

Optical properties of Gd, Dy, and Tb[†]

J. L. Erskine, G. A. Blake, and C. J. Flaten

Department of Physics, University of Washington, Seattle, Washington 98195

(Received 8 February 1974)

Optical constants in the spectral range 1.5–5.5 eV are presented for the heavy rare-earth metals Gd, Tb, and Dy. The samples are thin films prepared by vacuum evaporation at pressures below 10^{-9} torr, and are studied *in situ* using a precision ellipsometric technique. The optical spectra are broadly similar but differ slightly in their temperature dependence. The optical data complement recent magneto-optic spectra, and the significance of their difference is discussed in terms of existing electronic-structure models and the microscopic origin of the two spectra.

Index Headings: Gadolinium; Dysprosium; Terbium; Films; Ellipsometry; Refractive index; Absorption.

In this paper, optical spectra of Gd, Tb, and Dy covering the 1.5 to 5.5 eV spectral range are presented. These metals are consecutive members of the rare-earth series having respectively 7, 8, and 9 4*f* electrons, and all become ferromagnetic at sufficiently low temperature. In the atomic state, they have the same valence configuration ($5d^16s^2$) and as metals they exhibit very similar chemical and physical behavior.

Although the rare-earth metals are difficult to study experimentally as well as theoretically, the variety of unique physical properties associated with their localized 4*f* moments has attracted the attention of an increasing number of investigators. The bulk magnetic behavior of these metals has been fairly well established,¹ and primary efforts are now being directed towards obtaining a microscopic understanding of their properties. Recent theoretical work² has yielded fairly detailed band models and quantitative estimates of electronic-structure parameters; several of the standard experimental techniques, including optical absorption³ and photoemission⁴ have been used to obtain experimental data. In addition, some less-conventional experimental methods have been applied such as spin-polarized photoemission,⁵ spin-dependent tunneling,⁶ and magneto-optic measurements,⁷ all of which yield information about the magnetic electrons.

Part of our motivation for measuring optical constants of Gd, Tb, and Dy is that optical constants are needed for the reduction of magneto-optic data, and are also helpful in analyzing photoemission results. Optical properties of a few rare-earth metals have been previously studied, although not extensively. The agreement between existing optical data for rare-earth metals is poor, and in many cases the results do not agree, even qualitatively. This paper is primarily intended to fill an existing gap in available experimental information on rare-earth metals.

CONDUCTIVITY TENSOR

Because Gd, Dy, and Tb have hcp structure, the optical properties of single crystals of these metals or of polycrystalline samples with preferred alignment cannot be strictly represented by a diagonal conduc-

tivity tensor. However, measurements on polycrystalline samples with random alignment yield an average over all crystallographic directions and the conductivity can then be represented by a scalar function. This average unfortunately loses information about anisotropies associated with preferred crystal directions, but greatly simplifies the macroscopic description of optical properties. We have performed optical measurements on samples with both random and preferred orientation of crystallites and have found that the results are basically the same, indicating that the anisotropy is small.

We therefore characterize the optical behavior of these metals by using a diagonal conductivity tensor with identical elements

$$\bar{\sigma}(\omega) = \sigma_{ii}(\omega) = \sigma_{ii}^{(1)}(\omega) + i\sigma_{ii}^{(2)}(\omega), \quad (1)$$

where $\sigma_{ii}^{(1)}(\omega)$ is the absorptive component of $\sigma_{ii}(\omega)$ and $\sigma_{ii}^{(2)}(\omega)$ is the dispersive component. The optical conductivity $\bar{\sigma}$ is related to the commonly used dielectric constant $\bar{\epsilon}$ by

$$\bar{\sigma}_{ij} = \frac{i\omega}{4\pi}(\bar{\epsilon}_{ij} - \delta_{ij}). \quad (2)$$

EXPERIMENTAL METHODS

Thin-film samples were deposited onto glass microscope slides by evaporation from resistively heated Ta boats in a continuously pumped ultra-high-vacuum system. Initial purity of the starting material was greater than 99.9%; x-ray analysis of the films showed no evidence of Ta or other impurities. Sample film thickness was greater than 5000 Å, as indicated by a crystal oscillator thickness monitor. Under visual inspection, the samples appeared opaque and free of pin holes or other imperfections.

X-ray analysis of a number of samples prepared under a variety of conditions revealed that samples with a high degree of *c*-axis orientation could be routinely produced, as well as samples with basically random crystallite orientation. Films prepared on substrates held at temperatures above 573 K at evaporation rates below 10 Å/s tended to have a high degree

of preferred orientation with *c*-axis direction normal to the substrate. Films prepared at lower substrate temperatures and at higher evaporation rates tended to have more-randomly oriented crystallites.

The samples were studied *in situ* under ultra-high-vacuum conditions. The vacuum system consisted of a standard Varian ion-pumped system with cryogenic forepumps and a specially designed high-vacuum stainless steel helium dewar. With this system, samples could be prepared and maintained at temperatures from 4 to over 670 K in the ultra-high-vacuum environment. Typical pressures during evaporation of rare-earth-metal samples were in the 10^{-9} torr range. After an evaporation, the system would routinely reach its ultimate pressure in the 10^{-11} torr range with a few minutes, and would remain at that pressure.

Optical access to the sample located inside the vacuum at the He dewar tip was provided by a pair of uv-grade fused-silica windows. The window ports were on axes that intersected the sample and formed a 140.2° angle, yielding a 70.1° angle of incidence for ellipsometry. The windows were carefully annealed and checked for birefringence, to avoid errors in ellipsometric data.

Optical constants were determined by use of an automatic ellipsometric technique similar to that described by Cahn and Spanier.⁸ The ellipsometer, constructed and described by Flaten,⁹ employed a continuously rotating prism to analyze the elliptically polarized light reflected from the sample. The analyzed light was detected by a photomultiplier tube; electronic circuitry converted the signal into two voltages that were related to the ellipsometric parameters $\tan\psi$ and Δ , which represent, respectively, the ratio of *s*- and *p*-reflection coefficients and relative phase shift of the two components. The two analog voltages gave directly θ_m , the analyzer angle at which the detected intensity was a maximum, and X , the ratio of the difference between maximum and minimum intensities to the sum of the two. These two quantities are related to the conductivity $\bar{\sigma} = \sigma_1 + i\sigma_2$ by

$$\sigma_1 = (\omega/2\pi)X(1-X^2)^{\frac{1}{2}} \cos 2\theta_m \sin^2\theta_i \\ \times \tan^2\theta_i (1+X \sin 2\theta_m)^{-2},$$

$$\sigma_2 = (\omega/4\pi)\{1 - \sin^2\theta_i - \sin^2\theta_i \tan^2\theta_i \\ \times [X^2(\cos^2 2\theta_m + 1) - 1][1 + X \sin 2\theta_m]^{-2}\},$$

where θ_i is the angle of incidence. These relations come from solving for $\tan\psi$ and Δ in terms of θ_m and X and substituting in the Drude equations for ϵ_1 and ϵ_2 .⁹ A complete error analysis of the ellipsometer, as used by Flaten to study silver-alloy systems, has been performed,⁹ and we have verified the accuracy by comparing our results for silver films with well-established results of other investigators. Our values for Ag agree to within $\pm 5\%$ with the results of Johnson and Christy¹⁰ over the 2.5–5.5 eV range. Consistency checks, made by measuring optical constants of Ag at various angles of

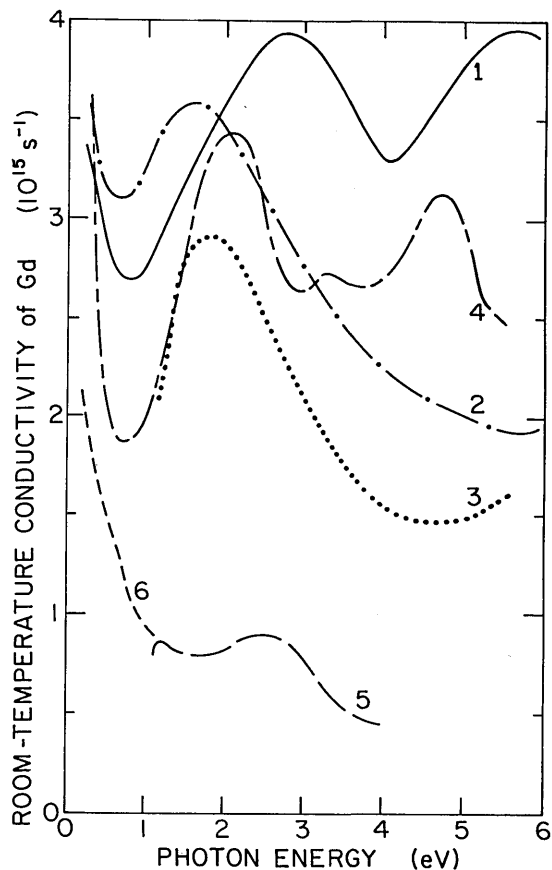


FIG. 1. Optical conductivity of Gd at room temperature after several authors (Ref. 2): 1—Petrakian, 2—Hodgson and Cleyet, 3—present work, 4—Schüler, 5—Knyazev.

incidence, show similar agreement. We believe that our data on rare-earth metals are also accurate to $\pm 5\%$ because the rare-earth metals are more strongly absorbing than Ag, and the parameters $\tan\rho$ and Δ are consequently easier to obtain with high accuracy at most wavelengths. Reproducibility of the data for separately evaporated samples was good; the structural features were always reproduced, and usually the measured spectra could be fit with less than a $\pm 5\%$ adjustment in scale factor.

EXPERIMENTAL DATA

Figure 1 shows the spectral dependence of the diagonal-element absorptive component, $\sigma_{xx}^{(1)}$, for Gd at room temperature, obtained by us, as well as results of several other authors. This figure illustrates the general disagreement that exists in the literature of the optical behavior of rare-earth metals. The basic reason for this disagreement most likely lies in the reactive nature of rare-earth metals. In many cases, adequate precautions are not taken to ensure that uncontaminated surfaces are studied.

Our room-temperature data for Gd are in fairly good agreement with the most-recent results of Hodgson

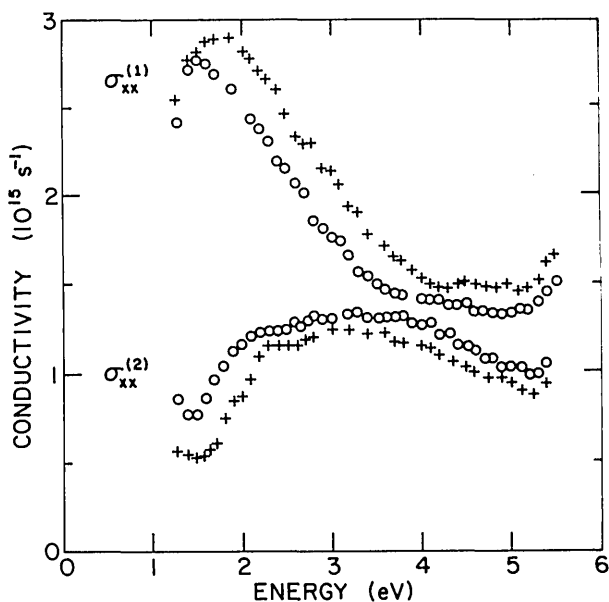


FIG. 2. Optical conductivity of Gd at temperatures above and below the Curie point, +80 K, \circ 300 K.

and Cleyet.¹¹ Petrakian's³ results, which he obtained using films held in ultra-high vacuum, utilizing reflection and transmission techniques, are an order of magnitude different than ours, and do not agree, even qualitatively. The qualitative features of Petrakian's data are somewhat similar to early results of Schüler,³ who also used reflectance and transmission methods. Some more-recent work by Schüler bears closer resemblance to our results and the results of Hodgson and Cleyet.³ The work most recently published is that of Knyazev,³ who applied ellipsometric methods to obtain optical constants of bulk Gd samples mechanically polished in a nitrogen atmosphere. We believe that the disagreement between our results and those of Knyazev are primarily due to contamination of the surface of his samples, despite his efforts to achieve smooth, uncontaminated surfaces.

The next three figures present optical spectra of Gd, Tb, and Dy at temperatures above and below their respective curve points,¹ 292.7, 219.6, and 88.3 K. Figure 2 shows the spectral dependence of the real and imaginary components of σ_{xx} for Gd at 300 K ($T > T_c$) and at 80 K ($T < T_c$). Figures 3 and 4 show the corresponding data for Dy and Tb. In all cases, the effects resulting from magnetic ordering are relatively small in the energy range investigated. In the case of Gd, the main effect appears to be a slight shift of the major peak (from 1.6 to 1.8 eV) and a slight broadening. Hodgson and Cleyet report a similar shift of the peak for Gd; however they report that the peak narrows. They also observe a new peak that occurs as a result of magnetic ordering slightly outside our energy range. Figure 5 shows the off-diagonal (magneto-optic) absorptive components $\sigma_{xy}^{(2)}(\omega)$ for Gd and Dy

normalized to full magnetic moment.^{7,12} In the discussion that follows, the relatively sharp structure exhibited by the magneto-optic spectra (as contrasted with the behavior of the optical spectra) is qualitatively related to the microscopic origin of the effect.

DISCUSSION

The general features of the optical absorption spectra of Gd, Tb, and Dy are similar which is not surprising because of the previously noted likeness of these metals. The spectral dependence is characteristically smooth and void of sharp structure that could be used to check detailed predictions of band models. The optical absorption of Gd is dominated by a broad peak centered around 1.6 eV. Band-structure calculations by Dimmock *et al.*² predict for Gd a high joint density of states in the 1–3 eV range and a large number of allowed interband transitions,¹³ which qualitatively accounts for the experimental results.

The optical absorption spectra of Dy is much broader than that observed for Gd. This suggests that the bands in Dy are more spread out in energy than those of Gd. Keeton and Loucks² calculated energy bands for several rare-earth metals, including Gd and Dy. For Gd, a potential corresponding to a free atom configuration of $4f^7 5d^1 6s^2$ was used. This was the same as the potential used by Dimmock *et al.*² in their calculations for Gd. The results agree fairly well, the main differences being splittings associated with the relativistic treatment of Keeton and Loucks. For Dy, Keeton and Loucks pointed out that there is uncertainty regarding the most-appropriate starting potential, and they therefore used starting potentials constructed from two atomic configurations: $4f^9 5d^1 6s^2$ and $4f^{10} 6s^2$. The band structures that resulted from these

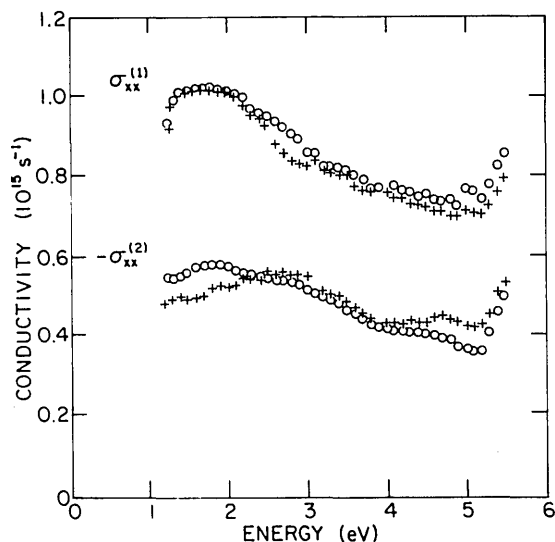


FIG. 3. Optical conductivity of Dy at temperatures above and below the Curie point, +80 K, \circ 300 K.

two potentials differ significantly. The density-of-states histogram for the $4f^{95}5d^{16}s^2$ potential is very similar to the results for Gd where, as in the case of the $4f^{10}6s^2$ potential, the conduction band is much broader, with less-pronounced peaks. The behavior of the joint density of occupied and unoccupied states for the band model based on the $4f^{10}6s^2$ potentials is in better agreement with the results of our optical measurements, suggesting that the $4f^{10}6s^2$ potential may be more nearly correct.

The temperature dependence observed in the present data is relatively small. More-pronounced temperature-dependent effects in Gd, Dy, and Tb have been observed in the 0.6–1.0 eV range by Cleyet.¹¹ The observed temperature dependence is more likely related to magnetic ordering than to lattice parameter changes. Measurements taken on Gd at temperatures up to 400 K were found to duplicate the 300 K data. In addition, the relative magnitude of the change in $\sigma_{xy}^{(2)}(\omega)$ for Gd over the spectral range covered is approximately what would be expected from the spin-polarized band calculations of Harmon and Freeman.¹⁴ On the other hand, simple arguments are unable to account for the fact that the temperature-dependent change in the Tb spectra is in the opposite direction of changes in the Gd and Dy spectra. It appears as though a suitable explanation could be based on the details of spin-up and spin-down *d*-band density-of-states of Tb, but these results do not appear to be available at this time.

The striking differences between ordinary optical absorption and magneto-optical absorption can be understood by considering the microscopic origin of the two effects. Magneto-optic effects are produced by a net spin polarization acting in conjunction with spin-

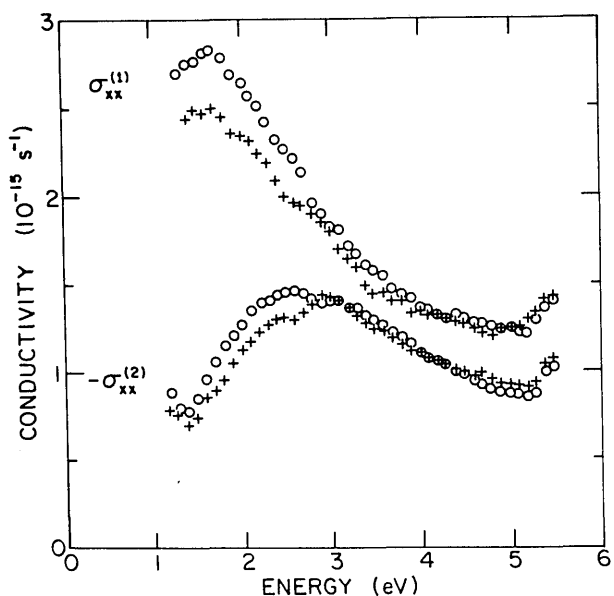


FIG. 4. Optical conductivity of Tb at temperatures above and below the Curie point, +80 K, ○ 300 K.

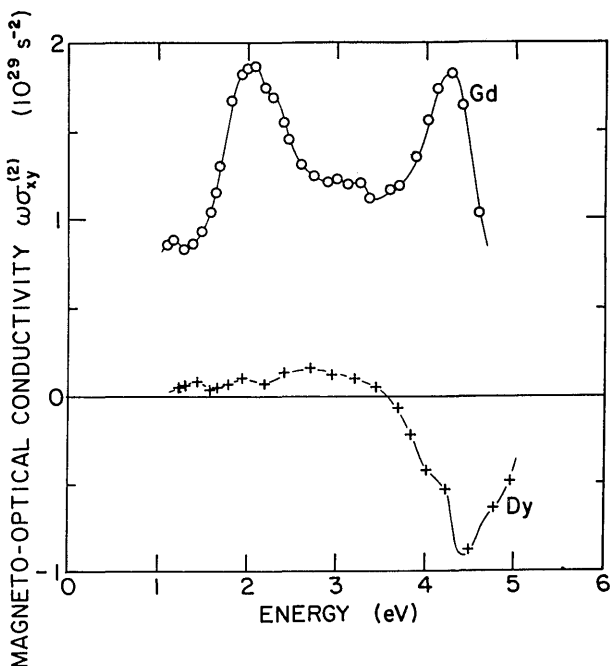


FIG. 5. Magneto-optical conductivity $[\omega\sigma_{xy}^{(2)}(\omega)]$ of Gd (○) and Dy (+) normalized to saturated moment magnetization ($T=0$). (Ref. 7.)

orbit coupling. This tends to enhance the contribution to magneto-optic effects in rare-earth metals produced by *d* states and *f* states and to suppress contributions from *s* and *p* states, even though *sp* optical matrix elements may be stronger than *pd* or *df* matrix elements. The ordinary optical absorption in Gd, Tb, and Dy results primarily from optical transitions of both *sp* and *pd* nature. In these metals, the *sp* and *d* bands are strongly hybridized and it is not appropriate to speak of *sp* or *pd* transitions in the strict sense. However, it is nevertheless justified to compare the relative weight of matrix elements. In Gd, Tb, and Dy, *sp* matrix elements are much larger than *pd* matrix elements, and therefore an appreciable portion of ordinary optical absorption is due to *sp* transitions.⁶ This is not the case for magneto-optic absorption.

The dependence of magneto-optic effects on spin polarization and spin-orbit coupling results in the magneto-optic absorption being dominated by transitions that involve *d* and *f* electrons. This has been verified quantitatively by calculations of the absolute weight of the integrated magneto-optic absorption in Gd.

In summary, the shapes of optical spectra of Gd, Tb, and Dy that we obtained by ellipsometry provide insight into the general features of the bands in these metals. Our results also show that temperature dependence of the optical spectra are not confined to the infrared region, as previously reported, but are also observed at higher energies. The distinct differences between optical and magneto-optical spectra clearly

illustrate that these two forms of spectroscopy are sensitive to different states in the solid and therefore should be considered complementary experimental techniques.

ACKNOWLEDGMENT

The authors would like to express their appreciation to B. Cleyet for useful communications concerning his work on optical properties of rare-earth metals, and to B. N. Harmon for sending his spin-polarized energy-band data for Gd.

REFERENCES

†Work supported in part by the Air Force Office of Scientific Research.

¹*Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliott (Plenum, New York, 1972).

²J. F. Herbst, D. N. Lowy, and R. E. Watson, *Phys. Rev. B* **6**, 1913 (1972). (All rare earths.) J. O. Dimmock, A. J. Freeman, and R. E. Watson, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 237. (Gd.) S. C. Keeton and T. L. Loucks, *Phys. Rev.* **168**, 672 (1968). (Gd, Dy.) C. Jackson, *Phys. Rev.* **178**, 949 (1969). (Tb.)

³C. Cr. Schüler, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 221; J. N. Hodgson and V. Cleyet, *J. Phys. C* **2**, 97 (1969); Yu. V. Knyazev, *Fiz. Met. Metall.* **30**, 214 (1970); *Fiz. Met. Metall.* **31**, 1099 (1971); *Fiz. Met. Metall.* **32**, 1189 (1971); J. P. Petrakian, *Thin Solid Films* **13**, 269 (1972); *C. R. Acad. Sci. (Paris) B* **270**, 624 (1970).

⁴F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, *Phys. Lett.* **45A**, 3, (1973); P. O. Heden, H. Lofgren, S. B. M. Hagstrom, and C. Norris, *Phys. Rev. Lett.* **24**, 1173 (1970); D. E. Eastman, *Solid State Commun.* **7**, 1967 (1969).

⁵G. Busch, M. Campagna, P. Cotti, and H. Ch. Siegmann, *Phys. Rev. Lett.* **22**, 597 (1969); G. Chrobok, M. Hofmann, and G. Regenfus, *Phys. Lett.* **26A**, 551 (1968).

⁶P. M. Tedrow and R. Meservey, *Phys. Rev. B* **7**, 318 (1973); *Phys. Rev. Lett.* **26**, 192 (1971).

⁷J. L. Erskine and E. A. Stern, *Phys. Rev. B* **8**, 1239 (1973).

⁸B. D. Cahn and R. F. Spanier, *Surf. Sci.* **16**, 166 (1969).

⁹C. J. Flaten, Ph.D. thesis (University of Washington, 1969).

¹⁰P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**, 4370 (1972).

¹¹Private communication; also see Ref. 3.

¹²E. A. Stern and J. L. Erskine, Proc. of the International Conf. on Magnetism, Moscow, Aug. 22-28 (1973).

¹³Schüler (Ref. 3) lists the allowed transitions; also see J. F. Cornwell, *Group Theory and Electronic Energy Bands in Solids* (North-Holland, Amsterdam, 1969).

¹⁴B. N. Harmon and A. J. Freeman, *AIP Conf. Proc. (U.S.A.)*, No. 10, Pt. 2, p. 1309 (1972); also B. N. Harmon (private communication).

COPYRIGHT AND PERMISSION

This Journal is fully copyrighted, for the protection of the authors and their sponsors. Permission is hereby granted to any other authors to quote from this journal, provided that they make acknowledgment, including the authors' names, the Journal name, volume, page, and year. Reproduction of figures and tables is likewise permitted in other articles and books, provided that the same information is printed with them. The best and most economical way for the author and his sponsor to obtain copies is to order the full number of reprints needed, at the time the article is printed, before the type is destroyed. However, the author, his organization, or his government sponsor are hereby granted permission to reproduce part or all of his material. Other reproduction of this Journal in whole or in part, or copying in commercially published books, periodicals, or leaflets requires permission of the Optical Society of America, Suite 620, 2000 L St., N.W., Washington, D. C. 20036.