavior. In our calculations the position of the empty *f* state is in close agreement with the optical spectroscopy results and so we are also able to suggest that. Furthermore the empty *f* states in TmN are actually at the Fermi energy as indicated in Table III. Extrapolating from the results for YbN suggests that undoped TmN might exhibit heavy-fermion or intermediate valent behavior as well.

IV. CONCLUSIONS

We have seen that the rare-earth nitrides display a wide range of electronic properties despite having the same crystal structure with only a small variation in lattice constant and superficially similar electronic structures. They show insulating (semiconducting), half-metallic, and full metallic behaviors. This is a consequence of the N p and the bandlike rare-earth f states occurring in the same energy window, in the vicinity of the Fermi level. This leads, at E_f, to strong hybridization of these states.

Our results suggest that rare-earth nitrides and their alloys may enable us to fabricate materials with a wide and continuous range of useful properties, particularly with regard to spin-filtering applications where they may provide alternatives to the rare-earth chalcogenides already in use for this purpose.[10–13]

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