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The excited-state properties of the light rare-earth elemental metals praseodymium, neodymium, and samarium are studied within the Hubbard-I formalism. This method describes the multiplets of the rare-earth f shell by an exact diagonalization of the two-body part of the Hamiltonian. Subsequently, the rare-earth ion is embedded in the solid environment by incorporation of the atomic self-energy into a solid Green's function, which is calculated using the local density approximation to density functional theory. After describing the method briefly, a systematic comparison with available photoemission experiments is made, and it is found that all main structures of the experimental spectra are reproduced by the approach, with the exception of the features immediately below the Fermi level which are interpreted as a mark of a mechanism different from an atomlike multiplet transition.

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I. INTRODUCTION

Through the history of modern science, the rare-earth series has always been a subject of great interest. Due to their intricate electronic structure, these elements are of interest from a purely scientific point of view, but in addition they offer numerous practical industrial applications.¹⁻⁵ This has its origin in the mixture of two rather different behaviors for the electrons: the $4f$ -derived states are localized and experience strong electron-electron interaction, contrary to the spd states which are reflecting the delocalized nature of the corresponding electrons. Therefore, it has always been a great challenge to describe the electronic structure of rare-earth systems from a fundamental level.

To be more specific, the light rare-earth elements from praseodymium to samarium share many properties that make theoretical studies of them interesting, and the present work addresses the electronic structure of praseodymium, neodymium, and samarium metals, exploiting a newly developed technique, the first-principles multiband generalization of the "Hubbard-I" approximation⁶ (HIA) extended to open f shells, which allows the combination of an atomic description of the f electrons with a band description of the remaining electrons of the metal. The very radioactive element promethium is excluded from our study, since experimental information is more scarce. Also, cerium is not considered here, since the validity of the atomic limit for the f electrons is less well founded.

A standard electronic structure method, like the density functional theory in the local density approximation (LDA), does not take properly into account the limited spatial extent of the f orbitals and leads to a too large energy dispersion when the $4f$ electrons are treated as bandlike valence electrons. On the other hand, treating the $4f$ states as part of the core but the remaining degrees of freedom by the LDA also experiences some difficulty especially for the early rare-earth

elements,^{7,8} although it seems that this approach describes most of the ground-state properties of the rare earths correctly.² More advanced electronic structure methods have been used as well, like the self-interaction-corrected LDA,⁹ the LDA+ U ,¹⁰ and the orbital polarization,¹¹ leading to various degrees of success^{12,13} concerning the ground-state properties of the rare-earth elements. However, the excited states, as measured, for example, in x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) experiments¹⁴ remain challenging in particular since one clearly observes the appearance of multiplet structures related to the localized nature of the $4f$ electrons. These effects are not captured in the theoretical treatments outlined above, which all resort to the one-electron picture, while multiplet formation is notoriously a many-electron phenomenon. Therefore, previous theories have invoked more approximate models to reproduce the excited-state properties of rare-earths, like parametrized multiplet calculations¹⁵⁻¹⁷ or the single-impurity Anderson¹⁸ model. Such methods permit a qualitative understanding of the physics but are often obscured by the number of parameters one has to adjust *ad hoc* in order to obtain agreement with experiments. Therefore, these approaches in general offer limited predictability.

The HIA approach employed in the present work can be considered somewhat intermediate between pure *ab initio* and model calculations. The open f shell is treated in a simplified model, but is subsequently embedded in a bath of delocalized electrons. Both the sea of conduction electrons and several of the parameters of the model are calculated from first principles in the LDA. The purpose of the present work is to study how well this method applies to the rare-earth elements praseodymium, neodymium, and samarium in their metallic phase. In Sec. II the calculational details of the HIA approach are outlined. Section III presents the calculated spectral functions, which are compared to experimental photoemission and inverse photoemission data. Finally, Sec. IV presents the conclusions of our work.

II. THE HUBBARD-I APPROXIMATION

In this section, we describe the details of the Hubbard-I approximation,^{6,19} which we used to study the excited-state properties of elements with strong electron-electron interaction. The HIA combines the effect of strong electron-electron interaction on a given rare-earth ion with a periodic lattice,¹⁹ enabling band formation. The method has previously been successfully applied to samarium²⁰ and thulium²¹ compounds, and here we provide an interesting example of its capabilities by studying the series of light rare-earth elements.

The central quantity to compare to photoemission spectra is the spectral function $A(\omega)$ of the solid state system:

$$A(\omega) = -\frac{1}{\pi} \text{Im} \sum_{\mathbf{k}} G_{\mathbf{k}}(\omega), \quad (1)$$

where the sum extends over the Brillouin zone (for angle-integrated photoemission). The Green's function is obtained as

$$G_{\mathbf{k}}^{-1}(\omega) = \omega - \Sigma^{at}(\omega) - H_{\mathbf{k}}^{LDA}. \quad (2)$$

Here $H_{\mathbf{k}}^{LDA}$ is the Hamiltonian as given by the LDA,²² i.e., containing the bands of the Kohn-Sham electrons, which move in the effective crystal potential including Hartree and exchange-correlation contributions. In the LDA calculation, the f electrons are treated as itinerant, which leads to narrow f bands near the Fermi level. The LDA calculation is performed using the tight-binding linear muffin-tin orbital method in the atomic sphere approximation.²³ The basis for the valence states is made of $6s$, $6p$, $5d$, and $4f$ orbitals, and the k -point mesh is constructed from a $10 \times 10 \times 4$ grid for Pr and Nd, while a $10 \times 10 \times 10$ grid is used for Sm. $\Sigma^{at}(\omega)$ contains the multiplet effects originating from the strong electron-electron correlations within the f shell. This part is calculated in a model describing only the f shell of a single ion:

$$H^{at} = \frac{1}{2} \sum_{\{m_j\}} U_{m_1 m_2 m_3 m_4} c_{m_1}^\dagger c_{m_2}^\dagger c_{m_3} c_{m_4} + \xi \sum_i \vec{l}_i \cdot \vec{s}_i - \mu \sum_m c_m^\dagger c_m. \quad (3)$$

Here, the index m_j labels the f orbitals (from 1 to 14), and c_m^\dagger and c_m are creation and annihilation operators. The first term in Eq. (3) is the electron-electron interaction, with the matrix element

$$\begin{aligned} U_{m_1 m_2 m_3 m_4} &= \int \int \frac{f_{m_1}^*(\mathbf{r}) f_{m_2}^*(\mathbf{r}') f_{m_3}(\mathbf{r}) f_{m_4}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &= \sum_{\ell} a_{\ell}(m_1, m_3, m_2, m_4) F^{\ell}, \end{aligned} \quad (4)$$

where $f_m(\mathbf{r})$ are the single-particle f orbitals. In the second equality of Eq. (4) the Coulomb integrals are expressed in terms of Slater integrals F^{ℓ} and vector coupling coefficients a_{ℓ} .¹⁹ Hence, the U matrix is in fact determined completely by only four parameters F^{ℓ} , $\ell=0,2,4,6$. We use the radial f waves from the self-consistent LDA calculation to evaluate the Slater integrals.

Since the $4f$ electrons are strongly localized, the spin-orbit coupling plays an important role and is included in the second term in Eq. (3). Here the sum extends over all electrons and ξ is the spin-orbit constant, which is obtained from the self-consistent LDA potential:

$$\xi = \frac{2}{c^2} \int \frac{dV(r)}{dr} |f_m(r)|^2 d\mathbf{r}'. \quad (5)$$

Other relativistic effects are incorporated through our scalar-relativistic implementation of the LDA. The last term in Eq. (3) contains the chemical potential μ and acts to absorb all one-body terms of the Coulomb interaction to avoid double counting, these interactions being already included in $H_{\mathbf{k}}^{LDA}$. In effect, the atomic Hamiltonian in Eq. (3) describes only the two-body part of the f - f interaction, which is the part that determines the multiplet splittings, and which is not included in the LDA.

The atomic Hamiltonian H^{at} is solved by exact diagonalization in the space of all possible Slater determinants for each of the f^n configurations needed in the calculation (typically for the ground-state configuration with n electrons and for the $n \pm 1$ configurations corresponding to excited states). The eigenvalues and eigenvectors, denoted, respectively, E_{γ} and $|\gamma\rangle$, are obtained, and the atomic Green function $G_{mm'}^{at}$ is calculated as

$$G_{mm'}^{at}(\omega) = \sum_{\gamma\delta} g_{\gamma\delta} \frac{\langle \gamma | c_m | \delta \rangle \langle \delta | c_{m'}^\dagger | \gamma \rangle}{\omega + E_{\gamma} - E_{\delta}}, \quad (6)$$

where the weight factor $g_{\gamma\delta}$ specifies the relevance of the $\gamma \leftrightarrow \delta$ transition. At thermal equilibrium,

$$g_{\gamma\delta} = \frac{1}{Z} (e^{-\beta E_{\gamma}} + e^{-\beta E_{\delta}}), \quad (7)$$

where $\beta = 1/k_B T$, and $Z = \sum_{\gamma} e^{-\beta E_{\gamma}}$ is the atomic partition function. In the calculations discussed in the present work, the value of the temperature is chosen to be close to zero, so that only the lowest multiplet state is populated, i.e., either γ or δ must belong to the ground-state multiplet. From G^{at} the atomic self-energy $\Sigma_{mm'}^{at}$ is finally extracted,

$$\Sigma_{mm'}^{at}(\omega) = \omega \delta_{mm'} - (G^{at})_{mm'}^{-1}(\omega), \quad (8)$$

to be inserted in Eq. (2).

The procedure outlined above combines in a unified framework the strong intrashell correlation effects related to the $4f$ electrons and the weaker interaction between spd electrons. Adding Σ^{at} to the LDA Hamiltonian on the right-hand side of Eq. (2) shifts the f weight from the narrow LDA bands into the energy positions corresponding to multiplet excitation energies. The matrix elements in the numerator of Eq. (6) ensure that the proper transition amplitudes, according to atomic selection rules, enter the spectral function. Not included in the description based upon Eq. (1) is the matrix elements between the outgoing photoelectron and the orbital of the left-behind hole. These matrix elements will depend on the angular character of the photohole. However, in the following we will focus on the f part of the spectral function only, and compare to photoemission spectra using photon

TABLE I. Values (in eV) of the calculated parameters used in the multiplet HIA model to compute the spectral function of Pr, Nd, and Sm.

	F^2 (eV)	F^4 (eV)	F^6 (eV)	ξ (eV)
Pr	10.20	6.30	4.50	0.10
Nd	10.92	6.76	4.84	0.12
Sm	11.86	7.35	5.26	0.16

energies chosen so as to enhance the f contribution.

As said, the parameters F^l and ξ are provided by radial integrals of the f partial waves obtained from a self-consistent LDA calculation.^{19,21} However, the first Slater integral F^0 has to be scaled down to account for screening: in the photoemission process, a hole created in the f shell is rapidly screened by the non- f -electrons, effectively reducing the value of the direct Coulomb interaction energy. For the elements studied here a value of $F^0=7$ eV has been used. This value is chosen in rough agreement with the study made by van der Marel and Sawatzky in Ref. 24 concerning the value of F^0 to be used for the entire $4f$ series. These authors derived a linear interpolation formula for F^0 as a function of the atomic number Z , starting from a value of 6.7 eV for $Z=57$ (La), which we have approximated by 7 eV for the early rare earth metals. There is no strict consensus on the appropriate value of F^0 to be used for the rare earths. For example, in Ref. 14, values close to or even below 6 eV are suggested for Pr, Nd, and Sm. As shown below, a constant value of 7 eV leads to very good agreement with experiment. Recent research aims at a fully *ab initio* description of these screening processes, but has as yet not been considered for f materials.²⁵

An important parameter of the present theory is the chemical potential μ in Eq. (3). This has to be adjusted to ensure a proper embedding of the atom in the solid. The value is set by the requirement that the correct atomic configuration f^n is in fact the ground state, and the lowest multiplet corresponding to this configuration is at the same energy as the Fermi level of the solid.

III. RESULTS

As explained in the previous section, the HIA model is dependent upon parameters such as the Slater integrals as well as the spin-orbit constant ξ . The values used here, obtained from LDA calculations are presented in Table I. One notices the slight increase of the values of all parameters through the series, which simply reflects the contraction of the radial part of the $4f$ wave function and the increase of the electron-electron interaction. These parameters are used in Eq. (3) for the respective element.

To begin our study, we consider elemental praseodymium. The crystal structure is the double hexagonal close packed (dhcp),²⁶ with $a=3.6721$ Å and $c=11.832$ Å, and Pr contains two electrons in the f shell. The XPS spectra correspond therefore to transitions from f^2 to f^1 whereas the BIS spectrum is simulated by calculating excitations between f^2 and

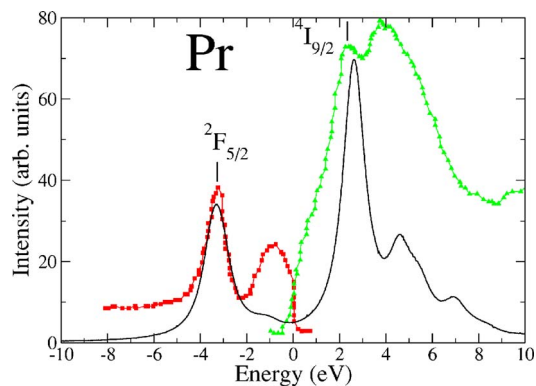


FIG. 1. (Color online) The calculated f contribution to the spectral function of praseodymium at the equilibrium volume computed within the multiplet Hubbard-I method (full line) compared with the XPS (squares) and BIS (triangles) spectra of Ref. 14. The Fermi level is at zero energy.

f^3 configurations. The resulting spectral function obtained within the HIA using the parameters presented in Table I is shown in Fig. 1. The overall agreement appears to be quite good. The structure around -3.5 eV (corresponding to a $^2F_{5/2}$ final state) is well placed in energy. The double structure of the BIS spectrum is also reproduced by the theory; however it is located at approximately 0.5 eV too high energy in comparison with the experimental spectrum. The long tail extending to high energies is also reproduced by the calculations, but the intensity of this feature seems too low in the theory, which could also be an effect of secondary processes in the experiment. One significant feature in the XPS experiment is not reproduced by theory, namely, the peak at ~ 1 eV binding energy. Similar structures are present in all elements studied here, and we return to a discussion of them below.

The next element in our study is neodymium. Like praseodymium, it crystallizes in the dhcp structure but contains one more electron in the f shell. The ground state therefore corresponds to an f^3 configuration (in a $^4I_{9/2}$ multiplet state). Due to the incomplete screening by this extra f electron of the increased nuclear charge, the lattice parameters used for the LDA part of our calculations decrease to $a=3.6583$ Å and $c=11.7966$ Å.²⁶ The excited states here are the f^2 and the f^4 configurations, and the corresponding spectrum obtained with the HIA is presented in Fig. 2.

The agreement between theory and experiment is similar to that found for praseodymium: the states below the Fermi level, corresponding to photoemission into a 3H_4 final state, are accurately described, while the part of the spectrum above the Fermi level has the same qualitative form in theory and in experiment, but the peaks are found at slightly too high energies and have too low intensity in the calculations.

The next element in the lanthanides series is promethium (Pm), which has a radioactively unstable nucleus and therefore has not been studied by XPS or BIS. Hence, we will disregard it in our study and rather consider samarium. For Sm metal, the unit cell is rhombohedral²⁶ (with $a=8.9834$ Å and $\alpha=23^\circ 49.5'$), or can also be viewed as hexagonal, the atoms being placed in the cell according to a

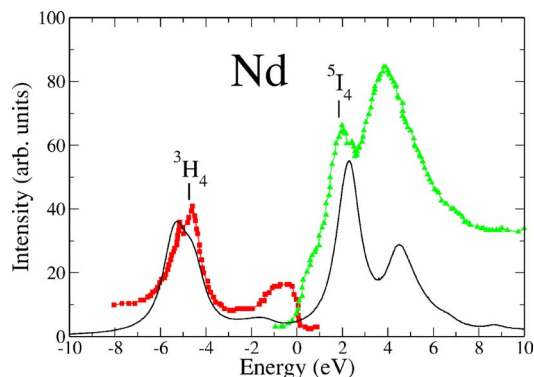


FIG. 2. (Color online) The calculated f contribution to the spectral function of neodymium at the equilibrium volume computed within the multiplet Hubbard-I method (full line) compared with the XPS (squares) and BIS (triangles) spectra of Ref. 14. The Fermi level is at zero energy.

mixture of fcc and hcp positions (in the so-called Sm-type crystal structure).²⁷ The XPS and BIS spectra, presented in Fig. 3, are more complex than the Pr and Nd spectra, due to the larger number of multiplets which can be reached in the final state. The states below the Fermi level, corresponding to $f^5 \rightarrow f^4$ transitions, are made up of four structures corresponding to 5I_4 , 5F , 5G , and 5D final states. The calculations reproduce all of these peaks, although the ones at highest binding energy are found to be located at ~ 0.5 eV too high binding energy. For the positive frequency states, corresponding to $f^5 \rightarrow f^6$ transitions, the agreement is quite satisfactory since the two structures around 1 and 4 eV are well reproduced.

One key feature missing from all our calculations in comparison with experiments is the hump between 0 and -2 eV, seen for Pr, Nd, and Sm. This structure has been interpreted^{28,29} to arise from a $4f$ hole screened by an f electron (corresponding to $f^n \rightarrow f^n$ transitions) merged with the contribution from spd electrons to the photoemission spectrum (which happens to be in the same range of binding energy). This second channel (in opposition to the first $f^n \rightarrow f^{n-1}$ channel corresponding to a screening by a conduction electron) is made possible by the fact that the f electrons are not completely localized⁸ in the light rare-earth series and therefore may contribute to the screening of the hole. Although the present theory is able to reproduce the spd contribution, as can be seen either by plotting directly the s , p , and d spectral functions or by noticing the hump around -1 eV in the spectral function (see Figs. 1–3) due to spd - f hybridization, the resulting structure is obviously too weak compared to the experimental features. Hence we conclude that further theoretical development is needed to account for the screening of the f hole by other f states. The effect is particularly important for praseodymium for which the f electrons are most delocalized among the ones studied here. Also, the f interaction with the conduction bands can be of a more subtle nature than just simple band formation, for ex-

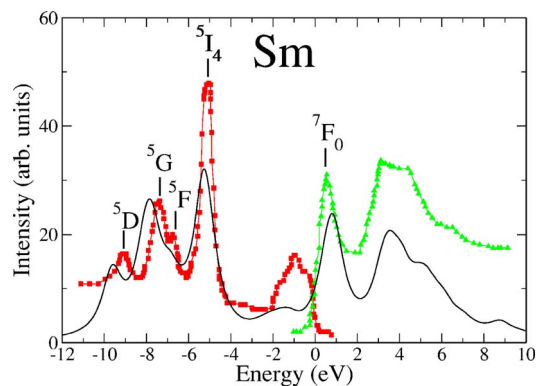


FIG. 3. (Color online) The calculated f contribution to the spectral function of samarium at the equilibrium volume computed within the multiplet Hubbard-I method (full line) compared with the XPS (squares) and BIS (triangles) spectra of Ref. 14. The Fermi level is at zero energy.

ample, correlation effects beyond the Hubbard-I approximation. Finally, it can also not be excluded that surface effects or defects can cause this contribution in the experimental spectra.

IV. CONCLUSION

In summary, we have calculated the XPS and BIS spectral functions of praseodymium, neodymium, and samarium by using the multiplet Hubbard-I approximation. The results have been compared to available experimental data and the agreement is found to be rather good, despite the complexity of the phenomena involved. In particular, the parameters of the model are calculated (except for the first Slater integral) and not adjusted to reproduce experiments, as is often the case to simulate multiplet effects in crystals. An interesting development would be to actually calculate the value of the first Slater integral by taking into account the screening effects from spd electrons, as was done, for example, in Ref. 25. This will bring the present method closer to an almost complete *ab initio* scheme. Minor deviations between the calculated spectral functions and experimental spectra occur at low binding energies and are suggestive of the relevance of f -non- f interaction channels of a character not accounted for in the present theory. Further applications of the HIA could be used to compute the excited-state properties of the mixed-valent SmB_6 and the Kondo insulator YbB_{12} . These systems exhibit spectra rich in detail that have not been calculated so far with the HIA.

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