

<sup>7</sup>A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **39**, 1781 (1960) [*Sov. Phys. JETP* **12**, 1243 (1961)].

<sup>8</sup>As usual, contributions which correspond to diagrams with crossing impurity lines are neglected.

<sup>9</sup>Y. Nagaoka, *J. Phys. Chem. Solids* **27**, 1139 (1966).

<sup>10</sup>M. J. Zuckermann, *Phys. Rev.* **168**, 390 (1968).

<sup>11</sup>A. Griffin, *Phys. Rev. Lett.* **15**, 703 (1965).

<sup>12</sup>K. Maki, *Phys. Rev.* **153**, 428 (1967).

<sup>13</sup>A. Griffin, in *Superconductivity*, edited by P. R. Wallace (Gordon and Breach, New York, 1970), Vol. II, p. 598 ff and p. 617.

<sup>14</sup>The position of the pole of the scattering amplitudes within the energy gap generally has to be determined numerically also, from a boundary condition (see Ref. 1).

<sup>15</sup>H. Shiba, *Progr. Theor. Phys.* **40**, 435 (1968).

<sup>16</sup>J. G. Huber and M. B. Maple, to be published.

<sup>17</sup>K. H. Bennemann, *Phys. Rev.* **183**, 492 (1969).

<sup>18</sup>G. Morandi, *Solid State Commun.* **6**, 561 (1968).

<sup>19</sup>A. B. Kaiser, *J. Phys. C: Proc. Phys. Soc., London* **3**, 409 (1970).

<sup>20</sup>M. B. Maple, J. G. Huber, B. R. Coles, and H. C. Lawson, *J. Low Temp. Phys.* **3**, 137 (1970).

<sup>21</sup>One might expect U in Th to exhibit a spin of 1, but the best fit is definitely obtained with  $S = \frac{1}{2}$  here.

<sup>22</sup>M. B. Maple and K. S. Kim, *Phys. Rev. Lett.* **23**, 118 (1969).

<sup>23</sup>J. Zittartz and E. Müller-Hartmann, *Z. Phys.* **212**, 380 (1968).

<sup>24</sup>E. Müller-Hartmann, *Z. Phys.* **223**, 267 (1969).

## 4f Electronic States in the Metals Nd, Sm, Dy, and Er Studied by X-Ray Photoemission

P. O. Hedén and H. Löfgren

*Chalmers University of Technology, Gothenburg, Sweden*

and

S. B. M. Hagström

*Department of Physics, University of Linköping, Linköping, Sweden*

(Received 16 November 1970)

Photoelectron spectra excited by x radiation are reported for the band-structure part on clean films of the rare-earth metals Nd, Sm, Dy, and Er. The dominant part of the spectra is due to excitation of 4f electrons. The spectra exhibit a complex and extended structure which is interpreted in terms of multiplet splitting of the final state in the photoemission process.

In this Letter we wish to report on x-ray photoemission studies of the rare-earth metals Nd, Sm, Dy, and Er. In particular we have studied the location and structure of the 4f electrons. We have previously reported<sup>1,2</sup> on similar studies of Eu and Yb. In contrast to these results the present spectra for rare earths with a 4f shell which is not filled or half-filled show a much more complicated and widened structure. An interpretation of this in terms of multiplet splitting is given.

The technique of x-ray photoemission spectroscopy (XPS) or electron spectroscopy for chemical analysis has been described elsewhere.<sup>3</sup> Here only some details pertinent to the present experiments will be discussed. The electron spectrometer is of the electrostatic type with direct analysis of the photoelectrons without any retardation. With Al  $K\alpha$  radiation for excitation, a resolution of 1.6 eV full width at half-maximum is obtained using a gold sample. As a measure of the sensitivity of the spectrometer one can use

the maximum counting rate of the Au 4f electron line at a given resolution. In the present instrument this figure is 2000 counts/sec at the above resolution. The vacuum system is an all-metal-gasket chamber. All samples were prepared by repeated evaporation *in situ* from 99.9% pure ingots in tungsten baskets at a working pressure of  $5 \times 10^{-7}$  Torr or better. The cleanliness of the sample surface was checked by monitoring the appearance of the oxygen photoelectron line. To maintain an oxide-free sample a new evaporation had to be made every 5 min. The energy scale of the spectrometer was calibrated using a Pd sample for which the Fermi level is located at the inflection point of the steep high-energy edge of the 4d band. The calibration was also checked by comparing with uv photoemission measurements (UPS).

The metals studied in this investigation all belong to the so-called normal rare earths. The crystal structures are dhcp (double hexagonal close packed) for Nd, rhombic for Sm, and hcp

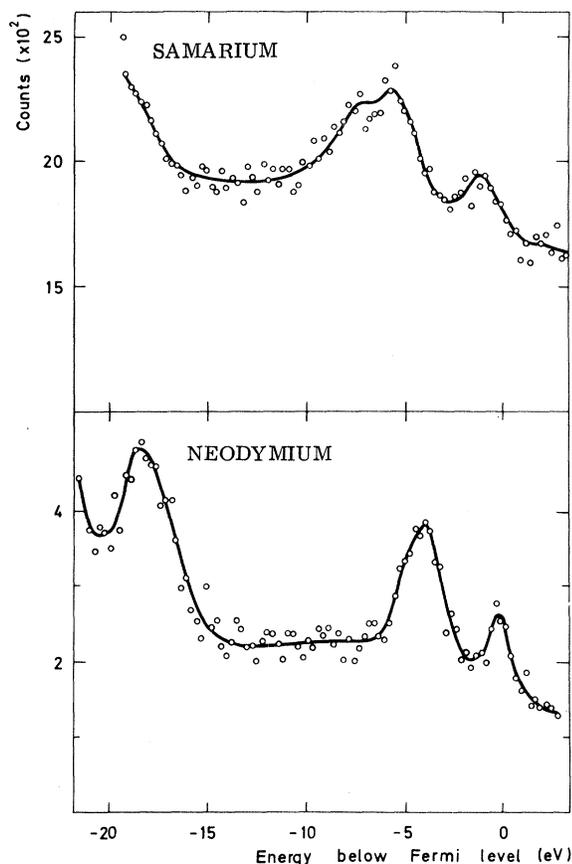


FIG. 1. Photoelectron spectrum of outer energy levels excited with Al  $K\alpha$  radiation from clean neodymium and samarium metal films.

for Dy and Er. In the metallic phase the outer electronic configuration apart from the  $4f$  electrons consists of  $5d^1$  and  $6s^2$  states. These states overlap and are strongly mixed. The  $4f$  configuration is  $4f^3$ ,  $4f^5$ ,  $4f^9$ , and  $4f^{11}$  for Nd, Sm, Dy, and Er, respectively.

The recorded spectra obtained by excitation with Al  $K\alpha$  (1486.6-eV) photons are shown in Figs. 1 and 2. The Fermi level is chosen as the zero of the energy scale. As has been observed earlier,<sup>1</sup> the oscillator strength for exciting the  $4f$  electrons in the rare earths is considerably higher in the XPS case than in the UPS one. This fact is also evident from the present recordings where the dominant structure in the upper part of the spectrum originates from  $4f$  electron transitions, as ascertained by comparison with recordings on Ba.<sup>4</sup> However, in contrast to previous recordings on Eu and Yb,<sup>1,2</sup> the present ones show much more structured and widened spectra.

A slight oxidation of the sample gives a more structured appearance to the  $4f$  levels<sup>4</sup> due to a

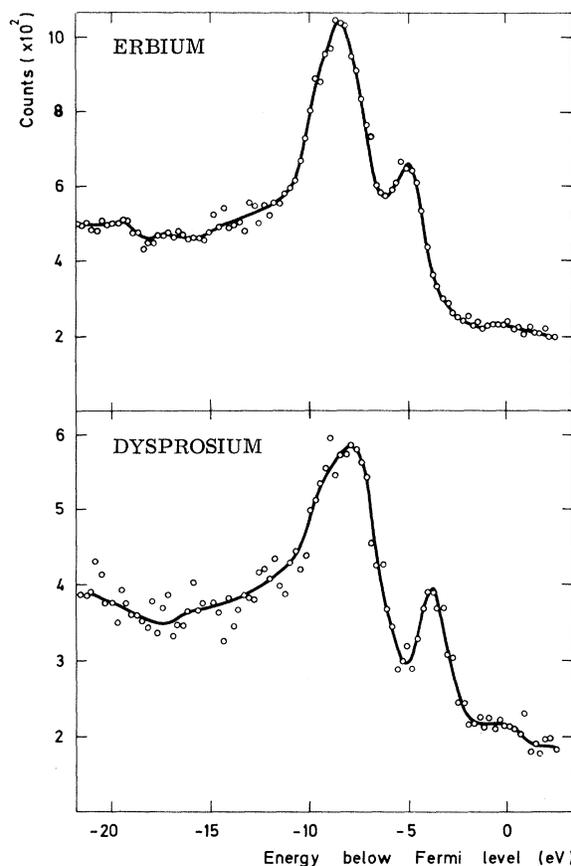


FIG. 2. Photoelectron spectrum of outer energy levels excited with Al  $K\alpha$  radiation from clean dysprosium and erbium metal films.

chemical shift of the  $4f$  electrons and the oxygen  $2p$  states. However, the nonappearance of any signal from the oxygen  $1s$  level in the present experiments excludes this possibility. We therefore conclude that the recorded spectra are representative of the pure metals. Another explanation for the structure would be that part of it is due to characteristic energy losses of the photoexcited electrons. The flatness of the spectrum on the low-energy side of the second peak rules out this explanation.

The Nd spectrum shows a peak just below the Fermi level ( $-0.4$  eV) and a stronger one at  $-4.2$  eV. The peak at  $-18.4$  eV is the photoelectron line from the atomic  $5p$  states in Nd. The Sm spectrum is similar with a small peak at  $-1.2$  eV. However, in this case the slight asymmetry of the second peak has developed into two peaks at  $-5.8$  and  $-7.5$  eV. The peaks in the Dy spectrum are located at  $-3.8$  and  $-8.0$  eV. The dominant peak again shows asymmetry which becomes more pronounced in the Er spectrum

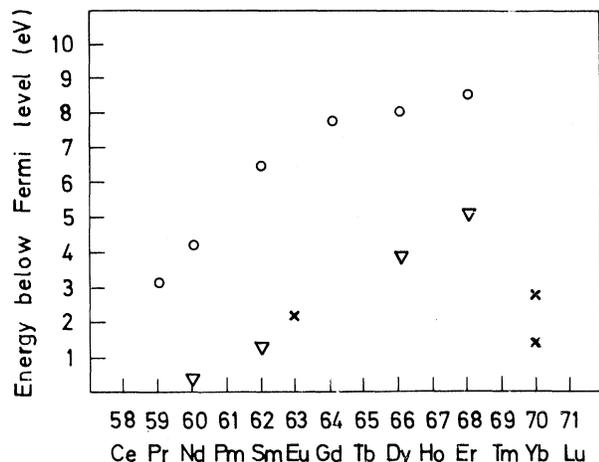


FIG. 3. Locations of peaks in the x-ray photoelectron spectra of some rare-earth metals as a function of atomic number.

where the peaks are located at  $-5.0$  and  $-8.5$  eV.

The spectra of Dy and Er also show weak structure just at the Fermi level. This could possibly be due to the  $5d$  states which are known to be located at the Fermi level. In the case of Nd and Sm this structure would be concealed by the shallow  $4f$  peak.

The positions of the peaks as a function of the atomic number are shown in Fig. 3. The experimental uncertainty is  $\pm 0.4$  eV on an absolute scale while splittings, for instance, can be determined with higher accuracy. The data for Eu, Yb, and Gd are taken from Ref. 4, while we have used preliminary data for the element Pr. As can be expected, there is a regular change towards increasing binding energies with increasing atomic number except for Eu and Yb which exhibit very shallow  $4f$  states. Gd,<sup>4</sup> which, like Eu, has a half-filled  $4f$  shell and only shows one  $4f$  peak, seems to behave regularly.

In interpreting photoelectron spectra it is essential to bear in mind that the kinetic energy of the outgoing electron is in principle the difference between the energies of the final state and the initial state. If the final state can be one of a number of excited states of the system, the

photoelectron spectrum will reflect these excitations. This is particularly illustrated in work on free molecules in gaseous samples where the photoelectron spectrum reflects not only the different ionization potentials of the molecule but also its vibrational and rotational levels. For solid samples an analogous case has been observed in the splittings of core levels due to the coupling of a hole in a metal-atom subshell to an unfilled valence subshell.<sup>5</sup>

The recorded photoelectron spectra of the  $4f$  electrons have a simple structure if the  $4f$  shell is half-filled (Eu, Gd) or filled (Yb). Yb shows a double peak with an energy separation of 1.3 eV in agreement with the two lowest spin-orbit-split states of the  $f^{13}$  ion. As for Eu and Gd, the measured width of the single observed peak is consistent with the multiplet structure of the  $f^6$  ion.

The metals we are concerned with show a structure that extends over roughly 10 eV. This large width rules out explanations in terms of crystal-field effects. Thus also in these cases the recorded spectra seem to reflect the host of final states available for the photoexcited system. We therefore interpret the observed structure as being due to multiplet splitting of these states.

We wish to acknowledge valuable discussions with G. Brodén and other members of the Optical Group at Chalmers University of Technology. This work has been supported by the Swedish Board for Technical Development.

<sup>1</sup>G. Brodén, S. B. M. Hagström, P. O. Hedén, and C. Norris, in *Electronic Density of States*, National Bureau of Standards Special Publication No. 323 (U.S.G.P.O., Washington, D. C., 1970).

<sup>2</sup>S. B. M. Hagström, P. O. Hedén, and H. Löfgren, *Solid State Commun.* **8**, 1245 (1970).

<sup>3</sup>K. Siegbahn *et al.*, *Nova Acta Regiae Soc. Sci. Upsal.* **20**, 1 (1967).

<sup>4</sup>P. O. Hedén, H. Löfgren, and S. B. M. Hagström, to be published.

<sup>5</sup>C. S. Fadley and D. A. Shirley, *Phys. Rev. A* **2**, 1109 (1970).