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Optical constants of gadolinium and terbium films obtained from *in situ* reflection measurements in ultra high vacuum

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Abstract. The optical constants n , k and $\sigma(\omega)$ of paramagnetic gadolinium and terbium have been determined from *in situ* reflection measurements on opaque films prepared in ultra high vacuum ($\sim 10^{-10}$ Torr). Optimized reflection ratio measurements at oblique incidence in the photon energy range 1.8 to 3.1 eV give evidence of direct optical transitions at 1.95, 2.15, 2.50, 2.75 and 3.1 eV for gadolinium and at 1.90, 2.20 and 2.45 eV for terbium. Deductions from electronic band structure calculations for the bulk materials predict optical transitions at 2.0, 2.2, 2.4 to 2.6, 2.8 and 3.1 eV for gadolinium, and at 1.9, 2.2 and 2.5 eV and other energies for terbium. Previous experimental work on gadolinium has failed to isolate these predicted transitions, and no previous n , k or $\sigma(\omega)$ values exist for terbium.

1. Introduction

There is an increasing research interest at present in the optical properties of the rare earth metals as a means of testing electronic band structure calculations. In this paper we describe the behaviour of the optical constants n , k and $\sigma(\omega)$ of paramagnetic gadolinium and terbium over the visible part of the spectrum (1.8 to 3.1 eV). The complex refractive index of a metal is defined in terms of n and k ($\tilde{n} = n - ik$), and the optical conductivity $\sigma(\omega)$ at an angular frequency ω is given by $\sigma(\omega) = nk\omega/2\pi$. The variation of $\sigma(\omega)$ with the photon energy $\hbar\omega/2\pi$ gives information about the optically induced electronic transitions within the metal, and therefore provides a check on the theory used to predict such transitions. Deductions from electronic band structure calculations for gadolinium and terbium predict a large number of optically excited transitions for photon energies between 1.8 and 3.1 eV. One of the purposes of optical studies is therefore to investigate the existence of such transitions.

There have been three published accounts concerning measurements of the optical properties of gadolinium. Schüler (1966) and Pétrakian (1972) examined gadolinium above 289 K, the Curie point, and Hodgson and Cleyet (1969) investigated both paramagnetic and ferromagnetic states. All three studies produced $\sigma(\omega)$ dispersion curves over a wide energy range, which show no evidence of individual, direct optical transitions in the visible part of the spectrum. There is, moreover, considerable disagreement between the shapes of the three curves. There is no detailed published account of optical experiments on terbium, but Schüler and Pétrakian each give a dispersion curve of transmission through a thin, paramagnetic terbium film.

Gadolinium and terbium are easily oxidized and react with other atmospheric gases

almost as readily. It is therefore necessary to prepare samples, for subsequent optical studies, by evaporating the metals onto substrates at very low pressures. Hodgson and Cleyet (1969) prepared their films of gadolinium in vacua of approximately 10^{-8} Torr and Pétrakian prepared his films under an initial vacuum better than 5×10^{-10} Torr.

In this paper we demonstrate that individual optical transitions in paramagnetic gadolinium and terbium can in fact be observed. In view of the importance of specimen preparation in this type of work, we describe in some detail the method used to obtain opaque films at pressures in the 10^{-10} Torr range for subsequent *in situ* reflection measurements. Values of n and k were deduced by the optimized reflection ratio technique (measurement of $R_{\parallel}/R_{\perp}$ at two selected angles of incidence), devised by Miller *et al* (1972). This is followed by a simple interpretation of the observed $\sigma(\omega)$ dispersion curves, and a comparison is made between these curves and those previously obtained.

2. Specimen preparation

The ultra high vacuum (UHV) system used in the preparation of, and experiments with gadolinium and terbium films, has been described in detail by Taylor (1972) and Julien (1973). It was designed for thermal evaporations of rare earth metals and subsequent *in situ* optimized reflection measurements of the evaporated films.

The system consists of a service chamber containing equipment required for thin film production and manipulation, together with a UHV pumping group. All vacuum components are of stainless steel and the optical access ports for reflection measurements are of fused quartz, so that the system is bakeable to 300°C . A diode ion pump with titanium elements gives a pumping speed of 140 l s^{-1} and reduces the pressure to approximately 1×10^{-9} Torr in the service chamber after baking. In addition, a four element titanium sublimation pump and an internal liquid nitrogen tank, give an estimated speed of 4000 l s^{-1} . The pumps produce an ultimate pressure of approximately 3×10^{-10} Torr within the main chamber. The total integrated pressure is measured by a Bayard-Alpert ionization gauge, and the residual gas partial pressures are analysed by a mass spectrometer. A typical residual gas composition before and after an evaporation is given in table 1.

Table 1. Residual gas composition within main chamber of UHV system before and after evaporation

Residual gas constituent	Partial pressure (Torr)
H ₂ O	1.2×10^{-10}
N ₂ + CO	8×10^{-11}
CO ₂	2×10^{-11}

Evaporant material from a tungsten filament in the main service chamber falls normally onto a vertical substrate at a distance of 18 cm. The substrate may be manipulated by means of a goniometer head in the top of the chamber. The evaporant beam may be externally shuttered and is also screened from the optical ports. Shutter and screens, substrate holder and supports are made of electropolished stainless steel.

Before placing the tungsten evaporation filament in the UHV chamber it is electrically heated to white heat in an ordinary high vacuum (OHV) system and then allowed to cool

in a pressure of approximately 10^{-6} Torr. The evaporation filament was removed from the OHV system and lengths of 99.9% pure gadolinium (Koch Light Laboratories Ltd) or 99.9% pure terbium wire (Rare Earth Products Ltd) were placed within the filament helix. The loaded filament was heated in the OHV system to melt and partially evaporate the gadolinium or terbium. This OHV treatment outgasses both filament and evaporation material to approximately 2×10^{-6} Torr, and thereby saves considerable time when outgassing these items in the UHV system.

The substrates were float glass microscope slides and each was cleaned in the following way: a slide was immersed in a solution of 'Decon 75' (a cleaning agent for glass, made by Medical Pharmaceutical Developments Ltd) so that it did not touch the walls of the containing beaker. The beaker and slide were then placed in an ultrasonic cleaner for about an hour. After ultrasonic cleaning the 'Decon 75' was displaced by passing a continuous flow of distilled water into the bottom of the beaker. A few tens of litres of distilled water were sufficient to rinse away the cleaning fluid. The slide was removed from the water, rapidly dried in a current of dry nitrogen and then mounted in the substrate holder inside the UHV system. The cleaning procedure prevented any film of cleaning agent or dust from forming on the substrate surfaces.

Normal vacuum practice is to anneal substrates by heating them for an hour or so under vacuum, before evaporation, so as to relieve surface stresses and release adsorbed gases. In our case, the substrate is annealed during the bakeout cycle, during which the whole vacuum system is at a temperature of 280°C and the pressure below 10^{-6} Torr. Bakeout lasts 48 h during the latter part of which the pressure is in the 10^{-8} Torr range.

Once bakeout was finished and the base pressure had been reached, a further outgassing of the filament and its charge was performed as follows: the filament was heated until the pressure in the system rose into the 10^{-9} Torr range at which point the current through the filament was switched off to allow it to cool and the pumps to clear the evolved gases. Successive heating and cooling of the filament finally gave an equilibrium pressure of less than 8×10^{-10} Torr during the pre-evaporation onto the shutter. This procedure produced some very low pressures during evaporation of the gadolinium and terbium. Gadolinium films were obtained by heating the filament with a current of 55 A for about 120 s during which time the pressure in the service chamber, measured with the Bayard-Alpert gauge, remained at or below 8×10^{-10} Torr. The temperature of the substrate surface was 27°C during the evaporation. Interferometric thickness measurements on a number of gadolinium films, showed the films to have height variations of no more than ± 2 nm about a mean thickness of 140 nm. Terbium was evaporated onto glass substrates in exactly the same way, but pressures before and during evaporation were generally lower than the gadolinium. Base pressures of $6\text{--}8 \times 10^{-11}$ Torr were usual after the UHV outgassing and preliminary evaporation, and pressures during evaporation were $3\text{--}5 \times 10^{-10}$ Torr. The residual gas composition before and after evaporation was similar to that obtained previously. Evaporation rates of about 1 nm s^{-1} were used in producing films of terbium 140 nm thick.

It is important with reactive materials such as gadolinium and terbium to have fast evaporations and to have a rapid return to base pressure after the evaporation has stopped. The first requirement was achieved by producing films in *one* evaporation, and the second requirement met by using fast pumps, which achieve a base pressure 30 s after stopping the evaporation. The very low residual gas pressures in the system meant that subsequent optical reflection measurements from the film surface could be completed at any time within about 10 h of film growth, during which time only about a monolayer of residual gas would arrive at the surface.

3. The reflectometer and method of reflection measurement

Optical constants n and k of the gadolinium and terbium films prepared in UHV were obtained from *in situ* measurements of the reflection ratio $R_{\parallel}/R_{\perp}$ at two angles of incidence. The determination of n and k values from measurements of $R_{\parallel}/R_{\perp}$ at two angles of incidence, from surfaces of bulk material and nontransmitting films, was first used by Avery (1952). The method has been studied in detail by Miller and Taylor (1971) as a method of obtaining n and k of transmitting films of material. All three workers used graphical techniques of extracting n and k values from the reflection ratio measurements. However, a computational technique has been developed (Miller *et al* 1972), which relieves the tedium of drawing graphs, for deducing n and k values from the reflection measurements obtained from surfaces of bulk material and opaque films. Experimentally, the reflection ratio method has many advantages and these have been stated by Avery (1952) and Miller and Taylor (1971). In addition, the method can be optimized so that angles of incidence may be chosen for a given degree of uncertainty in the measured quantities, (Miller *et al* 1972, and Julien 1973). In this way, the optimum design may be produced for a reflectometer capable of measuring $R_{\parallel}/R_{\perp}$ at two angles of incidence from film surfaces within the service chamber of the UHV system. The design, construction and performance of such a reflectometer have been described by Julien (1973) and therefore we only give a brief description here.

The instrument utilizes a white light source, a graded wavelength filter for producing monochromatic light, a quartz collimator, a Glan-Thomson prism for polarizing the light beam incident on the film and a photomultiplier (EMI 9558QB) which can be set to receive either the incident beam or the reflected beam from the film surface, through the optical ports in the UHV system. Voltages across the photomultiplier anode load resistor are recorded by a digital voltmeter with a five digit display.

The light source is a vertical filament 200 W quartz iodine bulb mounted in a water cooled housing and powered by a stabilized D/C supply. Measurements with the photomultiplier and voltmeter showed short term fluctuations in the light output of 1 or 2 in the fifth digit displayed, and there was no drift over times of less than 30 min. Measurements of $R_{\parallel}/R_{\perp}$ could be obtained in times much less than this.

A parallel beam of light emerges from the collimator with a maximum divergence of less than 2 mrad and the optical path length from collimator to film surface is 80 cm. The light then passes into the monochromator, which is a circular graded wavelength filter, housed in a light tight box, and is calibrated to transmit light of any wavelength in the range 400–700 nm (3.2–1.8 eV) with a maximum half band width of ± 10 nm. The monochromatic beam of light then passes through a Glan-Thomson prism, which is mounted in a circular scale, coaxial with the collimator, by means of which the polarization azimuth may be set to within $\pm 0.1^\circ$. The light incident on the specimen can thus be polarized perpendicular or parallel to the plane of incidence.

Incident or reflected light passes through a ground glass screen placed immediately in front of the flat end window of the photomultiplier. It was found advantageous, in terms of noise level, to set the photomultiplier cathode voltage to considerably less than the permissible maximum, but still within the linear portion of the tube's characteristic curve.

Before commencing a set of reflection measurements, the incident beam was calibrated to give the incident intensity ratio, of light polarized perpendicular and parallel to the plane of incidence. This calibration was carried out over the entire spectral range in photon energy steps of 0.1 eV. Preliminary determinations of the optical constants

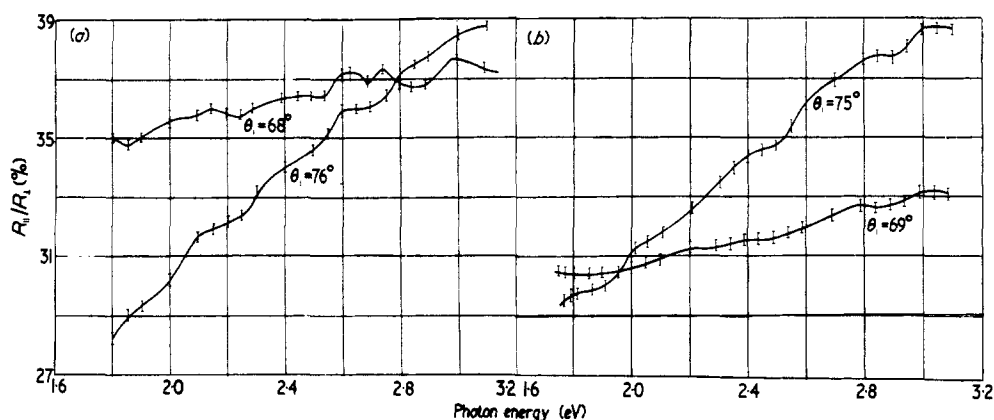


Figure 1. Reflection ratio $R_{||}/R_{\perp}$ for (a) gadolinium and (b) terbium measured at two angles of incidence.

of gadolinium and terbium obtained by Taylor (1972) allowed suitable angles of incidence to be selected (Miller *et al* 1972) for measuring $R_{||}/R_{\perp}$ from films in the UHV system. These angles of incidence were set and measured from the calibrated rotational part of the goniometer head which controlled the orientation of the film with respect to the incident light beam. Angles could be measured to within $\pm 0.2^\circ$. Reflection ratio measurements for gadolinium were made at angles of incidence of 68° and 76° and for terbium at 69° and 75° . Reflection measurements over the entire spectral range were completed at one angle, the angle changed and measurements completed at the other angle. This procedure was preferable to obtaining both measurements together for each wavelength, because repeated rotation of the film between the two angles could cause spurious effects through small differences in angle of incidence. For one film of each material the reflection ratio $R_{||}/R_{\perp}$ at each wavelength was determined several times and the mean square uncertainty was found to be $\pm 0.3\%$ for all wavelengths. The reflection measurements on films of each material were completed within 4 h of growth.

4. *In situ* reflection ratio measurements in the energy range 1.8–3.1 eV

Figures 1(a) and 1(b) show plots of $R_{||}/R_{\perp}$ against photon energy ($\hbar\omega$) obtained at the angles of incidence shown, for a gadolinium and a terbium film respectively. Both films were 140 nm thick. In both figures we note that: (i) there is a larger variation of $R_{||}/R_{\perp}$ with photon energy at the higher angle compared with that at the lower angle of incidence, and (ii) the curves at both angles show considerable structure.

The results shown in figure 1 are typical of those obtained on five gadolinium and four terbium films. The general shape of each curve was the same, and structure appeared at photon energies which differed from film to film by only ± 0.05 eV.

5. Film surface and structure

Some gadolinium and terbium films were examined by scanning electron microscopy

and x ray reflection diffraction. This necessitated removal of the films from the UHV and so we are not sure that the properties revealed by these studies existed during the reflection measurements in UHV. The electron microscope studies showed no significant surface details, other than one or two minor tears probably caused by handling, and also that the films were smooth on a scale sufficient for valid optical measurements (Taylor 1972). The x ray diffraction produced weak, arced patterns typical of a textured polycrystalline deposit and consistent with the hcp structure of both metals, with c/a ratios close to those reported in the literature. It was estimated that the film grain size was greater than 25 nm in a direction perpendicular to the plane of the film and less than 15 nm in the film plane. The relative intensities of the diffraction arcs indicated some fibre orientation with a (0001) plane parallel to the film surface. This means that in both the gadolinium and terbium films a proportion of crystallites lay with their c axis perpendicular to the plane of the film. We are reasonably sure, therefore, that the films produced in the UHV system were polycrystalline with some degree of preferred orientation.

6. The optical constants and optical conductivity of gadolinium and terbium

Optical constants n and k , and associated errors Δn and Δk arising from the uncertainties in $R_{\parallel}/R_{\perp}$ and θ , were deduced from the reflection ratio data using the computational scheme of Miller *et al* (1972). Table 2 gives n and k values and estimates of Δn and Δk obtained from typical gadolinium and terbium films. The n and k values at each wavelength for different films of the same material fell within $\pm 10\%$ of calculated mean

Table 2. Optical constants of gadolinium and terbium and associated errors for energies 1.80–3.10 eV

Photon energy (eV)	Gadolinium				Terbium			
	n	k	Δn	Δk	n	k	Δn	Δk
1.80	2.34	3.28	± 0.013	± 0.015	1.82	2.55	± 0.016	± 0.002
1.85	2.20	3.14	± 0.010	± 0.011	1.82	2.55	± 0.017	± 0.003
1.90	2.19	3.14	± 0.011	± 0.013	1.80	2.54	± 0.018	± 0.006
2.00	2.10	3.10	± 0.013	± 0.018	1.67	2.38	± 0.033	± 0.035
2.10	1.96	2.98	± 0.010	± 0.014	1.62	2.32	± 0.038	± 0.047
2.15	1.95	3.00	± 0.011	± 0.015				
2.20	1.91	2.93	± 0.012	± 0.018	1.57	2.26	± 0.043	± 0.061
2.25	1.88	2.89	± 0.010	± 0.015				
2.30	1.79	2.82	± 0.010	± 0.015	1.48	2.11	± 0.049	± 0.081
2.40	1.73	2.77	± 0.010	± 0.016	1.42	2.02	± 0.053	± 0.102
2.50	1.70	2.74	± 0.009	± 0.016	1.40	1.97	± 0.054	± 0.107
2.60	1.60	2.66	± 0.009	± 0.017	1.30	1.80	± 0.057	± 0.139
2.70	1.59	2.62	± 0.009	± 0.017	1.27	1.75	± 0.057	± 0.148
2.75	1.58	2.64	± 0.009	± 0.018				
2.80	1.48	2.46	± 0.008	± 0.016	1.23	1.68	± 0.056	± 0.162
2.90	1.45	2.41	± 0.008	± 0.017	1.23	1.70	± 0.056	± 0.160
3.00	1.43	2.44	± 0.008	± 0.018	1.19	1.58	± 0.055	± 0.178
3.10	1.41	2.39	± 0.008	± 0.017	1.19	1.58	± 0.055	± 0.181

values. Figures 2(a) and 2(b) show the optical conductivity $\sigma(\omega)$ of a gadolinium and terbium film, each plotted as a function of photon energy. In §8 we compare these curves with those obtained by other experimenters.

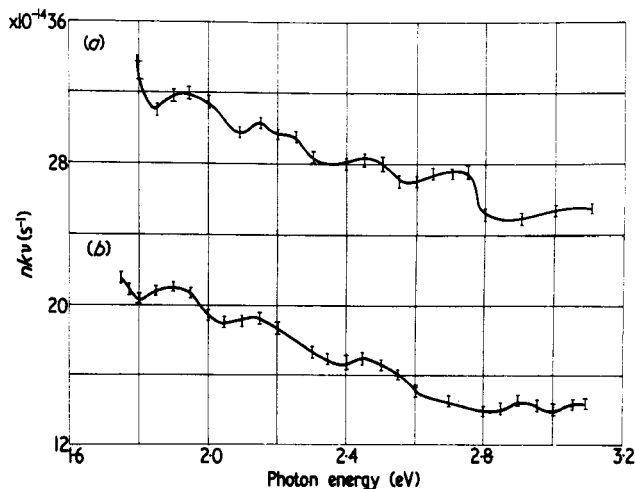


Figure 2. Observed dispersion of optical conductivity for (a) gadolinium and (b) terbium.

In figure 2(a) we notice distinct peaks in the $\sigma(\omega)$ curve at photon energies: 1.95, 2.15, 2.50, 2.75 and 3.1 eV. Such peaks were found in all the curves obtained from the different gadolinium films, and their positions varied by no more than ± 0.05 eV from film to film. In figure 2(b), the curve for terbium, peaks occur at photon energies: 1.9, 2.15 and 2.45 eV. Of these peaks, the first two varied in position from sample to sample by no more than ± 0.05 eV, but the peak at 2.45 eV did not vary in position from one sample to the next. All the terbium films investigated gave $\sigma(\omega)$ curves with some rather ill defined structure in the energy range 2.7 to 2.9 eV, and we are reluctant to quote any peak positions in this range.

7. Interpretation of the optical conductivity curves

In order to explain the optical conductivity curves of gadolinium and terbium it is necessary to know the electronic configuration of the neutral atoms. All of the rare earth metals have, as a stable inner core, the electronic configuration of xenon. The rare earth electron structure is given in general by

$$\text{Xe}(1s-4d)4f^n5s^25p^65d^{(1)}6s^2 \quad n = 0-14.$$

The parenthesis for the 5d state is used to indicate that in many of the elements, once the 4f shell contains electrons, the 5d electron is transferred to the 4f shell. For gadolinium $n = 7$, and for terbium n has been variously reported as 8 or 9. The atomic numbers of gadolinium and terbium are 64 and 65 respectively. Starting potentials derived from electronic configurations and the symmetry properties of the crystal lattice have been used to derive the electronic energy bands for gadolinium (Dimmock and Freeman 1964, and Dimmock *et al* 1966) figure 3 and terbium (Jackson 1969) figure 4. Selection

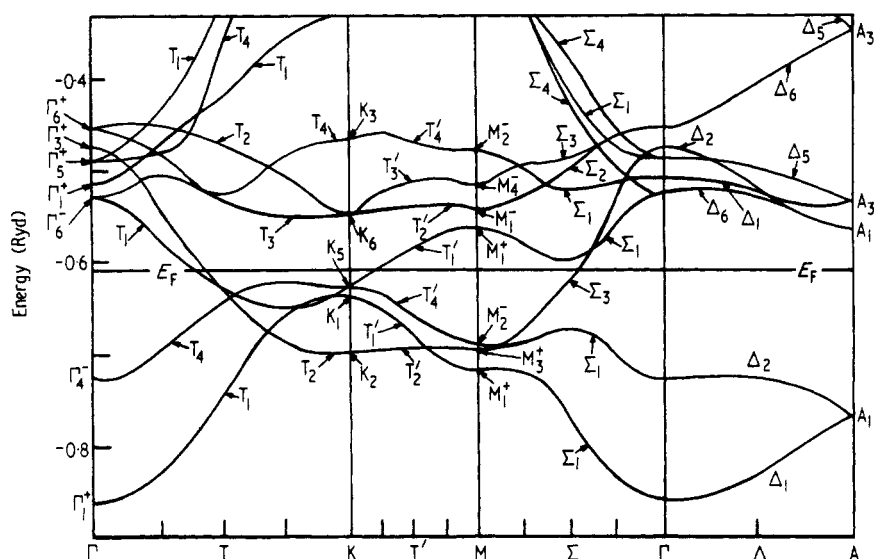


Figure 3. Electronic band structure diagram for bulk hcp gadolinium (Dimmock and Freeman 1964).

rules for predicting how optically excited electrons can move from one energy band to another have been derived for the hcp crystal lattice by Pétrakian (1972). From the symmetry conditions, we would expect the bands to be of zero slope, and therefore parallel, at symmetry interband points; thus, at these points there is a high joint density of states. Where the joint density of states is high, optical transitions are likely, resulting in observable changes in slope of the $\sigma(\omega)$ curve. It is, therefore, reasonable to expect that many, if not all, of the features in the experimental $\sigma(\omega)$ curves, may be due to transitions, at symmetry interband points, from below to above the Fermi level. Our interpretation of the $\sigma(\omega)$ curves of gadolinium and terbium is presented on this basis, and is given in the usual group theory notation.

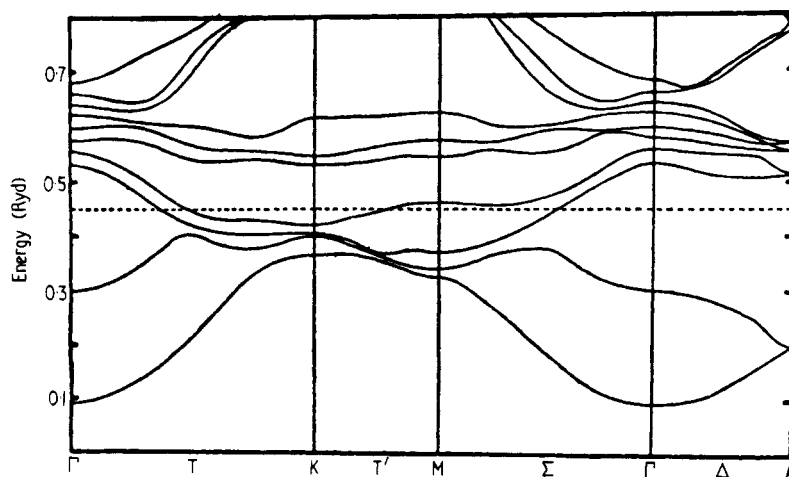


Figure 4. Electronic band structure diagram for hcp terbium (Jackson 1969).

Table 3. Allowed optical transitions between certain symmetry points for first Brillouin zone of hcp Gd

Symmetry direction	Symmetry points of allowed transition		Associated energy (eV)
M	M_2^-	M_1^-	1.76
M	M_3^+	M_1^-	2.045
K	K_2	K_6	2.045
K	K_3	K_3	2.24
M	M_3^+	M_4^-	2.385
H	H_2	H_1	2.44
L	L_1	L_1	2.44
L	L_1	L_2	2.48
H	H_1	H_1	2.58
M	M_1^+	M_4^-	2.79
A	A_1	A_1	2.84
M	M_3^+	M_2^-	2.93
K	K_2	K_3	3.17
A	A_1	A_3	3.185

Table 3 gives the allowed optical transitions between certain symmetry points within the first Brillouin zone of the hcp crystal lattice of gadolinium. These points were selected for their relevance to our photon energy range (1.8 to 3.1 eV), and were compiled assuming no spin-orbit coupling.

In order to predict at what photon energies structure should occur in the $\sigma(\omega)$ curve, the following procedure was adopted. We made the simplifying assumption that all the allowed transitions, given in table 3, were equally probable. Furthermore, the optical absorption, measured by the quantity $\sigma(\omega)$, arising from interband electronic transitions at a photon energy E was assumed to be proportional to the number of allowed transitions in the range $E \pm \delta E$. From table 3 the interband points corresponding to optical transitions were obtained, and the associated energy differences between these points obtained from figure 3. The number of possible transitions at each value of E in the range $E \pm 0.05$ eV could then be obtained for values of E from 1.8 to 3.1 eV, the experimental range of energies. A plot of the number of allowed transitions at each photon energy versus photon energy is shown in figure 5(a), where the energy scale is the same as in figure 2(a). Clearly the peak positions shown in figure 5(a) will have an uncertainty of ± 0.05 eV, which is equal to the experimental uncertainty in the positions of the observed peaks. We hope that, despite our simplifying assumptions, plots such as figure 5(a) will give at least a good indication of peak positions in the experimental $\sigma(\omega)$ curve.

The first thing we notice when figures 2(a) and 5(a) are compared is the good energy match between the peaks in both plots. It seemed reasonable, then, to associate our experimentally observed peak positions at 1.95, 2.15, 2.50, 2.75 and 3.1 eV, with the predicted ones at 2.0, 2.2, 2.4 to 2.6, 2.8 and 3.1 eV respectively. For each observed peak we assigned likely interband transition points within the first Brillouin zone and produced a list, shown in table 4. According to this scheme the structure in the optical conductivity curve for gadolinium can be explained as being predominantly caused by direct transitions between symmetry interband points in the first Brillouin zone.

Interpretation of the observed $\sigma(\omega)$ curve for terbium can be carried out in much the same way. Figure 4 shows the energy bands of terbium calculated by Jackson (1969),

Table 4. Optical transitions in gadolinium for the energy range 1.8–3.1 eV

Transition	Energies (eV)		Assigned transition points
	Observed	Estimated	
1.95	2.00		$K_2 \rightarrow K_6$ $M_3^+ \rightarrow M_1^-$
2.15	2.20		$K_5 \rightarrow K_3$
	2.40		$M_3^+ \rightarrow M_4^-$
2.50	2.50		$L_1 \rightarrow L_2$
	2.60		$H_1 \rightarrow H_1$
2.75	2.80		$M_1^+ \rightarrow M_4^-$
3.10	3.10		$A_1 \rightarrow A_3$ $K_2 \rightarrow K_3$

who assumed an outer electronic configuration of $4f^9 5s^2 5p^6 5d^{(0)} 6s^2$. It will be noticed that the bands are not labelled as they are in figure 3. The reasons for this are associated with the methods employed by Jackson to calculate the energy bands at points in the Brillouin zone. In order to label the diagram it would be necessary to use the original computer programme to determine the appropriate symmetries at the points used. This would be a long and difficult task and so we have used a simple method of interpretation.

For gadolinium, not many electronic transitions with energies in the range 1.8 to 3.1 eV were excluded by the selection rules given in table 3. To a first approximation therefore, the selection rules may be relaxed and energy differences greater than 1.8 and less than 3.1 eV between bands below and above the Fermi level can be listed for each of the symmetry directions. These energy differences will then form a set of possible optical transition energies. As for gadolinium, we have produced in figure 5(b) a plot of the number of allowed transitions in the range $E \pm 0.05$ eV, versus energy E . Comparing figure 5(b) with the observed $\sigma(\omega)$ for terbium, figure 2(b), we again see the coincidence of peaks in both curves. The two theoretical graphs are quite similar, as are the two experimental $\sigma(\omega)$ curves. Because of the assumptions made when interpreting the terbium results, we were unable to assign symmetry interband points to all of the

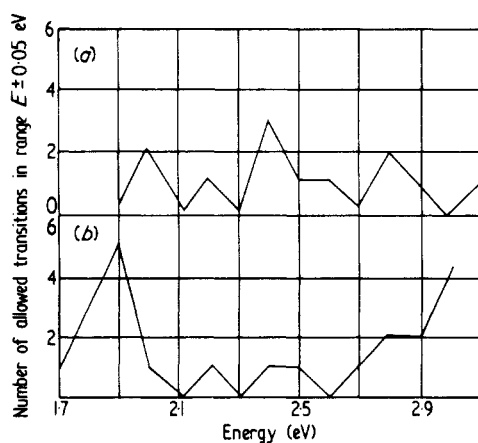


Figure 5. Theoretically estimated peak positions in $\sigma(\omega)$ dispersion curves for (a) gadolinium and (b) terbium.

peaks in the $\sigma(\omega)$ curve. However two assignments can be made. The observed peak at 2.15 eV is due to a transition along the K symmetry direction between points with a transition energy of 2.23 eV. The peak at 2.45 corresponds to a transition energy of 2.46 eV between points along the M symmetry direction. These symmetry band points were selected on the basis of the similarity at these points between the band structure diagrams of gadolinium and terbium.

8. Comparison with other experiments

Other workers have measured the optical constants n and k of gadolinium and terbium films, and deduced optical conductivity curves over a range of photon energies from 0.5 to 6 eV. Schüller (1966) obtained n and k for transmitting gadolinium films and deduced an optical conductivity curve at room temperature. He has obtained some n and k values for terbium but has not published them. Hodgson and Cleyet (1969) restricted their measurements to gadolinium for photon energies 0.5 to 2.8 eV. They deduced optical conductivity curves for gadolinium in the paramagnetic and ferromagnetic states. Pétrakian (1972) has obtained dispersion curves of reflection and transmission for a number of rare earth metals in the energy range 0.5 to 6 eV, and deduces an optical conductivity curve for gadolinium in this energy range. For terbium, Pétrakian gives only transmission dispersion curves. We can therefore only give a comparison of our results with other workers for gadolinium, and the results for terbium must stand alone.

Figure 6 shows all the different $\sigma(\omega)$ results to date for gadolinium in the energy range investigated by us. We note that the numerical values obtained by Hodgson are mostly within about 10% of the present results and show a similar downward trend with increasing photon energy. Schüller obtained $\sigma(\omega)$ values which were about twice those

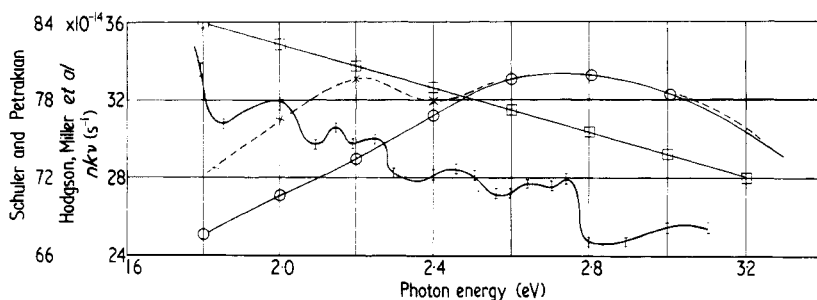


Figure 6. Comparison of various authors' $\sigma(\omega)$ dispersion curves. $\square$ Hodgson and Cleyet (1969); $\times$ Schüller (1966); $\circ$ Pétrakian (1972); $\cdot$ present work.

obtained by us. However, Hodgson suggested that Schüller's values of $\sigma(\omega)$ needed revision and this point was conceded by Schüller. The situation is further complicated in that recent results obtained by Pétrakian are in good agreement with the unrevised $\sigma(\omega)$ values of Schüller.

Figure 6 also indicates that ours is the only $\sigma(\omega)$ curve to date which shows any evidence of resolved structure. The other workers have experimented over a wider photon energy range than here, and have detected only the broader features in the optical conductivity curve. Schüller obtains an approximately flat $\sigma(\omega)$ curve between

2 and 4 eV, whilst Pétrakian's curve has a positive slope from 2 to about 2.6 eV, opposite to that obtained by Hodgson and by us. The additional detail in our curves may be due principally to higher energy resolution, and optimization of the reflectance measurements.

Possible causes of the variation between different observers' results are (i) different specimen structure and surface conditions, and (ii) different methods of measurement. Variations in the crystallographic nature and degree of surface contamination of the films prepared by different experimenters are to be expected, because of the different methods of preparation. Schüler prepared his films in ultra high vacuum but does not quote any pressures. To obtain values of k , he measured the transmission through different thicknesses of film, which he deposited sequentially, measuring the transmission after each evaporation. Producing a film by depositing successive layers at different times may be risky if the film is required for optical studies. It is possible for a layered film structure to be produced, of metal-metal oxide composition, which would be unlikely to have the same n and k as the metal alone. Although Pétrakian's system attained a static ultra high vacuum of 5×10^{-10} Torr before evaporation, the maximum pressure rise, during evaporation in the sealed vessel, was 1×10^{-6} Torr (Pétrakian 1972). Relatively insensitive normal incidence methods of obtaining the optical conductivity $\sigma(\omega)$ were used by Pétrakian, which could help to explain the difference between his results and ours. Hodgson and Cleyet (1969) used the glass-film interface of a specimen deposited on a glass prism for polarimetric determination of n and k of opaque gadolinium films. They used fast evaporation rates (200 nm s^{-1} compared with ours at 1 nm s^{-1}) and deposited their films at $6\text{--}8 \times 10^{-8}$ Torr. The base pressure of their UHV system was between 1 and 2×10^{-8} Torr, compared with our evaporation and base pressures of approximately 10^{-10} Torr. Films prepared in this way are likely to be polycrystalline with no preferred orientation. Our films, although polycrystalline, showed some degree of preferred orientation.

Although Schüler (1966) and Hodgson and Cleyet (1969) annealed their films immediately after deposition, we did not. With a reactive material like gadolinium, annealing would seem to increase the likelihood of contamination, because there will always be some further outgassing from the glass on heating, even if an attempt at outgassing has been previously made, and the outgassed material will certainly contaminate the film (Redhead *et al* 1968).

The considerable differences in experimental technique must, therefore, be borne in mind when comparing the results from the various optical studies.

9. Conclusion

The optical constants n , k and $\sigma(\omega)$ of opaque films of gadolinium and terbium in the paramagnetic state, have been determined for the photon energy range 1.8 to 3.1 eV. The observed $\sigma(\omega)$ curves of gadolinium and terbium show peaks which can be associated with optically excited transitions of electrons between interband points in the first Brillouin zone of the bulk metals.

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