Exchange Splitting in the 4*f* Photoelectron Spectra of the Rare Earths

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Splitting observed in the x-ray photoelectron spectra of rare-earth ions with more than half-filled 4*f* shells is shown to arise from the exchange-energy difference between final 4*f* states.

We have identified structure in the 4*f* photoelectron spectra of rare-earth (RE) trifluorides which arises from the difference in energy between spin-up and spin-down electrons in the final state of the ion left behind in the photoemission process. This ion is isoelectronic with the trivalent ion of the next lower Z. Existing optical data on the $Z-1$ ion can thus be used to interpret the observed spectra.

The data were obtained on RE trifluorides using a Varian model IEE 15 photoelectron spectrometer. Both Mg and Al $K\alpha$ radiation were used. Samples were prepared from freshly crushed crystalline material, which were mounted on double-sided Scotch tape. The F(1*s*) and F(2*s*) lines indicate that charging effects differ by only a few tenths of an electron volt from sample to sample. The peak of the F(2*s*) line was used as a reference level to remove this scatter from the data, but no attempt has been made to remove the charging effect itself which may amount to ≈ 3 eV. The F(1*s*) line was used to determine the energy-loss structure associated with the photoelectron lines. The major energy-loss line was found to be at ≈ 16 eV and therefore does not interfere with the measurements reported here.

Examples of the photoelectron spectra obtained for electron binding energies from 0 to 20 eV are shown in Fig. 1. The spectrum of PrF_3 shows that the 4*f* electrons initially lie well above the valence band (VB) which is composed of F(2*p*) orbitals hybridized with RE 5*d* and 6*s* wave functions. In GdF_3, with a half-filled shell, the 4*f* electrons coincide in energy with the VB.[1] In TbF_3 a new line appears 5.4 eV above the 4*f* line. It may be thought of as representing the eighth 4*f* electron. (A more rigorous interpretation is

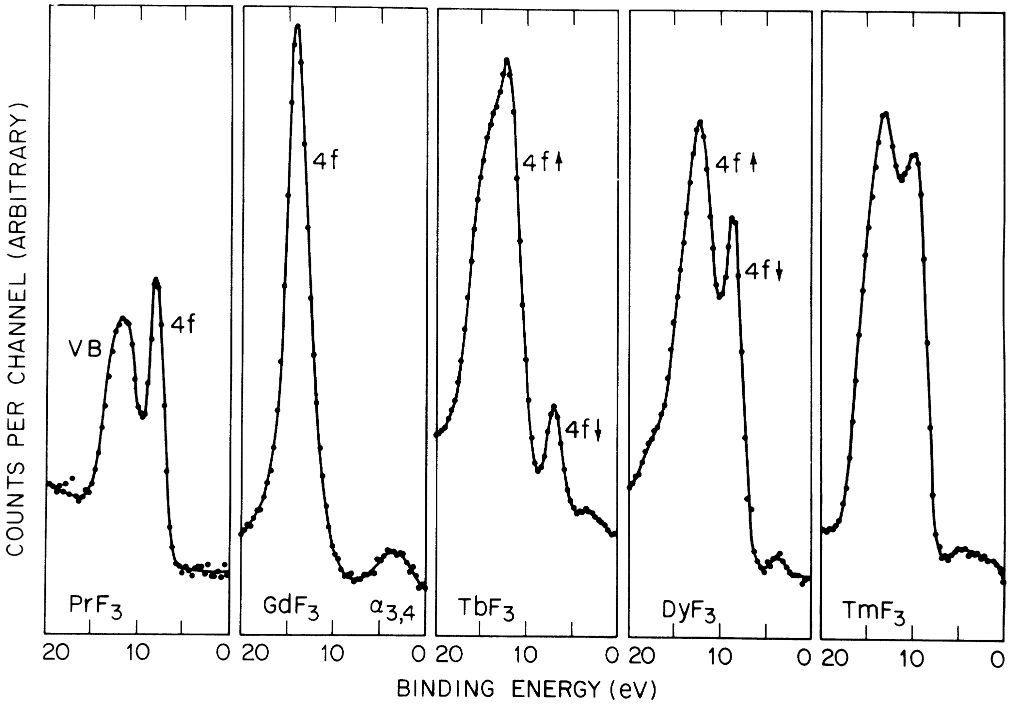

FIG. 1. X-ray photoelectron spectra of the valence and 4*f* electrons of trivalent Pr, Gd, Tb, Dy, and Tm ions in the fluorides. The binding-energy scale has not been corrected for charging effects.

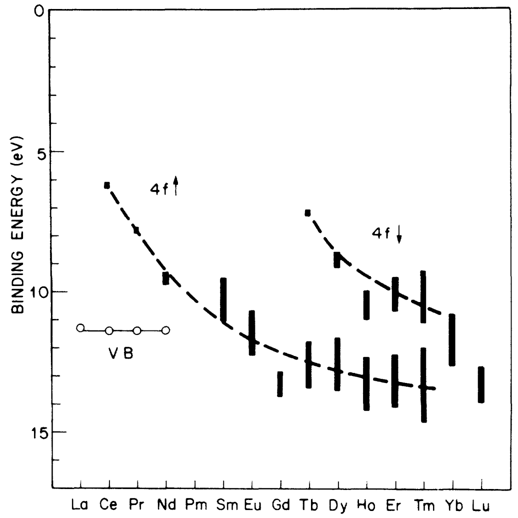

FIG. 2. Systematics of the binding energy of the $4f$ electrons in rare-earth trifluorides. The bars indicate the widths of the observed $4f$ lines. The binding-energy scale has not been corrected for charging effects.

given below.) The remaining data show how this part of the $4f$ structure grows and moves toward the main $4f$ line as the $4f$ shell is filled. It is worth noting that the "satellite" in this case lies at smaller binding energy than the main line. This immediately rules out various other mechanisms known to generate satellites, such as configuration interaction[2] and energy loss.

Results for the complete $4f$ series are summarized in Fig. 2. It is interesting to note the similarity in the behavior of the binding energy with increasing Z in the first and second halves of the $4f$ shell. The approximate location of the VB is also indicated for those compounds where it was clearly resolved. The bars indicate the width at half-height of the components of the $4f$ spectrum after correction for instrumental resolution. The $4f^1$ spectrum was not noticeably broadened. The widths of the Yb and Lu spectra correspond well to the known but unresolved spin-orbit splitting.[3,4]

The new line which appears in the terbium spectrum is best understood in terms of the final states of the photoemission process. The ground-state configuration of Tb^{3+} may be written $(4f{\uparrow})^7$-$(4f{\downarrow})^1\,{}^7F_6$. The final states after removal of one electron then are $(4f{\uparrow})^7\,{}^8S$ and $(4f{\uparrow})^6(4f{\downarrow})^1$. The former can be obtained in only one way, the latter in seven. The corresponding 1:7 intensity ratio is close to the one found. More interesting, however, is the observation that these two configurations describe the ground state and the first group of excited states of Gd^{3+}, whose energy separation is known. That is to say, the final states resulting from the $4f$ photoionization of Tb^{3+} are isoelectronic with those of Gd^{3+}. The known optical excited states of Gd include,[5] in order of increasing energy, only ${}^6P$, ${}^6I$, and ${}^6D$ whereas a large number of other sextet states are accessible in the photoemission process. The known states fall 32 000 to 41 000 cm^{-1} above the ground state for all L and J, which indicates that most of the excitation energy is required to turn over the spin, i.e., it represents the exchange energy with the remaining $4f$ electrons. The additional states accessible in photoemission presumably lie above those known from optical excitation. The measured energy of the satellite, 5.4 eV, is somewhat larger than that of the known optical levels, 4.0 to 5.0 eV. This difference has the expected sign since the energies in Tb^{4+} should be somewhat greater than those in isoelectronic Gd^{3+}. It is worth noting that the satellite corresponds to the unique ${}^8S$ ground-state configuration in the Tb^{4+} $4f^7$ final state and is therefore narrow, while the main line corresponds to the excited states and is broad.

The method of analysis used above can be readily extended to the other cases where this splitting is seen. The optical data[5] clearly indicate that the splitting decreases with increasing $4f$ population. They also show that the satellite line should broaden because there is now a multiplet of J states (or L and J states) for removal of either a spin-up or a spin-down electron. These conclusions are in good agreement with the experimental observations.

The interpretation of the splitting as an exchange effect is most compelling just beyond the half-filled shell, i.e., in Tb, Dy, and Ho where the corresponding optical states are well separated. For Er, Tm, and Yb these states overlap so that a simple identification of the components of the $4f$ spectrum with spin-up and spin-down electrons is no longer possible.

It is interesting to compare the results obtained for RE ions in insulating salts with those reported in the RE metals[6] themselves. In Dy and Er the spectra of the metals show satellites in the same position as the fluorides. This may be taken as an indication that the $4f$ wavefunctions are similarly localized in both cases. On the other hand the appearance of satellites in metallic Nd and Sm where none are seen or expected in the insulator indicates that this structure may contain contributions from conduction electrons.

We are indebted to D. N. E. Buchanan for assistance with the measurements.

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[1] In divalent fluorides of Sm, Eu, and Yb, the $4f$ level lies 6–7 eV above the position reported here for the trivalent compounds. See also D. E. Eastman, F. Holtzberg, and S. Methfessel, Phys. Rev. Lett. 23, 226 (1969).

[2] G. K. Wertheim and A. Rosencwaig, Phys. Rev. Lett. 26, 1179 (1971), and references cited therein.

[3] See, for example, W. Low, *Paramagnetic Resonance in Solids* (Academic, New York, 1960), p. 124.

[4] S. B. M. Hagström, P. O. Hedén, and H. Löfgren, Solid State Commun. 8, 1245 (1970).

[5] G. H. Dieke, *Spectra and Energy Levels of Rare-Earth Ions in Crystals* (Interscience, New York, 1968), 2nd ed., pp. 142, 250.

[6] P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Rev. Lett. 26, 432 (1971).

Onsager Phase Factor in Cadmium

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Precise de Haas–van Alphen phase measurements for the lens orbit in Cd with the magnetic field in the basal plane show that the Onsager phase factor γ for this orbit is $\frac{1}{2}$ and not $\frac{3}{4}$ as predicted recently by Hosack and Taylor. A spin-splitting zero is observed in the $(10\overline{1}0)$ plane, giving a value for $g \approx 1.6$.

Hosack and Taylor (HT) have recently published[1] calculations on energy levels of Bloch electrons in a magnetic field. A major conclusion of this paper is that for the "lens" orbit in hexagonal metals, with the magnetic field in the basal plane, the undetermined phase factor γ in the Onsager[2] relationship has the value $\frac{3}{4}$ rather than the free-electron value of $\frac{1}{2}$.

We have recently developed a technique[3,4] whereby the phase/field relationship of de Haas-van Alphen (dHvA) oscillations may be defined with very high precision. Under optimum conditions the phase can be measured to better than 0.01 cycle, and the field determined with a relative precision approaching 1 in 10^6. We have used this technique to test HT's prediction for the lens orbit in Cd. For this particular case we expect to be able to define the dHvA phase factor to a few hundredths of a cycle.

According to the dHvA data of Grassie[5] and the cyclotron resonance data of Galt *et al.*,[6] the lens orbit in Cd has a minimum frequency $\sim 6.25 \times 10^7$ G with the field in the basal plane, and the cyclotron mass at this point is $\sim 0.52 m_0$. Grassie explains his relatively strong second-harmonic signals on the basis of the product gm^*/m_0 being close to unity (the spin-splitting zero condition for the fundamental) but makes no estimate of g. It is important for the present study to know whether gm^*/m_0 is in fact greater or less than 1 since there is an ambiguity of $\frac{1}{2}$ in the phase according to the sign of the spin-splitting factor $\cos(\pi p g m^*/2m_0)$, where p is the harmonic number.

In our experiments we measure the second derivative of magnetization. If we consider the oscillatory part of the signal to be

$$d^2m/dH^2 \propto \cos[2\pi(F/H + \varphi)],$$

then $\varphi = \frac{1}{2} - p\gamma \mp \frac{1}{8} \pm \frac{1}{4}$; see, for example, Shoenberg.[7] We see that φ includes γ, the phase factor; p, the harmonic number; $\mp\frac{1}{8}$, according as the extremal area is a maximum or minimum; and $\pm\frac{1}{4}$, according as the spin-splitting factor is positive or negative. For the case of the lens in Cd, where the cross section is a maximum, where γ may be $\frac{1}{2}$ (free electron) or $\frac{3}{4}$ (HT), and where gm^*/m_0 is close to 1, we may tabulate the possible values of φ for the fundamental and second harmonic as shown in Table I.

Using the technique referred to above, we studied dHvA oscillations from the lens orbit in a sample of Cd with the magnetic field aligned to within $\sim 1°$ of the $\langle 10\overline{1}0 \rangle$ axis. The value of φ for the fundamental was obtained experimentally by extrapolating to $1/H = 0$ dHvA phases measured over a field range of 17–48 kG. The phase of second-harmonic signals were extracted by Fourier analysis over the range 36–48 kG, and the corresponding value of φ was derived by reference to the precise dHvA frequency obtained from the slope of the fit to the fundamental phases. We