Measurement of the 4*f*-shell optical edge in Gd metal*

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Vacuum-ultraviolet absorption techniques are used to study 4*f*-shell optical excitations in Gd metal. The results provide insight into the discrepancy between 4*f*-shell excitation thresholds reported from x-ray absorption and x-ray photoemission studies. The different threshold energies are attributed to different screening configurations in the final states, or to spurious shifts of the x-ray photoemission peaks.

Much recent interest has centered on the excitation spectra of rare-earth metals as probed by optical,[1] electron energy loss,[2] and x-ray photoemission[3] (XPS) methods. Closely related theoretical investigations have also appeared.[4] This paper reports on the first optical detection of excitations from the 4*f* shell of a rare-earth metal, in this case Gd, and suggests several possible explanations for the existing discrepancy between the 4*f* excitation thresholds reported from x-ray absorption and XPS techniques.

Optical-absorption measurements were made through the energy range 4–12 eV by comparing the light intensities transmitted by two Gd films having different thicknesses (from 100 Å to 400 Å), using an apparatus described elsewhere.[5] The films were prepared *in situ* at He temperatures on a LiF substrate and covered with a Ne film to prevent contamination in the 2×10^{-7} Torr vacuum. The comparison method eliminates reflectivity corrections (multiple-bounce effects are negligible since $n^2 \ll k^2$ for Gd) and the rare-gas coating has been found to maintain even alkali metals clean. Calibration runs established both the relative background transmissivities of the two substrate halves and the relative efficiencies of detection, and these effects were eliminated from the data to yield the absorption $K(\omega) = [2\omega k(\omega)/c]\Delta x$, with Δx the thickness difference between the two films.

The index of refraction n was calculated from the absorption by Kramers-Kronig analysis using additional data for $\hbar\omega \lesssim 5$ eV and $\hbar\omega > 12$ eV. The present data agreed to 3% in the overlap range 4.5–5.5 eV with precise ellipsometric studies of thin Gd films held at 10^{-11} Torr.[1] The ellipsometric data were judged to have the higher absolute precision and the present results shown in Fig. 1 were therefore normalized to the earlier results, also shown in Fig. 1. The results obtained in this way agreed well in ratio of slope to amplitude with absorption results calculated from electron energy-loss measurements by Daniels *et al.*[2] These results have been corrected (decreased) for an apparent scale discrepancy of ~25% in order to obtain the best consistent results shown in Fig. 1. Wing corrections outside the range 0.2–40 eV used in the Kramers-Kronig analysis were made by standard methods using n and k from the ellipsometric measurements.

Figure 2 shows the number $N(\omega)$ of electrons per atom contributing to the absorption according to the equation

$$N(\omega) = \frac{m}{2\pi^2 e^2}\int_{\omega_0}^{\omega} \omega\epsilon_2(\omega)\, d\omega + \frac{2m}{\pi m^*} N \tan^{-1}(\omega_0\tau)\,.$$

The second term here allows for Drude response at $\omega < \omega_0$ with $\hbar\omega_0 = 0.2$ eV; it is model dependent but not large. For one s electron having $m^* = m_e$ and two d electrons with $m = 4m_e$, together with Hodgson's[1] value for τ, $\hbar/\tau = 0.4$ eV, one finds the value 0.45 electrons with perhaps a 50% uncertainty.

With the reliability of Fig. 2 thus established there can be no question that for $\hbar\omega \gtrsim 10$ eV, far below the 5*p* edge at 20 eV, $N(\omega)$ calculated from the data exceeds the limit $N = 3$ set by the number of Gd valence electrons. The excess clearly origi-

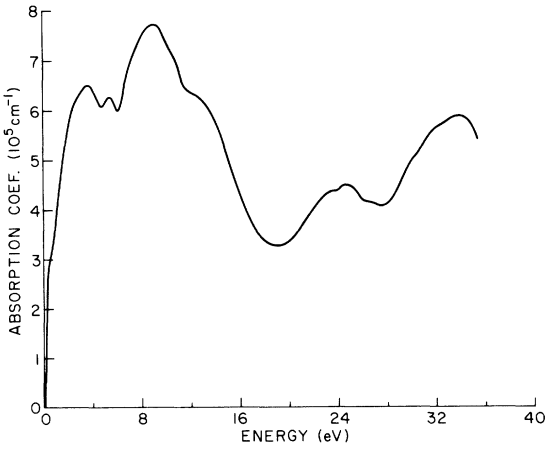

FIG. 1. Optical absorption spectrum of Gd metal.

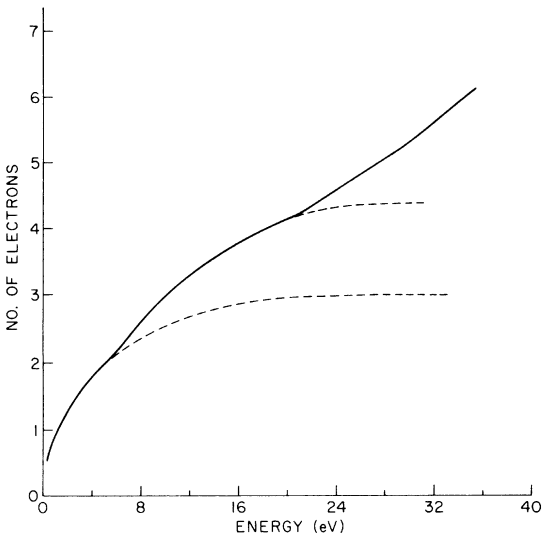

FIG. 2. Number of electrons N contributing to absorption as a function of energy. Solid line, computed value based on the equation given in the text. Dashed lines suggest component contributions to N due to three conduction electrons (lower curve) and due to $4f$ electrons (upper curve).

nates from the break in slope of $N(\omega)$ at $\hbar\omega \simeq 6.1$ eV in Fig 2, and hence from the sharp absorption threshold evident in Fig. 1 at 6.1 eV. This threshold is therefore associated unambiguously with transitions originating on the f state of the Gd $4f^7$ ($^8S_{7/2}$) core. We note that the total strength of $f \rightarrow g$ matrix elements are expected to exceed $f \rightarrow d$ matrix elements by a factor of[6] 5 so that the latter may contribute in all only ~1.4 electrons to the sum rule. In addition a sharp and quickly exhausted $f \rightarrow d$ transition threshold is predicted, whereas the $f \rightarrow g$ transition is delayed in energy and possesses a gradual threshold. The observed absorption and behavior of $N(\omega)$ above 6 eV are thus consistent with their assignment to $f \rightarrow d$ core transitions. This analysis constitutes the first detection by optical methods of $4f$ excitations in metals.

Theories of optical absorption and photoemission from metals are not yet sufficiently developed to permit a detailed analysis of the data. Coarse features may, however, possess useful qualitative interpretations. Into this category falls the discrepancy between the single peak at 8.1 eV observed in XPS studies of Gd, and the present sharp threshold at 6.1 eV. We note that M_{III} absorption studies[7] and early predictions from uv photoemission spectroscopy[8] (5.5 and 5.8 eV, respectively) yield $4f$ thresholds that fall close to our optical results, and the agreement with the theoretical prediction of[9] ~7 eV (although model sensitive) is very satisfactory. The discrepant threshold of the XPS[3] results thus requires explanation.

The final states reached by optical and XPS processes coupling to the $4f$ shell must both contain $4f^6$ (^7F) cores, but a variety of conduction electron configurations are possible. It is nevertheless clear that whatever process occurs, final states that persist for a time exceeding the plasma period must be self-consistent. Sharp structure ~1 eV wide certainly satisfies this criterion, so that the core holes produced in both optical and XPS experiments are fully screened by a deformation of the electron gas. It remains to be seen whether or not the local self-consistent excited configuration left in the lattice by the two processes are identical.

We can offer only two possible explanations for the observed difference between the XPS and absorption thresholds: (i) the two processes reach different final states and thus require different excitation energies; or (ii) the XPS peak is spuriously shifted. It is well known that XPS results are sensitive to work function changes induced by surface contamination. In addition chemical shifts of $4f$ shell XPS peaks in[10] Gd are compatible both in sign and magnitude with the discrepancy between the XPS and absorption thresholds. Although a third possibility could involve oxidation of the thin films used in this study, absorption measurements made on deliberately oxidized films allow us to clearly distinguish between the metal and metal oxide absorption spectra and thereby rule out this possibility. Based on all available data, one cannot rule out the possibility that the threshold discrepancy is genuine, and results from differences between the final states reached by the optical absorption and XPS processes.[11] Presumably these would represent different conduction band screening configurations for the $4f$ hole. Different optical absorption and XPS thresholds are observed in insulators and these can be attributed to the unscreened charge. In metals, the electron gas eliminates this possibility, but alternative screening charge distributions cannot be ruled out.

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[1]J. L.Erskine, G. A. Blake, and C. J. Flaten, J. Opt. Soc. Am. 64, 1334 (1974); G. A. Blake, private communications; J. N. Hodgson and B. Cleyet, J. Phys. C 2, 97 (1969).

[2]J. Daniels, Opt. Commun. 3, 13 (1971).

[3]F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A.

Shirley, Phys. Lett. A 45, 227 (1973); P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Rev. Lett. 26, 432 (1971).
[4]J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972).
[5]D. J. Phelps, R. A. Tilton, and C. P. Flynn, Phys. Rev. B (to be published).
[6]F. Combet Farnoux, C. R. Acad. Sci (Paris) B 264, 1728 (1967); S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968); U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).
[7]J. M. Mariot, R. C. Karnatak, and C. Bonnelle, J. Phys. Chem. Solids 35, 657 (1974).
[8]A. J. Blodgett, Jr., W. E. Spicer, and A. Y-C. Yu, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland, Amsterdam, 1966), p. 246.
[9]J. O. Dimmock, A. J. Freeman, and R. E. Watson, in Ref. 8, p. 237.
[10]P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Status Solidi B 49, 721 (1972).
[11]A 2 eV difference between XPS and optically determined 4*f* binding energies has also been observed in GdSb and GdS: G. Güntherodt, in *Advances in Solid State Physics XVI*, edited by J. Treusch (Vieweg, Braunschweig, 1976), p. 95.