

## Systematics of 4f electron energies relative to host bands by resonant photoemission of rare earth doped optical materials

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### Abstract

Relative energies of 4f<sup>n</sup> electronic states and crystal band states are important for a fundamental understanding of rare-earth-doped optical materials and a practical understanding of each material's potential performance in specific applications. With this motivation, the 4f<sup>n</sup> ground state binding energies of rare earth ions have been studied in the gallium garnets using resonant photoemission spectroscopy and compared with the aluminum and iron garnets. The 4d to 4f photoemission resonance was used to separate and identify the 4f<sup>n</sup> and valence band components of the spectra, and theoretical 4f photoemission spectra were fit to experimental results to accurately determine electron binding energies. A two-parameter empirical model was used to successfully describe the relative energies of the 4f<sup>n</sup> ground states in these materials. The success of this empirical model indicates that measurements on as few as two different rare earth ions in a host are sufficient to predict the energies of all rare earth ions in that host. This analysis shows that systematic shifts in the relative energies of 4f<sup>n</sup> states and crystal band states between different garnets arise entirely from shifts of the band states, while each rare earth ion maintains the same absolute binding energy for all garnets studied. These results suggest that further studies of additional host compounds using both photoemission and optical spectroscopy will rapidly lead to a broader picture of the host crystal's effect on 4f electron binding energies.

**Keywords:** 4f binding energies, resonant photoemission, rare earth garnets

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## 1. Introduction

Interactions between the localized  $4f^n$  electronic states of rare earth ions and the de-localized band states of the crystal lattice can strongly affect the optical properties of technologically important rare-earth-doped materials. In contrast to the well-developed understanding of the electronic structure of the  $4f^n$  states, relatively little is known about the relationships between these states and the electronic states of the crystal. In recent years, the body of knowledge on this topic has steadily grown due to the strong interest in developing ultraviolet lasers and more efficient phosphor and scintillator materials. The performance of rare-earth-activated optical materials in these applications can be enhanced, reduced, or even entirely inhibited by energy exchange and charge transfer processes between the rare earth ions and the host crystal [1]. This has made it increasingly important that the systematic trends and behavior of rare earth energies relative to crystal band states be explored and characterized.

Several experimental techniques have been used to explore the relationships between the  $4f^n$  states and the host electronic states, including vacuum-ultraviolet and excited-state absorption, photoconductivity, and photoelectron spectroscopy. Absorption spectroscopy provides one of the most direct methods for measuring interactions between the rare earth ions and the host crystal and also allows the study of exciton and other localized charge transfer processes that do not directly involve the host band states. However, interpretation is often difficult because of uncertainty in the assignment of initial and final states for observed transitions. Photoconductivity measurements can unambiguously assign the final state of a transition as involving either an electron in the conduction band or a hole in the valence band, although the presence of electron acceptor or donor defects in the lattice can also create ambiguity regarding the origin of observed signals. Photoelectron spectroscopy, or photoemission, measures the energies of occupied electronic states relative to a common energy reference, providing information that can complement optical methods. Combined with the methods of inverse photoemission or bremsstrahlung isochromat spectroscopy, which measure the energies of unoccupied electronic states, photoemission can be used to provide a clear picture of the electronic states in a material. The primary difficulties in applying photoemission to the study of optical materials are the requirement of ion concentrations of at least a few atomic percent and complications arising from electrical charging due to the highly insulating nature of the materials being studied. However, in the garnets it has been shown that energies determined from measurements on highly concentrated samples accurately reflect the energies in low-concentration samples and that sample charging problems can be overcome by combinations of experimental techniques and data analysis [2].

This paper briefly reviews the empirical model previously applied in the analysis of  $4f$  electron binding energies in the aluminum garnets and then presents the analysis of new results obtained from resonant photoemission of rare earth gallium garnets (REGG).

## 2. Systematics of the $4f$ binding energies

A variety of theoretical models have been used to predict and explain the  $4f$  electron binding energies observed in materials ranging from rare-earth-doped insulators

to the elemental metals. One model well suited to rare-earth-doped insulators is the electrostatic point charge model [3,4]. In this model, we view the free-ion binding energies of the 4f electrons—which correspond to the free-ion ionization potentials of the rare earth ions—as being shifted through electrostatic interactions with the host lattice. The largest contribution arises from the large negative electrostatic potential, or Madelung potential, at the rare earth's lattice site. This lattice potential raises the energies of the rare earth's electrons, resulting in a corresponding decrease in their binding energies. Other significant contributions must also be considered, such as the lattice polarizability, inter-atomic repulsive energies, and van der Waal's energies [3]. Due to the chemical similarity of the rare earth ions and the non-bonding character of the 4f electrons, the net shift in binding energy is similar for all rare earth ions in a particular material. Deviations from this constant shift are viewed as resulting from changes in the ionic radius and the corresponding changes in bond lengths [4]. Although these effects can be calculated for highly ionic materials, in practice the information that is needed is only known for special cases where the precise changes in bond lengths and the lattice relaxation effects can be accurately estimated. Recently it has been demonstrated that an empirical form of this model can be successfully applied to the description and extrapolation of measured 4f binding energies in optical materials [2]. This empirical model characterizes the effect of the host lattice on 4f electron binding energies with two empirical parameters, where one parameter describes a constant shift experienced by all rare earth ions and the second parameter describes a smaller dependence on the rare earth's ionic radius. These parameters may be determined from measurements on two different rare earth ions, or, in certain cases, from measurements on the host lattice itself [2].

Another advantage of an empirical treatment is that it may be extended to covalently bonded materials where the ionic picture fails. This is understood by considering the shift in binding energy experienced by 4f electrons in a semiconducting or metallic material. In this case, we again view the free-ion values as being shifted from interactions with the charge distribution inside of the host lattice, with the largest contribution arising from the average Coulomb interaction between the 4f electrons, the charge distributions of the bonding electrons, and the screened nuclear charges of the ligand atoms. Since the lattice may contain mobile charges, particularly in the metals, we must also consider a variety of relaxation effects including screening provided by free electronic charges as well as the dielectric polarizability. The resulting shift is related to the chemical cohesive energy of the lattice site and is similar for all rare earth ions due to their similar chemical properties [5]. However, both the cohesive energy and the screening properties are affected by the increase in effective nuclear charge across the rare earth series that results from the imperfect screening provided by the additional 4f electrons [5]. Thus, we obtain a model in which the binding energies are shifted by a constant value and a smaller effect that varies with the effective nuclear charge. Since the change in effective nuclear charge is directly correlated to the rare earth ion's ionic radius, the empirical two-parameter model for the effect of the host lattice successfully describes the systematic variation of 4f electron binding energies in semiconductors and metals as well as insulators.

As an example of this model's success in describing 4f electron binding energies in covalent solids, Fig. 1 shows the application of this model to the elemental rare earth

metals. The data in Fig. 1 are the 4f electron binding energies relative to the metal's Fermi energy measured by Lang, Baer, and Cox [6]. The number of 4f electrons can be unambiguously determined from the structure of the 4f photoemission spectrum, which provides a unique 'fingerprint' of the electron configuration. These photoemission spectra show that rare earth atoms in the metals have the same number of 4f electrons as trivalent ions, except for Eu and Yb, which have a divalent 4f configuration. The 4f binding energy of Ce was not resolved; however, the range of energies in which it lies is indicated on the graph. The solid line is our fit of the model to the binding energies in the trivalent metals, and the error bars indicate the uncertainty in the values of the free-ion ionization potentials used in the model. This model gives remarkable agreement with the observed binding energies. It is interesting that Sm metal agrees well with the model though its crystal structure is different than the other trivalent metals, indicating that the difference in crystal structure has a small effect on the 4f electrons in this case or possibly that both the Fermi energy and 4f binding energy experience equal shifts of the same sign.

### 3. The 4f photoemission spectra

The 4f electron photoemission often overlaps photoemission from the host valence band, making interpretation of features and measurement of energies difficult. Resonant photoemission removes this difficulty and allows the 4f component of the spectrum to be unambiguously identified and separated from the host photoemission. This technique relies on the enhancement in 4f photoemission that occurs when employing photon energies resonant with the  $4d^{10}4f^n$  to  $4d^94f^{n+1}$  transition of the rare earth ion [7]. By comparing spectra taken on- and off-resonance, the large change in 4f photoemission cross-section allows the 4f component to be extracted. Since the energy of the resonance is specific to both the ion and its valence, this technique also provides the advantage of being able to separate and identify different rare earth ions or valence states simultaneously present in a single material.

The 4f electron photoemission exhibits structure originating from the excited states of the  $4f^{n-1}$  electronic configuration that results from the removal of an electron during the photoemission process [6,7]. Since the 4f binding energy is the minimum energy required to remove a 4f electron, it corresponds to the component of this photoemission 'final state' structure with the smallest binding energy. To accurately determine the 4f electron binding energies from the observed 4f photoemission, we fit theoretical 4f photoemission spectra to the measured spectra for each sample studied using the method described in Ref. [2].

### 4. Materials and apparatus

This work was carried out on the Iowa State/Montana State ERG/Seya beam line at the University of Wisconsin-Madison Synchrotron Radiation Center using the apparatus and techniques described in Ref. [2]. The absolute binding energy scale was established by placing the C 1s photoemission peak arising from adventitious carbon contamination at a binding energy of 290 eV relative to the vacuum level.

The single crystal EuGG, TbGG, ErGG, and YbGG samples studied in this work were grown from flux by S. Mroczkowski at the Department of Applied Physics, Yale University.

## 5. Results and Analysis

To locate the energies of the 4f electrons relative to the host band states, the precise energy of the valence band must be determined for each sample. The valence bands of the gallium garnets and aluminum garnets have very similar density of states [8], and the technique previously used by Thiel, *et. al.* [2] for yttrium aluminum garnet was used to locate the valence band maximum (VBM), which is the highest energy valence band state. A value of 8.3 eV was obtained for the binding energy of the VBM by comparing the observed spectrum to the theoretical photoemission cross-section as estimated using the atom-resolved partial density of states [8]. No shift in the VBM was observed between samples to within the experimental accuracy of several hundred meV. The VBM is significantly shifted to lower binding energy compared to the value of 8.7 eV measured in yttrium aluminum garnet. A shift is expected since the gallium garnets have a band gap of ~5.5 eV, while the aluminum garnets have a larger band gap of 6.5 eV.

An example photoemission spectrum for EuGG is shown in Fig. 2 (a). To extract the 4f contributions to the photoemission, spectra were taken using photon energies of 137 eV, 139 eV, and 144 eV. By taking the difference of the spectra at 144 eV and 139 eV, the Eu 4f electron spectrum can be extracted as shown in Fig. 2 (b). The calculated contributions to the photoemission cross-section due to final state structure are shown as vertical lines and the dotted line is the fit to the observed spectrum, indicating a 4f electron binding energy of 11.9 eV, or 3.6 eV below the VBM.

A feature unique to EuGG was the presence of a weaker second resonance attributed to the presence of divalent Eu at the surface of the crystal. Sm, Eu, Tm, and Yb are known to sometimes form divalent surface layers that can be clearly distinguished from the trivalent ions in the bulk [5]. By comparing spectra taken at 139 eV and 137 eV, the divalent component of the spectrum was extracted as shown in Fig. 2 (c). The corresponding theoretical final state structure and fit are also shown, giving a binding energy of 6.2 eV. The lower photon energy of the photoemission resonance and the binding energy difference between the two components are both consistent with this second feature arising from a divalent surface component.

Once the 4f components of the spectrum are obtained, they may be subtracted out of the photoemission spectrum at 137 eV to obtain the photoemission due to the host, as shown in Fig. 2 (d). The position of the VBM at 8.3 eV is indicated by the vertical line.

By repeating this process for TbGG, ErGG, and YbGG, we obtain 4f binding energies of 7.8 eV, 10.9 eV, and 11.6 eV, respectively. The binding energies relative to the VBM are plotted in Fig. 3. The model for the binding energies relative to the VBM is given by  $E_{4f} = I - E_L + \alpha_R(R - R_0) - E_{VBM}$ , where  $E_{4f}$  is the 4f binding energy relative to the VBM,  $I$  is the free-ion ionization potential,  $E_L$  is the uniform shift experienced by the rare earth ions,  $\alpha_R$  is the binding energy shift per unit change in ionic radius,  $R$  and  $R_0$  are the effective ionic radii of the trivalent rare earth ion and the ionic radius reference (the ionic radius of yttrium,  $R_0 = 1.019 \text{ \AA}$ , is used to be consistent with the earlier work on yttrium

aluminum garnet) [9], and  $E_{\text{VBM}}$  is the binding energy of the valence band maximum ( $E_{\text{VBM}} = 8.3$  eV). Fitting this model to the observed binding energies in the gallium garnets gives values of  $E_{\text{L}} = 31.65$  eV and  $\alpha_{\text{R}} = 9.2$  eV/Å for the two empirical parameters. The fit of the model is shown in Fig. 3 as the solid line and the error bars represent the uncertainty in the known values of the free-ion ionization potentials used in the model. Note that the relative energy of the bottom of the conduction band for the gallium garnets would lie at about -5.5 eV in Fig. 3. The fit of the binding energies in the aluminum garnets from Ref. [2] is also shown for comparison as the dotted line in Fig. 3.

If we compare the values of the empirical parameters for the gallium garnets to the values of  $E_{\text{L}} = 31.6$  eV and  $\alpha_{\text{R}} = 8.3$  eV/Å measured in the aluminum garnets [2], we see that they are essentially identical. The difference in the  $\alpha_{\text{R}}$  values only represents a relative binding energy shift of  $\sim 70$  meV from Yb to Eu, which is within the experimental accuracy of several hundred meV. This shows that the systematic shift in relative energies of the 4f electrons and the host valence band is entirely due to the shift in the gallium garnet valence band, with the 4f electrons having the same absolute binding energies in the gallium and aluminum garnets.

We may also compare these results to the binding energy of the 4f electrons in Yb iron garnet, which has been measured using x-ray photoelectron spectroscopy [10]. These measurements show that the 4f electron binding energy is 11.5 eV and the VBM is at  $\sim 8$  eV. The absolute binding energy of the Yb 4f electrons is essentially the same as for the other garnets while the VBM is shifted to lower binding energy as expected from the smaller band gap of the iron garnets.

In summary, we have used resonant photoemission to study 4f electron binding energies in the garnets and have found that the results are well described by a two-parameter model for the effect of the host lattice. A systematic shift in the relative energies of the 4f electrons and the valence band is observed in the gallium garnets when compared to the results of measurements on the aluminum garnets. This shift was shown to originate entirely from a shift in the valence band while the measured 4f electron binding energies maintained the same values for all the materials studied.

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## Figures

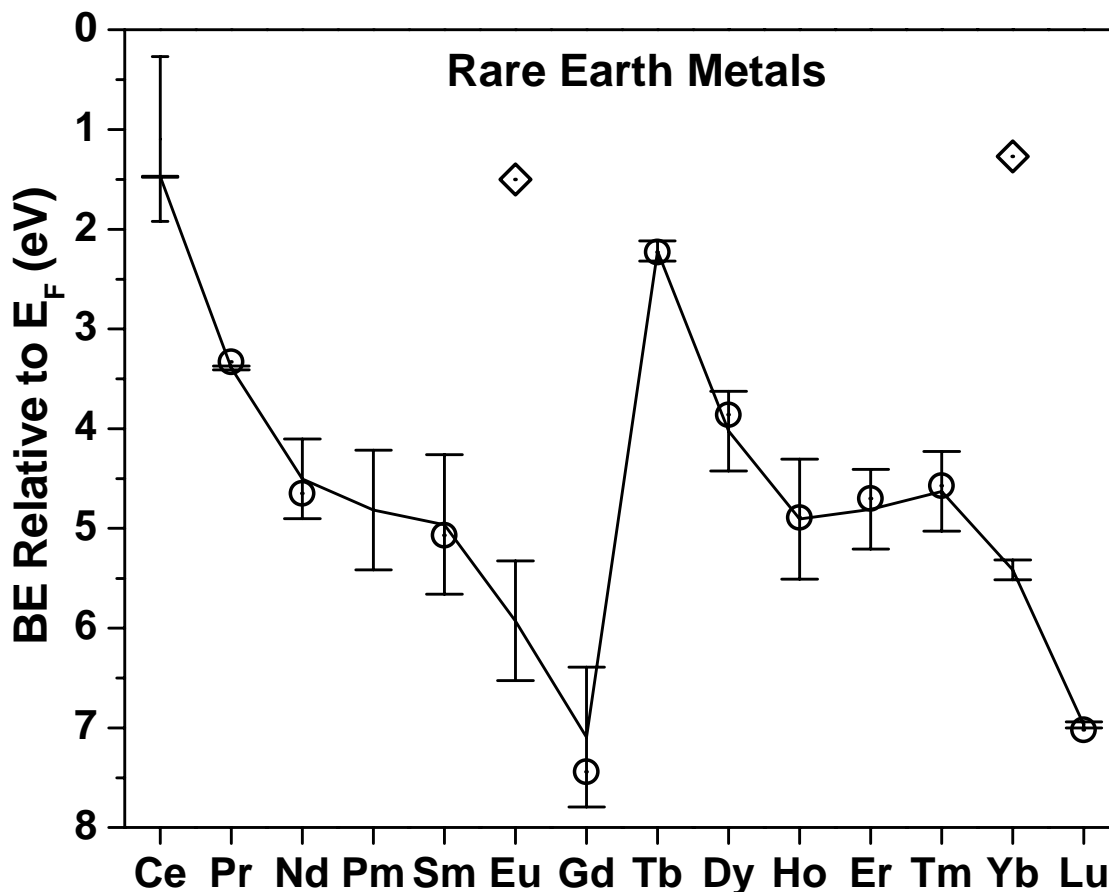


Fig. 1. Systematic behavior of 4f binding energies in rare earth metals. Circles and diamonds represent measured binding energies of 4f electrons relative to the Fermi energy ( $E_F$ ) from Ref. [6]; following the usual convention, states with negative binding energies have absolute energies greater than  $E_F$  while positive binding energies lie below  $E_F$ . The range in which Ce lies is represented by a vertical bar. Circles represent metals with the same number of 4f electrons as trivalent ions; metals with the same number of 4f electrons as divalent ions are represented by diamonds. The solid line is the fit of the model to the measured binding energies (circles), and the error bars represent uncertainty in the free-ion ionization potentials.

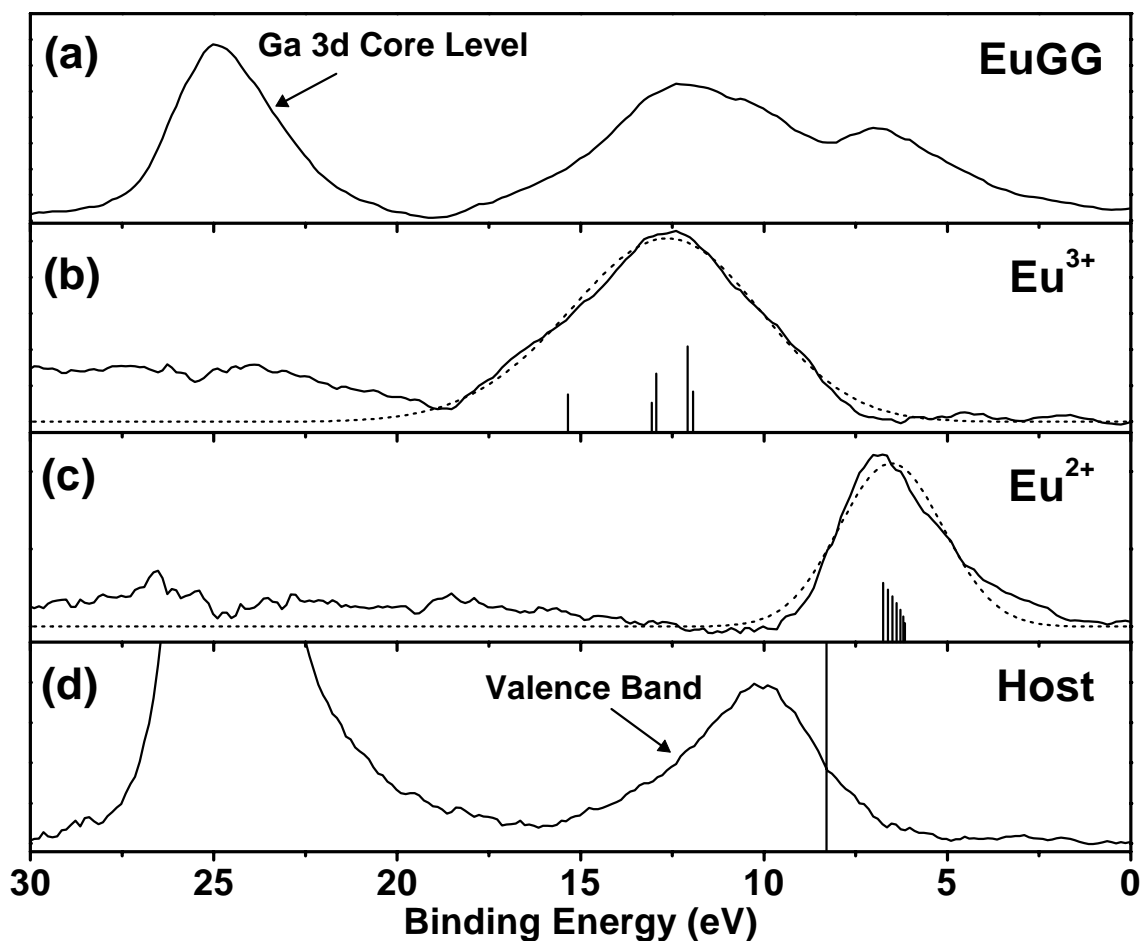


Fig. 2. Extracted  $4f^n$  photoemission spectra for EuGG. a) Photoemission spectrum taken with a photon energy of  $h\nu = 144$  eV. b)  $\text{Eu}^{3+}$  4f photoemission spectrum obtained from difference of spectra at  $h\nu = 144$  eV and  $h\nu = 139$  eV. c)  $\text{Eu}^{2+}$  4f spectrum obtained from difference of spectra at  $h\nu = 139$  eV and  $h\nu = 137$  eV. In (b) and (c), vertical lines represent underlying photoemission final state structure and dotted lines are fits to the observed spectrum. d) Photoemission spectrum with the 4f components in (b) and (c) removed. The estimated VBM energy is shown as a vertical line.

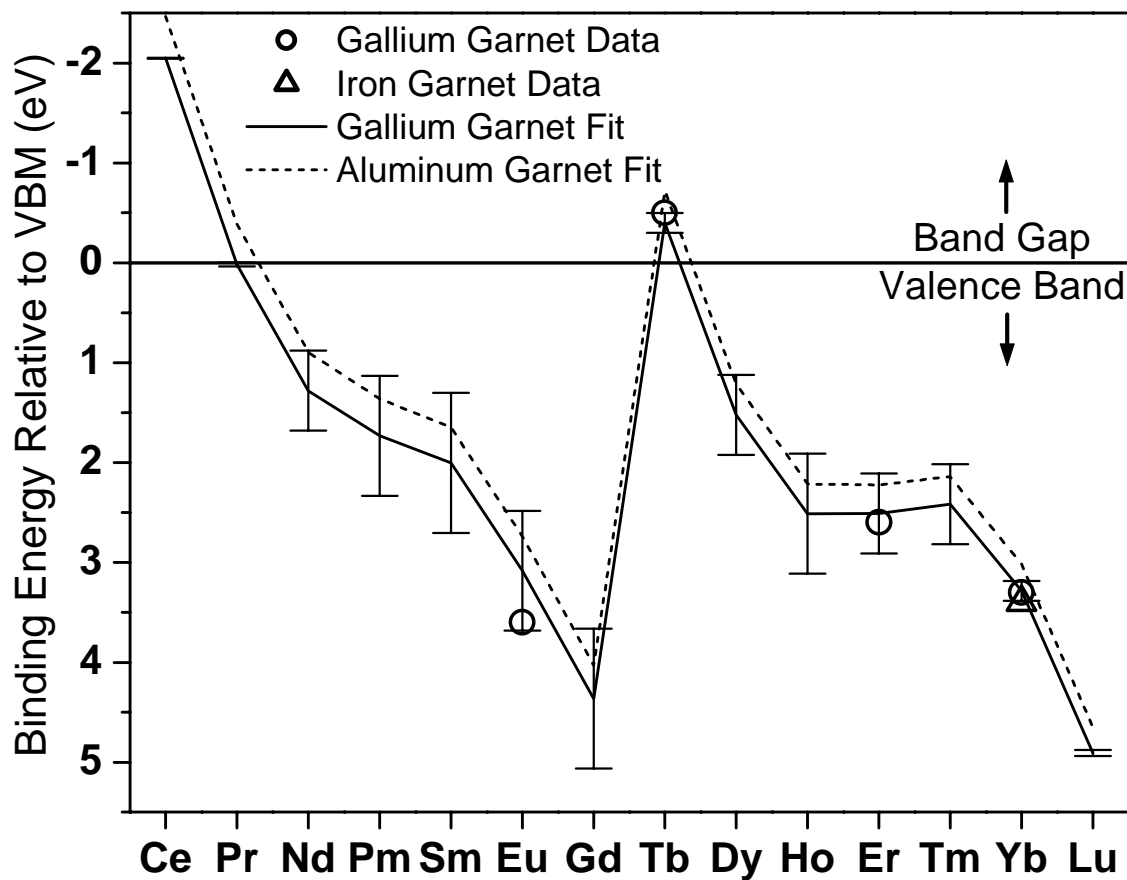


Fig. 3. Systematic behavior of 4f binding energies relative to the VBM in garnets. Circles represent measured binding energies relative to the VBM (at 8.3 eV) for 4f electrons in gallium garnets; negative binding energies are within the band gap and positive binding energies are below the VBM. The solid line is the fit of the model to our measured energies and error bars represent the uncertainty in the values of the free-ion ionization potentials. The dotted line is the fit of the model to 4f binding energies in the aluminum garnets from Ref. [2]. The triangle represents the measured 4f binding energy in Yb iron garnet from Ref. [9].