

commences. However, an important difference exists between the two systems in that the ordering of CuNi as a function of (T/T_0) is unaltered by the annealing treatment. We may hypothesize that at the concentrations used, i. e., $(\text{Ni})/(\text{Cu}) \approx 1$, the low-temperature anneal produces a departure from randomness in the "long-range" compositional order which alters the strength of the exchange interaction but leaves the exchange forces long range in character in all cases.

Most of the previous investigations of clustering

have been on Ni-Cu and have employed classical magnetization measurements. The large paramagnetic moments, e. g., $8-10 \times 10^{-6} \mu_B$, are generally interpreted as magnetically coupled clusters of Ni. Magnetization measurements on Au-Fe combined with heat treating would be of value. At present, it can be said only that Mössbauer experiments below the ordering temperature suggest the presence of iron-rich magnetically coupled clusters, with a continuum of magnetic ordering temperatures.

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Multiplet Splitting of the 4s and 5s Electrons of the Rare Earths

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The multiplet splitting of 4s and 5s electrons of trivalent rare-earth ions has been measured by photoelectron spectroscopy. This splitting represents the energy difference between the s-electron spin-up and spin-down final states.

Photoelectron lines arising from the s shells of rare-earth (RE) ions should be split by the interaction of the s shell with the partly filled 4f shell. Such splitting, called the multiplet splitting, has been observed previously¹ in the 3d elements. We report here the first observation of this splitting in the rare earths, and measurements of its magnitude for the 4s and 5s shells of a number of these elements. A simple approach is used to explain the major part of the Z dependence of the splitting.

The x-ray photoelectron² measurements were carried out with a Varian IEE-15 spectrometer, using Mg K α radiation. The instrumental resolution yielded a linewidth of 1.65 eV on the Au(4f) or graphite C(1s) lines. The samples, all RE trifluorides, were in the form of freshly crushed crystalline powders mounted with double-sided adhesive tape. Since we are here concerned only

with line splitting, no attempt was made to determine the magnitude of the charging effect. However, the fact that lines of instrumental width were obtained for the F(1s) electrons in these materials indicates that charging effects do not contribute to the linewidths.

A major concern in all x-ray photoelectron spectra (XPS) measurements is the condition of the 10-30-Å surface layer which is actually under observation. Many materials, especially metals, are covered by an oxide layer of almost this thickness after exposure to air. Other materials, e. g., (RE)₂O₃, adsorb large quantities of water. Fortunately the XPS technique makes it possible to determine the chemical composition of the layer under investigation. In the samples reported here the O(1s) line, indicative of adsorbed H₂O, or partial conversion to oxide, hydroxide, or carbon-

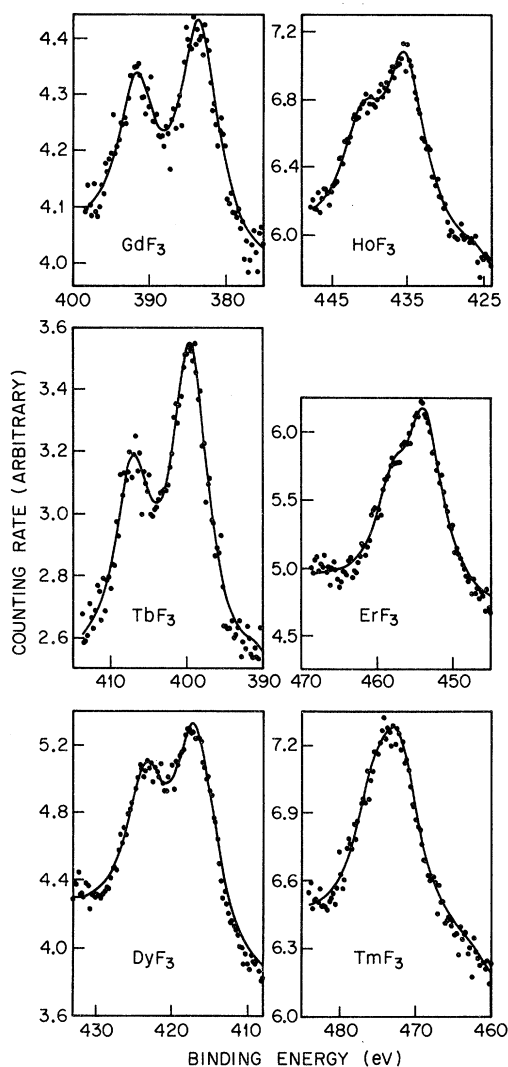


FIG. 1. X-ray photoelectron spectra of the 4s electrons of the trivalent rare-earth ion in the compounds indicated. The binding-energy scale has not been corrected for charging effects.

ate, was never more than one tenth of the $F(1s)$ intensity even though the photoelectric absorption coefficient for O and F is approximately equal for Mg $K\alpha$ radiation. We are therefore confident that the data correspond to the fluoride compound.

Examples of the data obtained are shown in Figs. 1 and 2 for the 4s and 5s electrons, respectively. The binding energy scales have *not* been corrected for charging effects. The data were analyzed using a nonlinear least-squares computer program in which the background was approximated by a sloping straight line and in which each Lorentzian line is accompanied by its $K\alpha_{3,4}$ satellite³ of fixed relative area and position. The widths of the two lines were constrained to be the same. The free param-

eters were the two line positions and amplitudes, the linewidth and the background position and slope. The results of this analysis are given in Table I.

The widths of the 4s lines were all found to be close to 6 eV, i. e., well above the instrumental width. This, together with the Lorentzian shape, indicates that they are lifetime widths due mainly to the Coster-Kronig decay mechanism. The width of the 5s lines increased strongly with increasing Z . This, together with the fact that they are superposed on the energy-loss tail of the RE($5p$) electrons, makes them more difficult to analyze, especially in the second half of the rare-earth series.

A simple model of the anticipated line structure can be made on the assumption that the exchange interaction of the 4s or 5s hole in the final state is larger than the L - S coupling energy of the 4f electrons. Then the spin, $s = \frac{1}{2}$ of the 4s or 5s shell, can couple with the spin S of the 4f shell to yield $S' = S \pm \frac{1}{2}$, so that the coupling results in a doublet. Since the 4f configuration is not changed in s -electron photoemission, the S' can be coupled with the original L to give all the final states of the ion. The intensities of the two components of the doublet

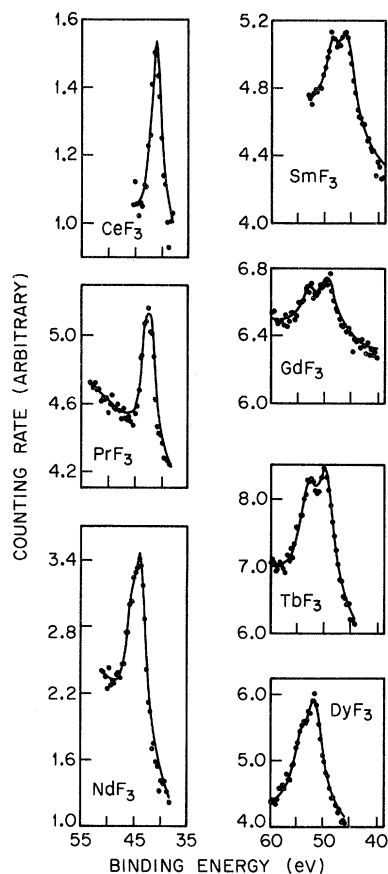


FIG. 2. Photoelectron spectra of the 5s electrons.

TABLE I. Results of least-squares analysis of multiplet spectra.

Element	Splitting (eV)	Linewidth (eV)	Amplitude ratio experimental	Amplitude ratio theory
Gd(4s)	8.2±0.2	6.0±0.3	1.5±0.2	1.29
Tb	7.5	5.9	1.7	1.33
Dy	6.4	6.5	1.4	1.40
Ho	5.6	6.6	1.7	1.50
Er	4.3	5.9	2.0	1.67
Tm	3.4	6.9	1.6	2.00
Tm	3.5	7.0	a	2.00
Ce(5s)	b	2.3±0.2	...	3.00
Pr	1.2±0.2	1.8	1.0±0.2	2.00
Nd	1.7	2.5	1.9	1.67
Sm	2.8	3.6	1.4	1.40
Gd	3.7	3.7	1.5	1.29
Tb	3.4	4.0	1.4	1.33
Dy	2.7	3.7	1.9	1.40

^aHeld fixed at theoretical value.

^bFitted with single line.

should be proportional to the respective final-state multiplicities $(2S'+1)(2L+1)$; with the S' given above, and the unchanging L , the intensity ratio becomes simply $1+1/S$. This has been listed in Table I for the ions we have studied.

The two multiplet components are of course further split by the L - S coupling, but this splitting is small in comparison to the 6-eV lifetime-limited linewidths. Some additional and asymmetric line broadening undoubtedly results from this mechanism, and is probably one of the primary contributors to the differences between the calculated and measured line-intensity ratios.

The size of the splitting between the multiplet components can be obtained from Hartree-Fock calculations. Comparison with such theoretical calculations⁴ shows that the measured 5s splittings agree fairly well with the Hartree-Fock estimates but that the 4s splittings are somewhat smaller. A simple picture to describe the Z dependence of the splitting can be obtained using a model proposed

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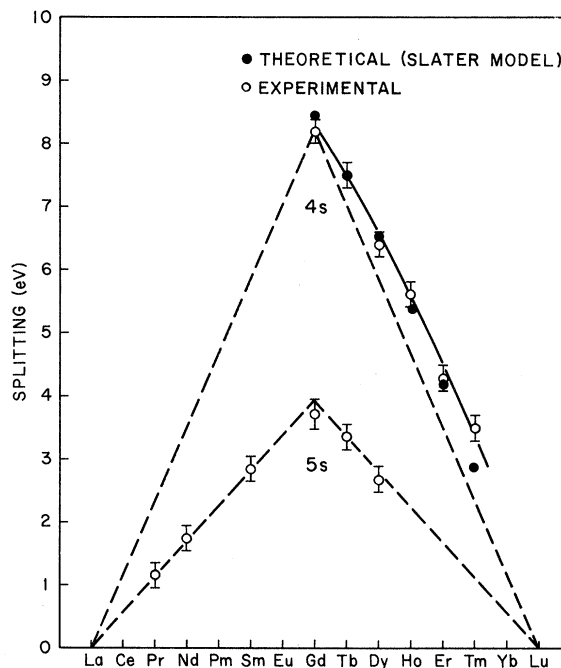


FIG. 3. 4s and 5s multiplet splitting in the trivalent rare earths.

by Slater,⁵ which uses a different effective potential for the "spin-up" and "spin-down" electrons. The observed splittings then correspond to the different binding energies for the two s electrons. Ignoring the change in wave functions with Z , the multiplet energy difference is then expected to be proportional to S (the total spin of the $4f$ shell), and to the binding energy itself. This function, scaled to match the observed splitting in Tb, closely follows the measured splittings for the 4s electrons, as can be seen from Fig. 3. The splitting of the 5s electrons is too small to show observable deviations from proportionality to S .

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³This satellite is due to the $K\alpha_{3,4}$ emission in the exciting x-ray beam, not to processes in the sample itself.

⁴We are indebted to R. E. Watson for permission to quote these results prior to publication.

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