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Electronic structure of EuN: growth, spectroscopy, and theory

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We present a detailed study of the electronic structure of europium nitride (EuN), comparing spectroscopic data to the results of advanced electronic structure calculations. We demonstrate the epitaxial growth of EuN films, and show that in contrast to other rare-earth nitrides successful growth of EuN requires an activated nitrogen source. Synchrotron-based x-ray spectroscopy shows the samples contain predominantly Eu$^{3+}$, but with a small and varying quantity of Eu$^{2+}$ that we associate with defects, most likely nitrogen vacancies. X-ray absorption and x-ray emission spectroscopies (XAS and XES) at the nitrogen K-edge are compared to several different theoretical models, namely LSDA+$U$ (local spin density functional theory with Hubbard $U$ corrections), dynamic mean field theory in the Hubbard-I approximation, and QS$GW$ (quasiparticle self-consistent $GW$) calculations. The DMFT and QS$GW$ models capture better the density of conduction band states than LSDA+$U$. Only the Hubbard-I model contains a correct description of the Eu 4$f$ atomic multiplets and locates their energies relative to the band states, and we see some evidence in XAS for hybridization between the conduction band and the lowest lying $^5S$ multiplet. The Hubbard-I model is also in good agreement with purely atomic multiplet calculations for the Eu M-edge XAS. LSDA+$U$ and DMFT find a metallic ground state, while QS$GW$ predicts a direct band gap at X for EuN of about 0.9 eV that matches closely an absorption edge seen in optical transmittance at 0.9 eV and a smaller indirect gap. Overall, the combination of theoretical methods and spectroscopies provides insights into the complex nature of the electronic structure of this material. The results imply that EuN is a narrow band-gap semiconductor that lies close to the metal-insulator boundary, where the close proximity to the Fermi level of an empty Eu 4$f$ multiplet raises the possibility of tuning both the magnetic and electronic states in this system.

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I. INTRODUCTION

The rare earth nitrides (RE-Ns) display especially strong coupling between spin and charge degrees of freedom. They are thus of interest both as candidates for use in spintronics devices and as a fundamental testing ground for theories of the electronic structure of correlated materials.1 Theoretical treatments predict that the series includes both half metals and ferromagnetic semiconductors.2–7 However, treating the atomic-like 4$f$ electrons within band theory is challenging, and the predicted electronic structures can be contradictory. Experimental investigations of the RE-Ns are also challenging, owing to the difficulty in preparing samples that are stoichiometric, and passivating them against oxidation in atmosphere. For most the magnetic state is known,8,9 but much less information is available regarding the electronic structure. Recent progress has been made, especially in the case of GdN, with the demonstration of epitaxial film growth,10–14 and studies of its electronic and magnetic properties.15–21 Far fewer experimental data concerning the rest of the series are available.22–26

Of particular interest are the properties of EuN,3,27–29 The ground state of the Eu$^{3+}$ ion, the charge state anticipated when Eu bonds to nitrogen, has total angular momentum $J = 0$, so is non-magnetic. However, the separate spin and orbital angular momenta are both large, and thus it is possible that magnetic ordering could exist in the form of “hidden ferromagnetism”.27 Accurate calculations of the electronic structure have proven difficult; for example, an LSDA+$U$ treatment that has been shown to be accurate for GdN3,17 was unable to determine whether EuN has Eu in the 2+ or 3+ charge state, due to the presence of Eu 4$f$ states close to the Fermi level.3 Thus, even the fundamental question of whether EuN is metallic or semiconducting remains unsettled.

There are presently few experimental studies that address the growth or electronic structure of EuN.30–32 Recently, we reported an x-ray magnetic circular dichroism (XMCD) study of EuN thin films, which demonstrated that Eu is predominantly in the 3+ charge state, but that a small quantity (a few %) of Eu$^{2+}$ is present in
the films.\textsuperscript{33} It appears that these 2+ ions are generated when low-lying empty Eu 4f levels become filled as a result of electron doping of the films, for example by nitrogen vacancies. The Eu\textsuperscript{2+} ions dominate the magnetic response, and the XMCD results raise the possibility that a sufficient density of 2+ ions could even support ferromagnetism against the Eu\textsuperscript{3+} background. More generally, such strongly localized levels close to the Fermi level can have a profound influence on conduction properties.\textsuperscript{34–36} These considerations highlight the substantial importance of developing theoretical techniques that can treat systems such as EuN.

Against this background we demonstrate epitaxial growth of EuN, and compare optical and x-ray spectroscopic data from the films with the predictions of several advanced electronic structure calculations, namely LSDA+U,\textsuperscript{3} quasiparticle self-consistent GW theory (QSGW),\textsuperscript{6,37} and Hubbard-F\textsuperscript{38,39} dynamic mean field theory.\textsuperscript{50,41} Each of the calculations brings a different perspective to the analysis of the electronic structure. Both the QSGW and DMFT calculations outperform the LSDA+U treatment in terms of accurately predicting the nitrogen p partial density of states (PDOS) measured by x-ray absorption and x-ray emission spectroscopies (XAS and XES, respectively). The results show that the previous LSDA+U calculations’ prediction of a mixed Eu-f–Eu-d like band near the Fermi level is an artifact of the difficulties in converging the LSDA+U calculations.

The QSGW calculation predicts a finite band-gap, in agreement with optical spectroscopy, while the DMFT results, which rely on an LSDA+U calculation as input, predict a metallic band structure. On the other hand, the location of the Eu 4f levels, measured by XAS and x-ray photoelectron spectroscopy (XPS), is best captured by the DMFT method due to its more accurate treatment of the multiplet nature of the correlated 4f states. The combination of XAS and DMFT provides evidence for the existence of a low-lying Eu \textsuperscript{8}S\textsubscript{5} level close to the conduction band minimum. The picture of EuN that emerges is of a heavily doped semiconductor, where the interaction between extended band states and atomic-like 4f levels can lead to interesting physics.

II. COMPUTATIONAL METHODS

A. LSDA+U

The LSDA+U method as described in Larson \textit{et al.}\textsuperscript{3} was used here to obtain N-p partial densities of states in the conduction band and compare them with the N K-edge XAS. The calculations are carried out using the FP-LMTO method.\textsuperscript{42,43}

The LSDA method was originally developed by Anisimov \textit{et al.}\textsuperscript{44–47} as a way to deal with strongly correlated narrow band electrons in the framework of the Hubbard model. Essentially it comes down to a Hartree-Fock level treatment of the \textit{f}-states, in interaction with the other orbitals being treated at the usual orbital independent local spin density functional approximation (LSDA) level. The double counting terms are treated in the so-called fully localized limit.\textsuperscript{45,48} What this means is that the total energies for the atomic limit of integer occupations of certain f-sublevels agree between LSDA and LSDA+U. The LSDA+U calculation then essentially describes how these f-level occupations are adjusted self-consistently by their interactions with the other orbitals. The particular implementation used in this and the previous work by Larson \textit{et al.}\textsuperscript{3} is described in Liechtenstein \textit{et al.}\textsuperscript{47} and is formulated in terms of the density matrix of the f-electrons.

An important issue is whether the LSDA+U solution is unique. Different starting point density matrices may lead to different solutions, and in principle we need to pick the lowest energy one. In Larson \textit{et al.}\textsuperscript{3} it was found that in most rare-earth nitrides the optimum density matrix is close to obeying Hund’s rules of maximal spin \textit{S}\textsubscript{z} and orbital angular momentum \textit{L}\textsubscript{z}. This solution breaks the cubic symmetry of the \textit{f}-states. On the other hand, EuN turned out to be one of the exceptions where a density matrix obeying cubic symmetry had lower energy. This is because the Hund’s rule solution converged to an Eu\textsuperscript{2+} like configuration by occupying the lowest empty \textit{f}-level of the Eu\textsuperscript{3+}. Similar convergence problems were mentioned by Johannes and Pickett,\textsuperscript{27} although they were able to stabilize a Hund’s rule-obeying Eu\textsuperscript{3+} configuration with slightly different \textit{U} parameters. Even within the solution obeying cubic symmetry, a band with mixed Eu \textit{f} – \textit{d} character was found to cross the Fermi level, predicting a metallic behavior. It is however not clear whether this metallic band would show up in transport because the mobility related to it might be low. The convergence problems in the LSDA+U treatment for EuN lead to a considerable uncertainty in this prediction. This uncertainty about the electronic structure of EuN makes it particularly interesting to study by spectroscopic methods and alternative theoretical treatments. In particular, we recognize that the problems have to do with the nature of the lowest empty \textit{f}-like states, and these are not yet accurately described in full within LSDA+U theory because it lacks a proper treatment of multiplet splitting effects.

On the other hand, in Larson \textit{et al.’s} LSDA+U treatment,\textsuperscript{3} a \textit{U}\textsubscript{d} shift of the \textit{d}-bands is also included to open a band gap. This parameter was adjusted for GdN, but significant uncertainty exists in its values for other RE-N such as EuN.

B. QSGW

The \textit{GW} method is a many-body perturbation theory\textsuperscript{49,50} for the self-energy of one-electron quasiparticle excitations. It is the first term in an expansion in terms of the screened Coulomb interaction \textit{W}, schematically,
\[ \Sigma(12) = iG(12)W(1^+2), \]  
where \( G(12) \) is the one-electron Green’s function. Here, \( 1 = \{ r_1, \sigma_1, t_1 \} \) is a short hand for position, spin and time and \( 1^+ \) means \( t_1 + \delta \). The one-electron Green’s function provides the polarizability

\[ \Pi(12) = -iG(12)G(21), \]

and hence the screening of the Coulomb interaction,

\[ W(12) = v(12) + \int W(13)P(34)v(42)d(34). \]

Its accuracy depends on the starting independent electron Hamiltonian \( H^0 \), which is usually taken as the LDA. Its Green’s function and the \( W \) constructed from it through the above equations are denoted \( G^0 \) and \( W^0 \). In quasiparticle self-consistent or QSGW,\(^{37}\) the one-electron Hamiltonian \( H^0 \) from which \( G^0 \) is constructed uses an exchange correlation potential,

\[ v_{xc}^{QSGW} = \frac{1}{2} \sum_{nm} |\psi_n\rangle \Re[\Sigma_{nm}(E_n) + \Sigma_{nm}(E_m)]|\psi_m\rangle, \]

which is itself extracted from the \( \Sigma \) of the previous iteration in such a way that the difference between quasiparticle energies \( E_i \), given by

\[ \int \frac{1}{2} \nabla^2 + v_{ext}(r) + v_H(r) \phi_i(r) + \int \Sigma_{xc}(r', r', E_i) \phi_i(r')d^3r' = E_i \phi_i(r), \]

and Kohn-Sham one-electron energies \( \epsilon_i \), given by

\[ H_0 \psi(r) = \left[ \frac{1}{2} \nabla^2 + v_{ext}(r) + v_H(r) + v_{xc}^{QSGW} \right] \psi_i(r) = \epsilon_i \psi_i(r), \]

approach each other upon self-consistency. In the above equations, \( v_{ext} \) is the external potential or interaction with the nuclei, \( v_H \) is the Hartree potential, and \( \Re \) means taking the Hermitian part.

This approach, along with the specific implementation in terms of the full-potential linearized muffin-tin orbital method (FP-LMTO) and a mixed basis set of product functions and interstitial plane waves, fully described in Refs. [51] and [52], was shown to give accurate band structures for a wide variety of systems.\(^{37}\) In particular, for most semiconductors, it provides accurate but slightly overestimated values for the band gap. The remaining overestimate is related to the random phase approximation (RPA) for the polarizability \([\text{Eq. (2)}]\) and is in practice well taken into account by scaling the final \( \Sigma \) by a factor 0.8. We will refer to this approximation as 0.8\( \Sigma \).

Specifically for \( 4f \) electrons, however, it was found that QSGW significantly overestimates the energy of the empty \( f \) electron states. This was shown for Gd metal, GdN, ErAs, etc.\(^{6} \) Nonetheless, this appears to be unimportant for the band gap region in GdN which is accurately obtained. In practice, here for EuN, we take an LSDA+\( U \) calculation as the starting point but the final self-consistent QSGW result should, in principle, be independent of starting point.

C. DMFT

In spite of its accuracy for moderately correlated systems, QSGW is still only the first term in a perturbation theory series. Essentially it still has a Hartree-Fock like structure with a screened Coulomb interaction similar to the LSDA+\( U \) level of treatment of the \( f \)-electrons. It does not yet take into account the more subtle correlation effects of the multiplet splittings of the \( f \) electrons. The latter arise from the different ways the electrons’ orbital and spin angular momenta can combine to give different total angular momentum states in multi-determinant wave functions. Such effects are mostly atomic-like and well understood since the work of Racah\(^{53} \) and described for example in Condon and Shortley’s book.\(^{54} \)

A method for combining these atomic multiplet effects with band structure approaches is provided by the so-called Hubbard-I approximation\(^{38,39} \) in dynamic mean field theory (DMFT).\(^{40,41} \) In these methods, the electronic structure of the localized orbitals is fully treated as a local decoupled impurity using atomic multiplet theory. The contribution of specific one-electron excitations between the multiplet states to the one-electron Green function are then calculated. These are expressed as a self-energy. This self-energy is now assumed to be Bloch wave vector \( k \)-independent and inserted in the Dyson equation for the crystal’s Green function with the coupling to other states turned back on. From this calculation, one obtains how these atomic type multiplet excitations are hybridizing with the other states of the system. In the present paper, this calculation is carried out using a tight-binding atomic sphere approximation implementation\(^{55} \) of the linearized muffin-tin orbital method.\(^{56} \) This method is shown to represent the band structure of RE-Ns similarly to the more accurate FP-LMTO provided adequate size of unit cells are chosen.\(^{57} \) The parameters of the model include the on-site Coulomb interaction \( U = 8.3 \) eV similar to the LSDA+\( U \) model, as well as atomic Slater integrals \( F^2 = 13.5, F^4 = 8.45 \) and \( F^6 = 6.07 \) eV. Spin-orbit coupling is included in the multiplet calculation at the \( j - j \) coupling level. The final multiplet states can approximately be labeled by their \( 2S+1L \) term label. The calculations consider the \( f^6 \rightarrow f^7 \) excitations reachable from the ground state term \( 7F \) of the \( f^6 \) configuration by a single \( f \)-electron creation oper-
an ion source producing 125 eV N\textsuperscript{2}− ions from a thermal source, and nitrogen supplied via a partial pressure of 10\textsuperscript{−4} mbar. The film was grown at a rate of 0.4 Å/s after the YSZ substrate had been outgassed for one hour.

Thus, all initial state multiplets of the d\textsuperscript{10} f\textsuperscript{6} and d\textsuperscript{9} f\textsuperscript{7} configurations are calculated. Spin-orbit coupling is included and the calculation is carried out in the intermediate coupling scheme. Calculations of the dipole allowed optical matrix elements corresponding to ΔJ = 0, 1 are carried out and produce a simulated spectrum. These calculations first of all provide a very different spectrum for Eu\textsuperscript{2+} and Eu\textsuperscript{3+} ions, and hence can be used as a fingerprint to determine the ratio of the contributions of these two valence states of the Eu in our samples. Secondly, however, the analysis provides us with approximate term labels of the initial and final state multiplets involved in each allowed transition as well as the labels of the corresponding pure f\textsuperscript{7} parent term. We can thus attempt to correlate the present more complete atomic multiplet calculation of the XAS spectrum with the simpler DMFT f-only multiplet calculations described in the previous section. As these two portions of the work were carried out independently, slightly different atomic parameters were used. The Slater F\textsuperscript{k} integrals in this part of the work are given by F\textsuperscript{2} = 11.263, F\textsuperscript{3} = 7.069 and F\textsuperscript{6} = 5.086 eV and the spin-orbit coupling parameter is 0.175 eV.

III. RESULTS

A. Epitaxial film growth

We begin by demonstrating epitaxial growth of EuN on [100] oriented YSZ. Figure 1 shows reflection high-energy electron diffraction (RHEED) images from a 75 nm thick film grown at a substrate temperature of 590°C in a Thermonics ultra-high vacuum system with a base pressure of 10\textsuperscript{−8} mbar. Eu metal (99.9% pure) was evaporated from a thermal source, and nitrogen supplied via an ion source producing 125 eV N\textsuperscript{2}− ions at a beam current of 0.24 mA. The overall N\textsubscript{2} partial pressure was 3.7 × 10\textsuperscript{−4} mbar. The film was grown at a rate of 0.4 Å/s after the YSZ substrate had been outgassed for one hour at 600°C. After growth the sample was capped with approximately 35 nm of AlN to allow \textit{ex situ} studies without oxidation of the film in air. The streaky and rather narrow RHEED patterns are indicative of two-dimensional high crystalline quality epitaxial growth. Weak streaks lying between the main streaks along the ⟨110⟩ direction suggest that there may be a (2 × 1) surface reconstruction under these growth conditions (see Fig 1(b) inset).

The x-ray diffraction pattern from this sample, shown in Figure 2, exhibits intense peaks corresponding to the [200] and [400] reflections of rocksalt EuN. Unlabelled narrow features correspond to substrate peaks that appear due to the slightly non-monochromatic x-ray source. A [111] peak weaker than the [200] by about two orders of magnitude is observed at 2θ = 64.3°. There is an even weaker shoulder at about 30.3° indicating a small amount of EuO in the film, which may be associated with a thin oxide layer forming at the film/substrate interface due to mobile oxygen in the YSZ.\textsuperscript{10} The measured EuN lattice constant is 4.98 Å, similar to the previously reported value of 5.02 Å.\textsuperscript{30,31} and a Scherrer analysis of the peak widths indicates an ordered length scale of approximately 20 nm. The RHEED and XRD results are comparable to those from the best gadolinium nitride films.\textsuperscript{10–12,14} A range of EuN samples have been grown under conditions similar to those described above, at temperatures...
between 475 and 590° C, but a clear correspondence between growth temperature and film quality has not been established. In fact, not all samples grown under nominally similar conditions to the sample described above have yielded epitaxial growth, with some growths instead leading to films with a strong [100] texturing but no evidence of epitaxy in RHEED. Thus, growth of EuN appears to be sensitive to the growth conditions. We have also grown samples under the conditions described above, but without using the ion source. X-ray diffraction from one such sample, included in Fig. 2, exhibits peaks from metallic europium, but does not show clear EuN peaks. This provides evidence that growth of EuN using nitrogen gas requires that the nitrogen source be excited. This is in contrast to other rare-earth nitrides such as GdN, SmN, or DyN, which can be grown under a non-excited nitrogen partial pressure, and sample Eu$^{2+}$ without nitrogen. Only Eu$^{2+}$AS, Eu$^{3+}$AS, and Eu$^{3+}$NSLS contain predominantly Eu$^{3+}$ corresponding to EuN, while Eu$^{2+}$AS and Eu$^{3+}$AS are largely metallic Eu. Spectra offset for clarity.

B. XAS/XPS analysis of sample quality

To further analyze the growth mode and properties of EuN we have carried out XPS and XAS at the Soft X-ray Spectroscopy Beamline of the Australian Synchrotron, and XPS, XAS, and XES at beamline X1B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, USA. At the Australian Synchrotron XAS data were recorded in total electron or fluorescence yield modes using the sample drain method. The overall XAS resolution was about 0.2 eV at the N K-edge and about 0.5 eV at the Eu M-edge. XES data were measured using a Nordgren-type grazing-incidence soft x-ray spectrometer with resolution of about 0.4 eV at the N K-edge. All data were obtained at room temperature. The XES and valence band XPS were calibrated by measuring the binding energy of the N 1$s$ core level (396.6 eV; calibrated to the Fermi level using the known location of the 4$f$ peaks of a gold reference sample).

For all synchrotron measurements samples were grown in situ at the synchrotron beamlines, thereby avoiding exposure of the samples to atmosphere and eliminating the need for a capping layer. At the Australian Synchrotron a thermal evaporator was used to evaporate the Eu onto YSZ [100] substrates, while nitrogen was introduced into the chamber via an ion source supplying 500 eV N$_2^+$ ions with a beam current of 7-10 mA. The partial pressure in the chamber was approximately 7×10$^{-6}$ mbar. The Eu deposition rate varied from 0.2–0.5 Å/s, calibrated using a quartz crystal microbalance. The substrate temperature, estimated using a thermocouple, was approximately 550°C for the first EuN growth (sample Eu$^{2+}$AS$_{thin}$) and 450°C for the second (sample Eu$^{2+}$AS$_{bulk}$) (the former sample is substantially thinner than the latter, as described below). For comparison a film (sample Eu$^{2+}$AS$_{N_2}$) was grown at 450°C with the ion source operating, but angled such that there was no line of sight to the substrate, thus allowing the role of the ion source to be investigated using films subject always...
obtained at the NSLS for the metallic sample EuNSLS.

At the NSLS samples were deposited onto Si [100] substrates in a growth chamber with base pressure 2 × 10⁻⁸ Torr (properties of a representative sample EuNSLS bulk are described below). The films were grown at a temperature of approximately 125°C using a thermal evaporator for the Eu and an Oxford Scientific ECR plasma source for the nitrogen. The plasma source was run at about 21 mA and with a N₂ partial pressure of about 3 × 10⁻⁴ Torr. The Eu deposition rate was estimated to be 0.7 Å/s. A reference Eu metal film (sample EuNSLS) was prepared without introducing nitrogen to the chamber.

The europium M-edge x-ray absorption spectra of all samples are shown in Figure 3. Also shown are calculated spectra for Eu²⁺ and Eu³⁺ ions obtained following Thole et al., as described in Section II D. All of the spectra are dominated by the expected Eu M4 and M5 absorption edges, with structure associated with multiplet levels. By comparison to the calculated spectra, we can conclude that the Eu metal sample EuAS is entirely Eu³⁺, with no detectable presence of Eu²⁺. Similar results were obtained at the NSLS for the metallic sample EuNSLS. Sample EuNSLS thin, grown with the ion source occluded, displays only a weak contribution from Eu³⁺, with the signal dominated by Eu²⁺. Only the samples grown using an activated nitrogen source (samples EuNSLS thin, EuNSLS bulk, and EuNSLS bulk) are dominated by Eu³⁺. The only plausible candidates for the origin of the 3+ signal are EuN and EuO₃, but if the latter were present significantly in samples EuNSLS thin and EuNSLS bulk we would also expect it in sample EuNSLS thin. Thus we attribute the Eu³⁺ to EuN, and conclude that Eu in EuN is predominantly in the 3+ charge state, and that, as found above, successful growth of EuN requires an excited nitrogen source.

The EuN samples EuNSLS thin, EuNSLS bulk and EuNSLS bulk also contain a small amount of Eu²⁺, as evidenced by the small shoulder at about 1132 eV. We cannot firmly establish whether this is a result of metallic Eu inclusions in the films, or defects, such as nitrogen vacancies or residual oxygen, altering the Eu charge state. Most significantly, sample EuNSLS bulk clearly contains the lowest Eu²⁺ concentration, so we conclude that it is the most close to stoichiometric of the films.

FIG. 4: (Color online) Normalized nitrogen K-edge XAS from a series of EuN samples grown under different conditions, along with the spectrum from GdN for comparison. The most nearly stoichiometric films are sample EuNSLS bulk and sample EuNSLS AS, and these bear the most resemblance to the GdN spectrum. Note however the shoulder at about 397 eV that does not appear in GdN, and which is likely related to the presence of an Eu 4f multiplet near the conduction band minimum. Spectra offset for clarity.

May not be fully representative of the bulk of the films. Therefore we do not attempt to calculate the stoichiometry of the films or the impurity content based on XPS data, simply noting that the near-surface region of the films is clearly subject to some disorder.

More revealing are XAS and XES results obtained at the nitrogen K-edge. XAS and XES are bulk probes (penetration depth ~ 50 nm), making them less sensitive to potential surface impurities, and they are element specific, picking out the partial density of empty (XAS) or filled (XES) states projected onto a nitrogen atom. Thus, to the extent that the electronic structure of EuN is influenced primarily by the local environment, these techniques are not directly influenced by impurities or off-stoichiometry. The nitrogen K-edge XAS from samples EuNNSLS thin, EuNNSLS bulk, and EuNNSLS bulk is shown in Figure 4. We also include in the figure the XAS from GdN published previously. The spectra have been aligned to the absorption onsets.

The most nearly stoichiometric film (sample EuNNSLS bulk) shows a structured XAS with clear peaks near 401 and 405 eV. Corresponding peaks can be identified in the GdN XAS at about 402 and 406 eV, and these have been shown to correspond to the t₂g and e₉ crystal field split Gd 5d states, respectively. This confirms the similar overall electronic structure of the two materials. The spectrum of sample EuNNSLS bulk displays the same main features as that of sample EuNNSLS bulk, but with an additional narrow peak near 400 eV that is most likely associated with molecular nitrogen trapped within the films, as seen also in disordered GaN films. Sample EuNNSLS thin, grown without direct exposure to the ion source, exhibits the same main spectral features as EuNNSLS bulk and EuNNSLS bulk.
but with substantially worse signal to noise ratio due to the minimal incorporation of nitrogen into this film. Sample EuN\textsubscript{AS}\textsubscript{thin} shows a less structured XAS with a single broad peak near 404 eV rather than the clearly identifiable $t_{2g}$ and $e_g$ peaks seen in samples EuN\textsubscript{AS}\textsubscript{bulk} and EuN\textsubscript{NSLS}\textsubscript{bulk}. This sample is substantially thinner than sample EuN\textsubscript{AS}\textsubscript{bulk}, as demonstrated by strong substrate peaks visible in the XPS of sample EuN\textsubscript{AS}\textsubscript{thin}, which is likely a result of re-evaporation of Eu at the higher growth temperature. The less structured XAS spectrum indicates a much larger degree of disorder in this film. Samples EuN\textsubscript{AS}\textsubscript{thin} and EuN\textsubscript{NSLS}\textsubscript{thin} both show evidence of molecular N\textsubscript{2}. Overall, we conclude that sample EuN\textsubscript{NSLS}\textsubscript{bulk} is the most representative of bulk EuN, and below we single this sample out for comparison to theory.

C. Comparison of spectroscopies with theory

The nitrogen K-edge XAS from sample EuN\textsubscript{NSLS}\textsubscript{bulk} is compared in Figure 5 with the N-$p$ PDOS in the conduction band calculated according to various models. As mentioned earlier, the LSDA+$U$ calculations of Larson \textit{et al.}\textsuperscript{3} obtained two competing solutions for the $f$-electron density matrix. One started from Hund’s rule Eu\textsuperscript{3+} but converged to a more Eu\textsuperscript{2+}-like solution. The other obeyed cubic symmetry and stayed Eu\textsuperscript{3+}-like but nonetheless was found to have an interesting hybrid $f-d$ like band crossing the Fermi level. This was found to be the lowest energy state. We can see in Fig. 5 that neither of these models fits the nitrogen K-edge well. Both overestimate the splitting between the $t_{2g}$ and $e_g$ peaks in the experiment, and the experiment does not show evidence for the low energy peak near 394 eV that arises from the filling of the low $f$-band and associated metallic character in this theory. On the other hand, the PDOS calculated in these models was taken to higher energy and does reasonably describe the peak in the 415–425 eV range.

The QSGW model is much better than LSDA+$U$ at matching the experimental $t_{2g}-e_g$ peak splitting, and the peak in the PDOS at 394 eV does not appear in this model. The DMFT PDOS also matches the N K-edge spectrum rather well. The most notable difference between the QSGW and DMFT is that the N-$p$ PDOS in DMFT shows a weak peak at about 396.5 eV. Comparison to the Eu $f$ PDOS, also shown in Fig. 5, shows that this peak in DMFT is clearly correlated with the occurrence of the $^8S_f^7$ multiplet term of the Eu ion, and is thus evidence of hybridization of this state with the conduction band. Experimental evidence for this hybridization exists as a shoulder at about 397 eV in the spectrum of sample EuN\textsubscript{NSLS}\textsubscript{bulk}. A similar shoulder is clearly evident in sample EuN\textsubscript{bulk}\textsubscript{AS} (Fig. 4), but a corresponding feature is not seen in the GdN spectrum. That the experimental and theoretical peak energies do not perfectly match is because these energies in the theory depend on the precise choice of the $U$ parameter and the Slater $F_k$ inte-
recognize that in particular the lowest high spin \(8f\) more accurate quantum number labeling in terms of the tum numbers in (up) and minority (down) spin. These are good quan-
to account. Neither LSDA+ pllet theory. Clearly, the multiplets are essential to take 
XAS with both the DMFT theory and the atomic multi-
ments. We indeed see that the full multiplet theory and 
DMFT multiplet theory that takes into account only the 
cluster of similar states as the DMFT theory. Although 
the XPS VBM is aligned with the N K-edge XES 
the main lines are labelled in spectroscopic notation.

by the degeneracies of these states rather than the in-
trinsic dipole matrix elements. In particular, we again 
note the low energy \(8S\) peak, which clearly corresponds 
to the shoulder of the spectrum. The \(M_5\)-edge spectrum 
appears to be a somewhat better fit with the DMFT 
splittings than the \(M_4\)-edge spectrum. The atomic mul-
ple theory including the correct dipole matrix elements 
accounts better for the shape of the \(M_4\) spectrum. The 
spitting between \(M_4\) and \(M_5\) is somewhat overestimated 
by the theory, indicating that the spin-orbit coupling of the 
3\(d\) states is overestimated.

The main point about DMFT however, is that this 
places the \(4f\) multiplets relative to the other bands in the 
system, whereas the purely atomic multiplet theory 
is of course not capable of doing this. As was pointed 
out in the previous discussion, this allows us to study 
hybridization effects between \(N-p\) and \(Eu-f\).

We now turn to the occupied states as measured by 
XPS and XES and shown in Figure 8. The XPS signal 
is heavily dominated by the \(Eu-f\) states that provide a large 
peak centered at about -7.5 eV and a much smaller peak 
below the VBM as those in DMFT, but again do not quite 
show the right splittings or locations to match the ex-
perimental data. Furthermore, there is no experimental
FIG. 8: (Color online) Comparison of XPS and XES measurements of the EuN valence band PDOS with various theories. Solid black line XPS; light blue line N K-edge XES; red line with labels DMFT theory of Eu $f^5$ multiplet PDOS; blue dashed line N-2s PDOS; pink dashed line N-2p PDOS; purple dotted line Eu-4f in LSDA+$U$. The XES energy scale has been shifted by -396.6 eV.

FIG. 9: Experimental optical transmittance of an epitaxial EuN film. The data show a clear absorption edge near 0.9 eV.

evidence for the low binding energy partially occupied peak right at the Fermi energy that is characteristic of the LSDA+$U$ model.

The N K-edge XES seen in Fig. 8 is not directly affected by contamination by Eu$^{2+}$, and it shows a shape that is consistent with that measured in other rare-earth nitrides. As expected the XES agrees well in shape with the calculated N-p PDOS in either LSDA+$U$ or GW theories.

To address the electronic state of EuN we have complemented the x-ray spectroscopies with optical transmittance measurements obtained at room temperature from the sample described in Section III A. As seen in Figure 9 the transmittance is large at low energies, but shows a clear absorption onset near 0.9 eV, with

the transmittance falling away towards the visible end of the spectrum. The structure in the spectrum below 0.9 eV is related to interference effects associated with the finite thickness of the film and the capping layer, and the small feature just above 1 eV is instrument related. The existence of an absorption edge is suggestive of a semiconducting state for EuN with a finite band gap. However, optical absorption is dominated by direct transitions, whereas the minimum gap is expected to be between $\Gamma$ and $X$ in the band structure, as found previously for GdN. We thus turn to an examination of the band structure calculated using $\text{QS}GW$, as shown in Figure 10. The calculation does indeed return a semiconducting and ferromagnetic ground state, with a direct gap at $X$ of 0.94 eV and a minimum indirect gap between $\Gamma$ and $X$ of 0.31 eV. The occupied majority spin 4f levels are visible as relatively dispersionless bands from about $-7$ to $-10$ eV, with an unoccupied majority spin band at about 4 eV that hybridizes somewhat with the conduction band. This lowest unoccupied 4f band is somewhat higher in energy than the $^{8}\text{S}$ multiplet level found in the DMFT calculation. Unoccupied minority spin 4f levels are located above 7 eV. The spin polarization leads to exchange splitting between the majority and minority spin states that is especially evident near the band edges.

The majority spin direct gap at $X$ is quite similar in energy to the measured optical absorption edge. However, it is uncertain whether EuN could order ferromagnetically, given the $J = 0$ ground state of the Eu$^{3+}$ ion, and our measurements have found no evidence for such ordering at the temperatures used for the optical spectroscopy. We have previously shown that for GdN the optical absorption edge in the paramagnetic state is reasonably well described by taking an average of the spin-down and spin-up direct band gaps. Following this approach we obtain a spin averaged direct QS$GW$ gap at $X$ of 1.59 eV for EuN, somewhat higher than the FM gap.
and the optical absorption onset. However, the QSGW method is known to provide a slight overestimation of band gaps for many semiconductors.\textsuperscript{37} It has successfully been applied to GdN\textsuperscript{6} for which it gives an indirect $\Gamma$-$X$ majority spin gap of 0.22 eV, while in the 0.8$\Sigma$ approximation it gives 0.05 eV for the indirect gap and a spin averaged gap at $X$ of 0.97 eV. Applying the 0.8$\Sigma$ approximation to the present calculation would yield an averaged gap closer to the experimental absorption onset. On the other hand it may be that the spin averaging approach is not valid here and the FM gap is closer to the paramagnetic gap.

In any case, like GdN, EuN appears to be very close to a metal-insulator transition with an almost zero indirect gap. Nevertheless, the results indicate that EuN lies on the semiconducting side of the transition under the conditions of our measurements. In contrast, for the DMFT calculation no attempt was made to adjust the $d$-bands, and thus a clear overlap of the valence bands at $\Gamma$ and conduction bands at $X$ is obtained, in other words, a semimetallic band structure. The LSDA+$U$ calculation does include a shift of the $d$ bands, but it finds a band with mixed $d$ and $f$ character crossing the Fermi level and it thus predicts an actual metallic band structure.

\section*{IV. CONCLUSIONS}

We have presented a detailed investigation of the electronic structure of EuN, drawing on both experimental results and a series of electronic structure calculations. We have demonstrated epitaxial growth of EuN, and have also shown using x-ray spectroscopy that the films typically contain a few atomic % of Eu$^{2+}$ ions amongst the predominant Eu$^{3+}$. X-ray absorption, x-ray emission, and x-ray photoelectron spectroscopic data have been compared to the results of LSDA+$U$, quasiparticle self-consistent $GW$, Hubbard-I dynamic mean-field, and atomic multiplet calculations, with different aspects of the theories being emphasized in different energy ranges. The conduction band density of states measured by XAS matches much better the QSGW and DMFT results than it does the LSDA+$U$ calculation. Our combined results make it clear that to understand the detailed features of the electronic structure it is essential to locate the atomic-like 4$f$ multiplets relative to band features, and here DMFT is most able to capture the 4$f$ electron physics. Of particular interest is the presence of a Eu $^8S^7 F^7$ multiplet level lying close in energy to the conduction band minimum. This offers the possibility of hybridization between conduction electrons and the atomic-like 4$f$ states. We believe that it is this level that becomes occupied in sub-stoichiometric EuN leading to the small concentration of Eu$^{2+}$ ions within the films. Optical absorption spectroscopy implies the presence of a direct band gap of around 0.9 eV at room temperature, which is most consistent with the QSGW band structure calculation, although the possibility remains that ferromagnetic EuN, if it exists, would have a small band overlap. Overall, the possibility of interacting conduction and 4$f$ electrons and the presence of a small concentration of magnetic Eu$^{2+}$ raises the possibility of complex and interesting physics in this material system.

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