Our experiment and its interpretation can contribute to the explanation of the puzzling result of the combined ESR and F-luminescence experiment by Ruedin and Porret.[14] They observed a decrease of the F luminescence (linear with the irradiated microwave power) when the system was tuned with the magnetic field into the resonance condition with $g = 1.984$. So far this effect could be ascribed only phenomenologically to the excitation of spin transitions in the F-center ground and/or relaxed excited state. The physical origin of this effect can now be understood to be the same as in our experiment: the presence of interacting F centers with reduced luminescence efficiency. As we showed that spin polarization *increases* the F luminescence, any microwave-induced spin flips—in the ground *or* excited F state—will *decrease* it. ESR experiments detecting microwave-induced luminescence decrease should be most promising for large magnetic fields (K-band) and F-center systems with strongly concentration-quenched luminescence.

A more detailed account of the experimental details, the derivation of the equations for the electron kinetics, and further experiments involving the magnetic-field–induced F-luminescence change will be published soon.

†Work supported by U. S. Air Force Office of Scientific Research Grant No. 69-1645.

*On a postdoctoral grant from Fonds National Suisse pour la Recherche Scientifique.

‡Present address: Universidade de São Paulo, Escola de Engenharia de São Carlos, Departmento de Fisica, São Carlos, Brazil.

§Final disposition delayed 4 months by loss of manuscript and correspondence in the U. S. Mail.

[1]H. Fedders, M. Hunger, and F. Lüty, J Phys. Chem. Solids 22, 299 (1961).

[2]F. Lüty, Z. Phys. 153, 247 (1958).

[3]F. Lüty, in *Halbleiterprobleme*, edited by W. Schottky (Vieweg, Braunschweig, W. Germany, 1961), Vol. 6.

[4]K. H. Becker and H. Pick, Nuovo Cimento Suppl. 7, 498 (1958); C. Z. Van Doorn, Philips Res. Rep. 13, 296 (1958).

[5]A. Mielich, Z. Phys. 176, 168 (1963).

[6]G. Chiarotti and U. M. Grassano, Nuovo Cimento 46B, 78 (1966).

[7]D. Schmid and H. C. Wolf, Z. Phys. 170, 455 (1962).

[8]J. A. Strozier and B. G. Dick, Phys. Status Solidi 31, 203 (1969).

[9]N. V. Karlov, J. Margerie, and Y. Merle-D'Aubigné, J. Phys. (Paris) 24, 717 (1963).

[10]D. Schmid and V. Zimmermann, Phys. Lett. 27A, 459 (1968).

[11]J. W. Hodby, J. A. Borders, and F. C. Brown, to be published.

[12]J. W. Hodby, private communication.

[13]L. F. Mollenauer, S. Pan, and S. Yugvesson, Phys. Rev. 175, 1133 (1968).

[14]Y. Ruedin and F. Porret, Helv. Phys. Acta 41, 1294 (1968).

Energy-Dependent Photoemission Intensities of "f" States in EuS, GdS, and US†

D. E. Eastman

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

Moshe Kuznietz*

Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 21 December 1970)

Photoemission measurements of f states and valence-band energies of EuS, GdS, and US for photon energies from 5 to 41 eV show characteristic energy-dependent emission strengths of "p," "d," and "f" states. These energy dependences permit the "l" character of various levels to be identified in many cases. For example, the emission strength of the $4f^7$ level in EuS increases about 100-fold relative to the 3-eV wide valence "p" band which lies just below the $4f^7$ level. GdS shows a deep $4f^7$ level at about 9 eV below the Fermi level E_F, and US shows an "f-d" band at E_F.

We report the extension of ultraviolet photoemission spectroscopy measurements of "f"-state energy levels in several NaCl-type rare-earth and uranium compounds (EuS, GdS, and US) up to photon energies of $\hbar\omega = 41$ eV. Previously, measurements were limited to 11.6 eV (LiF window cutoff) and $4f$-state emission was found to be weak for such energies.[1,2] The availability of a wide range of photon energies ($\hbar\omega = 16.8$, 21.2, 26.9, and 40.8 eV as well as $\hbar\omega$

≤ 11.6 eV) permits a determination of valence-band energy levels and bandwidths over a large energy range, i.e., in practice 20 eV or more below the Fermi level E_F. Also, in many cases this wide range of energies permits the determination of the angular-momentum character (i.e., "p"-, "d"-, or "f"-like) of the occupied energy levels. In EuS, the emission strength of the $4f^7$ level is observed to increase about 100-fold relative to the valence "p" band as $\hbar\omega$ increases from 10 to 41 eV. Photoemission measurements for US show $5f$ conduction-band electrons at E_F. To our knowledge, these are the first photoemission or optical measurements for actinide compounds.

The increase in absorption strength of $4f$ electrons at high energies has been reported in x-ray photoemission studies of Eu[3] and Yb[4] with $\hbar\omega \simeq 1500$ eV and for Yb with $\hbar\omega = 21.2$ eV.[5] However, the energy dependence of the $4f$ absorption strength could not be determined because of the lack of a range of photon energies. Our wide range of photon energies has permitted the first study of the energy dependence of $4f$- and $5f$-valence-electron absorption strengths.

EuS is a ferromagnetic semiconductor ($T_C = 16.8$°K), GdS is an antiferromagnetic metal ($T_N \simeq 50$°K), and US is a ferromagnetic metal ($T_C = 180$°K). Polycrystalline films of EuS, GdS, and US were evaporated onto heated substrates ($T \simeq 200$-300°C) using an electron beam gun. Starting material was stoichiometric bulk-sintered polycrystalline material. Sample chamber pressures rose from $\sim 10^{-8}$ to 10^{-7} Torr during evaporation ($\simeq 3$ Å/sec) and rapidly recovered to the 10^{-9} Torr range. The crystal structures of the films were confirmed by x-ray diffraction and the compositions were checked by comparison with the bulk material via electron-microprobe analyses.

Photoemission measurements for energies below 11.6 eV (LiF cutoff) were made using conventional techniques.[1] Measurements at 16.8, 21.2, 26.9, and 40.8 eV were made using a windowless photoemission spectrometer.[6] Radiation at 21.2 and 40.8 eV, and at 16.8 and 26.9 eV, respectively, is provided by the He I, He II, Ne I, and Ne II lines of cold-cathode He- and Ne- resonance lamps.

Photoemission-energy distribution curves (EDC) for EuS, GdS, and US are shown in Fig. 1. All curves are plotted versus the initial energy $E_i = E^* - \hbar\omega + \varphi$, where E^* is the measured kinetic energy and φ is the work function. This energy scale corresponds to the occupied energy levels

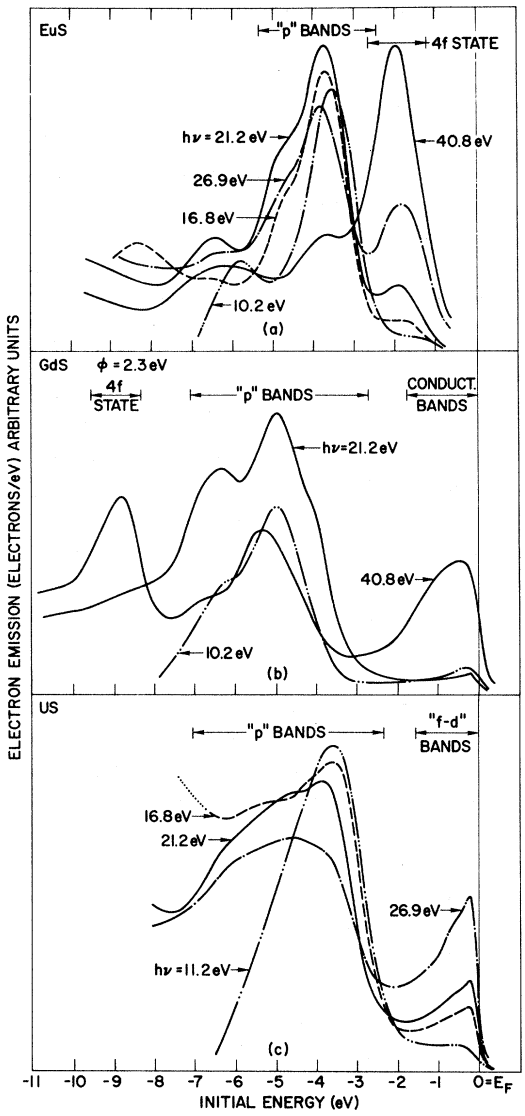

FIG. 1. Energy distributions for EuS, GdS, and US.

measured relative to the Fermi level E_F. All curves are plotted in arbitrary intensity units, i.e., quantum yields were not measured.

Previous photoemission studies[1,2] of EuS below 11.6 eV and spin-polarized photoemission studies[7] have concluded that the $4f^7$ level lies in the gap above the valence "p" band. As shown in Fig. 1(a), the rapid increase of the $4f$-level emission relative to the "p"-band emission in EuS with increasing photon energy provides a confirmation of this conclusion. The $4f^7$-multiplet binding energy is centered at ~1.8 eV below E_F and the filled valence band extends from ~2.3 to 5.2 eV below E_F. For $\hbar\omega < 11.6$ eV, the $4f$ emission is much weaker than the valence "p"-band emission; for $\hbar\omega = 10.2$ eV in Fig. 1(a), the emis-

sion strength (or absorption cross section σ) of the $4f$ level is only $\sigma_f/\sigma_p \simeq 0.03$ that of the "p" band. Here we assume for each EDC that absorption cross sections of the various electron states are proportional to the areas of their emission peaks. That is, we neglect the energy dependence of the electron-transport and -escape processes, which are small at the high energies involved. As the photon energy increases, the $4f$-level intensity increases very rapidly; σ_f/σ_p has increased to $\simeq 0.14$ at $\hbar\omega = 21.2$ eV, to $\simeq 0.32$ at $\hbar\omega = 26.9$ eV, and to $\simeq 3.0$ at $\hbar\omega = 40.8$ eV.

At 40.8 eV, the $4f^7 - 4f^6$ (^7F_J) multiplet excitation[1] is seen to have a full width of 1.3 eV at half-maximum. This width is expected to be only slightly affected by experimental broadening (resolution $\simeq 0.25$ eV at 40.8 eV). The structure in Fig. 1(a) at 6.5 eV below E_F was found to be sensitive to surface conditions and is believed to be due to impurity emission.

It is instructive at this point to summarize several experimental and theoretical studies of the energy-dependent optical-absorption cross sections of valence "p" states, valence "d" states, and $4f$ states and compare these results with our photoemission measurements. Since we are interested in the optical-absorption strengths (proportional to emission strengths) of different electron states in the same material, it is convenient to use the absorption cross section per electron state, which is defined by $\sigma(\omega) = \alpha(\omega)/(N_{at}Z_{at})$, where $\alpha(\omega)$ is the optical absorption coefficient [$\alpha(\omega) = 4\pi k/\lambda$, λ = wavelength, k = extinction coefficient, α^{-1} = absorption depth], N_{at} is the number of atoms per unit volume, and Z_{at} is the number of electrons per atom of the type considered.

A summary of absorption cross sections for several valence "p" states and valence "d" states and a calculation for $4f$ states in Ce is given in Fig. 2 for photon energies up to 70 eV. The cross sections are given in units of 10^{-18} cm^2, i.e., 10^{-18} cm^2 = 1 Mb. The solid lines show the measured cross sections per "p"-type electron for Ge[8] and MgO[9] and a calculation for the $4p^6$ level in Rb.[10] The dashed lines show the measured cross section per "d" electron for Pd[11] and a calculation for the $4d^{10}$ level of Sn.[10] The broken line shows the calculated cross section for a $4f$ electron in Ce (Ref. 10). The absorption cross sections for Ge, MgO, and Pd were derived from measured optical constants. The absorption cross sections for Rb, Sn, and Ce were calculated by Combet-Farnoux using a one-

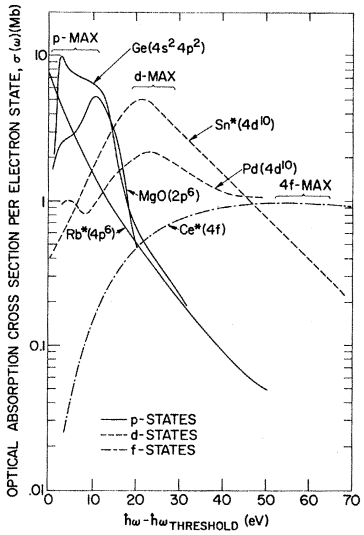

FIG. 2. Summary of the optical-absorption cross section $\sigma(\omega)$ versus photon energy for valence "p," "d," and $4f$ states. 1 MB = 10^{-18} cm^2. Here $\hbar\omega - \hbar\omega_{threshold}$ is the energy measured relative to the bottom of the empty conduction band or vacuum continuum (for atoms). The asterisks for Rb, Sn, and Ce denote calculated curves (see text).

electron model with a central potential.[10] Such calculations should be moderately accurate for well-localized orbitals such as the $4f$ orbitals.

Several qualitive trends in the absorption cross sections are shown in Fig. 2. The maximum cross section decreases with increasing l character, i.e., $\sigma_p{}^{max} > \sigma_s{}^{max} > \sigma_f{}^{max}$. At low photon energies ($\hbar\omega \lesssim 20$ eV) valence "p"-type electrons have the largest cross sections. Valence "d"-like electrons have maximum cross sections at higher energies, and $4f$ electrons have maximum cross sections at still higher energies. This trend is understandable in terms of a partial-wave expansion in spherical harmonics of a free-electron wave function $\exp(i\vec{k}\cdot\vec{r})$. The higher angular-momentum components increase with increasing energy, and electric-dipole selection rules require $\Delta l = \pm 1$. Thus for f electrons only $f \rightarrow d$ and $f \rightarrow g$ transitions are allowed ($f \rightarrow g$ transitions dominate for $\hbar\omega > 8$ eV),[10] and one must go to high energies to get appreciable g character in the "free-electron" wave functions.

A word of caution—the absorption cross sections shown in Fig. 2 are qualitatively valid for transitions into "free-electron-like" conduction bands and are not valid for resonance transitions. Thus resonance transitions such as $4f \rightarrow 5d$ excitations are not described by Fig. 2. In general, such excitations are expected to occur at low en-

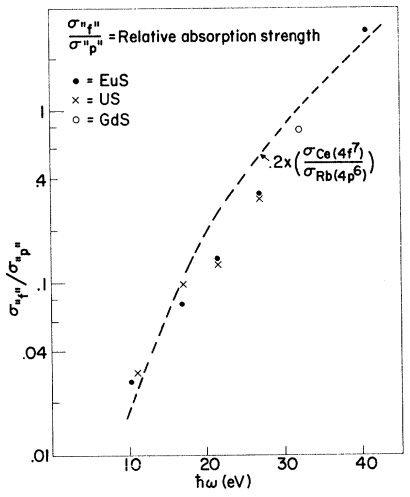

FIG. 3. Energy dependence of the "f"- to "p"- band absorption cross section σ_f/σ_p for EuS, GdS, and US. The dashed theoretical curve is taken from Fig. 2.

ergies ($\hbar\omega < 5$-10 eV) in the rare-earth and uranium compounds.

Returning to our data, in Fig. 3 we compare the ratio of the calculated $4f$- and "p"-band cross sections shown in Fig. 2 with our measurements for EuS. The measured cross-section ratio σ_f/σ_p for EuS increases by a factor of about 100 from 10 to 40 eV, and the energy dependence of the calculated curve (dashed line) agrees to within a factor of about 2 over this energy range. The magnitude of the calculated curve σ_f/σ_p was scaled by 0.2 to facilitate comparison of the energy dependence.

EDC's for metallic GdS are shown in Fig. 1(b). In contrast to EuS, which is a semiconductor, the EDC's of GdS show emission from states within ~1.5 eV of E_F. We associate this emission with a partially filled conduction band. The occupied valence "p" band is identified by the strong emission from 2.7 to 7 eV below E_F for $\hbar\omega = 10.2$ and 21.2 eV. It is the absorption edge of the "p" band $\rightarrow E_F$ transition which gives GdS its characteristic golden color. The conduction band at E_F is seen to have at least partial "d"-band character since its emission intensity relative to the valence "p" band increases from 21.2 to 40.8 eV (see Fig. 2). If the conduction band were only "s"-like, its relative intensity would decrease with increasing $\hbar\omega$.

The $4f^7$ level of GdS is observed in the EDC for $\hbar\omega = 40.8$ eV and is centered at an energy 8.9 eV below E_F with a full width at half-maximum of 1.2 eV. This $4f^7$ peak is seen as a strong peak in the EDC for $\hbar\omega = 40.8$ eV but is at best only a very weak shoulder for $\hbar\omega = 21.2$ eV. Its width is similar to that observed for EuS [Fig. 1(a)] and its relative intensity σ_f/σ_p for $\hbar\omega = 40.8$ eV is in agreement with the data for EuS. This $4f^7$ peak for $\hbar\omega = 40.8$ eV is weaker than for EuS at 40.8 eV because of its 9-eV binding energy, i.e., the f electron in GdS is excited 40.8–9.0 $\simeq$ 31.8 eV above threshold (see Fig. 3). Weak structure was previously observed for $\hbar\omega < 11.6$ eV at ~2.2 eV below E_F which was tentatively identified as the $4f^7$ level.[1] Our present measurements indicate that this previous assignment was incorrect.

EDC's for US are shown in Fig. 1(c). The valence "p" band is identified by its strong emission at low-photon energies and is seen to extend from 2.3 to 7.0 eV below E_F. The observed "p"-band width (~4.7 eV) and position (center at 4.7 eV below E_F) is consistent with the Korringa-Kohn-Rostaker energy-band calculations of Davis,[12] who determined a "p"-bandwidth of ~4.4 eV centered at ~5.5 eV below E_F.

For US, emission from the conduction band within ~2 eV of E_F is observed for all photon energies above the work function $\varphi = 4.6$ eV as determined from a Fowler plot. However, for $\hbar\omega < 11.6$ eV this emission is very weak [e.g., see 11.2 eV curve in Fig. 1(c)]. At higher energies, the relative emission intensity of these states increases rapidly with increasing photon energy. As with EuS, this indicates a higher l character for these conduction-band states than for the valence "p" band. The ratio of the measured conduction-band absorption cross section (states within 1.5 eV of E_F) and the "p"-band cross section is plotted in Fig. 3. This energy dependence is very similar to that observed in EuS and is consistent with substantial "f" character in the "f-d" conduction band of US.

Since the shape of the EDC's in Fig. 1(c) for conduction-band emission within 2 eV of E_F does not significantly change for $16.8 \leq \hbar\omega \leq 26.9$ eV, we expect this shape to resemble qualitatively the band density of states. This experimental conduction-band "optical density of states" within 2 eV of E_F is quite narrow, with a full width at half-maximum of about 1 eV. If we normalize this conduction band to contain 4 electrons, we obtain a density of states of 2.5 electron eV^{-1} (U atom)$^{-1}$ at E_F. This value, which at best is only accurate to a factor of about 2, is qualitatively consistent with the very large electronic specific heat of US, $\gamma = 23.3$ mJ K^{-2} mole^{-1} = 9.9 electrons eV^{-1} (U atom)$^{-1}$, reported by Westrum *et al.*[13] The band calculation of Davis[12] also in-

dicates a large density of states at E_F due to occupied "f-d" conduction bands.

Thus in summary, US has a broad "p"-band centered at ~4.7 eV below E_F and appears to have conduction bands of "f-d" character near E_F which are responsible for the observed large electronic specific heat and the magnetic ordering.

As we have demonstrated, the use of photoemission spectroscopy with a wide range of photon energies permits the character of "p," "d," and "f" states to be identified in many cases. The "f" states in EuS, GdS, and US are identified by their energy-dependent emission intensities for energies up to 40.8 eV. Our results clarify why $4f$ electrons are not observed in optical studies[14] and photoemission studies[15] of the rare-earth metals for $\hbar\omega < 11.6$ eV. For such low energies, optical transitions from "s," "p," and "d" states dominate the "f" states (see Fig. 2). Our results also show that care must be taken when translating observed emission intensities into a "density of states" since the emission strengths of "s," "p," "d," and "f" states are in general different at any given photon energy.[16]

We wish to thank M. A. Kanter for providing the US, F. Holtzberg for the GdS, M. W. Shafter for the EuS and for x-ray diffraction measurements, J. D. Kuptsis for electron microprobe analyses, and J. J. Donelon for his assistance with the measurements.

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†Based in part on work sponsored by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. F44620-70-0089 and the U. S. Atomic Energy Commission.

*Present address: Physics Department, Imperial College, London SW7, England.

[1]D. E. Eastman, F. Holtzberg, and S. Methfessel, Phys. Rev. Lett. 23, 226 (1969).

[2]G. Busch, P. Cotti, and P. Munz, Solid State Commun. 7, 795 (1969).

[3]G. Broden, S. B. M. Hagstrom, P. O. Hedin, and C. Norris, in "Electronic Density of States," edited by L. H. Bennett, National Bureau of Standards Special Publication No. 323 (U.S.G.P.O., Washington, D. C., to be published).

[4]S. B. M. Hagstrom, P. O. Hedin, and H. Lofgren, Solid State Commun. 8, 1245 (1970).

[5]G. Broden, S. B. M. Hagstrom, and C. Norris, Phys. Rev. Lett. 24, 1173 (1970).

[6]D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. 24, 310 (1970).

[7]G. Busch, M. Campagna, and H. C. Siegmann, Solid State Commun. 7, 775 (1969), and J. Appl. Phys. 41, 1044 (1970).

[8]R. E. LeVilla and H. Mendlowitz, J. Appl. Phys. 40, 3297 (1969).

[9]D. M. Roessler and W. C. Walker, Phys. Rev. 159, 733 (1967).

[10]F. Combet-Farnoux, C. R. Acad. Sci., Ser. B 264, 1728 (1967). For Ce, we computed the cross section using the radial matrix elements in Fig. 1.

[11]S. Robin, in *Proceedings of the International Conference on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965,* edited by F. Abelés (North-Holland, Amsterdam, 1966), p. 202.

[12]H. L. Davis, in *Plutonium 1970 and Other Actinides,* edited by W. N. Miner (The Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers, New York, 1970), Vol. 1, pp. 209-218. Also see references therein.

[13]E. F. Westrum, R. R. Walters, H. E. Flotow, and D. W. Osborne, J. Chem. Phys. 48, 155 (1968).

[14]J. G. Endriz and W. E. Spicer, Phys. Rev. B 2, 1466 (1970).

[15]D. E. Eastman, unpublished.

[16]A complete description of this work will be given in the Proceedings of the Sixteenth Annual Conference on Magnetism and Magnetic Materials held at Miami Beach, November 1970 (to be published).