fitted this model to the data, and the calculated form factor values are shown in Fig. 1 as the open circles. Considering the rather crude approximation for the Cl moments, the fit is remarkably good, with a $\chi^2 = 1.6$ ($\chi^2 = 1.0$ is ideal), while the fit without the Cl moments gave $\chi^2 = 17$. For clarity Fig. 3 shows the various contributions to the calculated form factor for a selected number of points. The final best-fit parameters are $\mu = 0.80\mu_B$ for the total moment, $M_{Cl} = 0.28$, and $\sigma = 0.06a$, which compare very favorably with the estimated[1,8] values of $\mu = 0.89\mu_B$ at $T = 0$ K, and $M_{Cl} \sim 0.3$. With the success of this simple model, it would certainly be desirable to have a more rigorous calculation of the magnetization density for the $IrCl_6$ complex.

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Magneto-optical Study of Gd Using Synchrotron Radiation

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The first measurements of magneto-optical effects in metals at energies above the quartz trasmission limit are reported. The discussion focuses on the results for Gd which exhibits a $4f$ transition threshold that confirms the result of recent optical studies. Details of the magneto-optical spectrum suggest that this technique provides a sensitive probe of core-state splittings as well as other features of optically excited states in ferromagnetic metals.

Recent work on ferromagnetic metals has stimulated new interest in the application of magneto-optical techniques as a probe of their electronic structure. In particular, interest in the $4f$ core levels of rare-earth metals is apparent from the x-ray-photoemission (XPS) studies of $4f$-core-state excitations[1] and from the $4f$-electron-binding-energy calculations that have recently appeared.[2] Additionally, several new experimental techniques that probe the spin polarization of conduction-band electrons in ferromagnetic metals have been developed. These techniques (spin-polarized photoemission and field emission, and spin-dependent tunneling) have raised new questions regarding the ground-state electronic structure of ferromagnets as well as the nature of the new probes.[3] The new interest in magneto-optical techniques stems from the fact that the same parameters, i.e., core-state splittings, $4f$ thresholds, spin polarization, and band properties, can, in principle, be obtained from magneto-optical studies. In addition, at energies

where core states are excited, magneto-optical measurements may provide new experimental information related to edge singularities, final-state interactions, and other many-body effects of current interest.

In this Letter, the first magneto-optical measurements of metals at energies above 6 eV are reported. Previous results have been limited to energies below the quartz transmission limit. The magneto-optical spectra of the ferromagnetic metals Fe, Ni, Co, and Gd have been determined to an energy of 12 eV; however, primary attention in the present discussion is focused on the results for Gd. In this case the excitations observed from $4f$ shells represent features that have not been observed in previous magneto-optical studies.

Magneto-optical measurements were performed at the Physical Sciences Laboratory Synchrotron Radiation Center in Stoughton, Wisconsin. A 1-m vertical Seya monochromator was used in order to maintain the high degree of linear polarization produced by the storage ring. The magneto-optical spectra were determined using the transverse configuration in which p-polarized light is reflected from a sample magnetized in the surface plane and perpendicular to the plane of incidence. In this configuration, a change in reflected intensity, ΔI, occurs upon magnetization reversal. Measurements of $\Delta I/I$ (where I is the average reflected intensity) at two angles of incidence, in addition to the optical constants, are sufficient information to calculate σ_{xy}, the off-diagonal components of the conductivity tensor, $\overleftrightarrow{\sigma}$. Measurements of $\Delta I/I$ at a third angle provide a consistency check of the data. Measurements of $\Delta I/I$ were made at 50°, 60°, and 70° angles of incidence using the experimental arrangement illustrated in Fig. 1. Samples were vacuum-evaporated thin films approximately 5000 Å thick. The Gd samples were measured at liquid-nitrogen temperature; the transition metals at room temperature. Reduction of the data is described elsewhere,[4] and a more detailed description of the experimental techniques will be given in a subsequent paper.[5]

Figure 2 shows $\omega\sigma_{xy}^{(2)}(\omega)$, the absorptive component of off-diagonal elements of $\overleftrightarrow{\sigma}$ multiplied by ω. Unlike $\sigma_{xx}^{(1)}(\omega)$, the absorptive component of diagonal elements also shown in Fig. 2, $\omega\sigma_{xy}^{(2)}(\omega)$ can have either positive or negative sign at a particular wavelength depending on whether the absorption of left- or right-circularly-polarized light dominates. The sign of $\omega\sigma_{xy}^{(2)}(\omega)$ is directly related to the spin polarization of states producing the magneto-optical absorption.[6] In Fig. 2, the dotted curve is previous data obtained using a null-detection ellipsometric method applied to the longitudinal configuration.[6] The solid line is data obtained using synchrotron

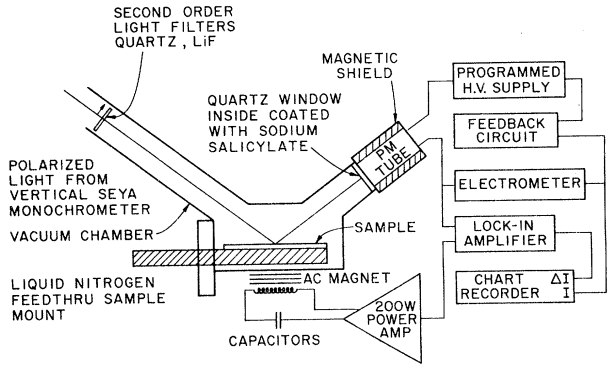

FIG. 1. Experimental setup. Light reflected from the magnetic sample has a constant component I, and an alternating component ΔI produced by the magneto-optic effect as the ac magnet reverses the sample magnetization at 33 Hz. Sodium salicylate and a photomultiplier tube convert the reflected intensity into an electrical signal. An electrometer measures I, a lock-in amplifier measures ΔI, and both of these quantities are recorded. Feedback circuitry is used to maintain I at a constant value by adjusting the tube gain. Capacitors are used to cancel the inductive reactance of the AC magnet.

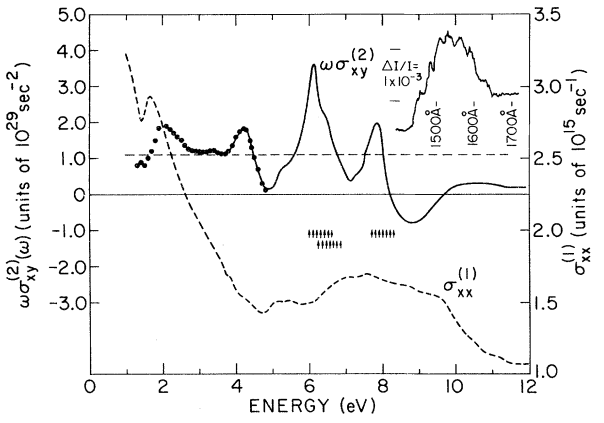

FIG. 2. Magneto-optical spectrum of Gd. $\sigma_{xy}^{(2)}$ is the absorptive component of the off-diagonal elements of the conductivity tensor $\overleftrightarrow{\sigma}$. $\sigma_{xx}^{(1)}$ is the absorptive component of the diagonal elements of $\overleftrightarrow{\sigma}$. Dotted line: previous data obtained using ellipsometric methods. Solid line: data obtained using synchrotron radiation and the transverse configuration as described in the text. Inset: structure at the 8-eV peak. Broken horizontal line: intraband component of $\sigma_{xy}^{(2)}$; see Ref. 6.

radiation as just described.

Previous model calculations estimate the absolute total weights, $\langle\sigma_{xy}^{(2)}\rangle = \int \sigma_{xy}^{(2)}(\omega)d\omega$, for interband magneto-optical absorption corresponding to allowed transitions in Gd and also predict the sign of this absorption at the threshold energy[6]:

$$\langle\sigma_{xy}^{(2)}\rangle_{p\to d} = +3.6\times 10^{28}\ \text{sec}^{-2},$$

$$\langle\sigma_{xy}^{(2)}\rangle_{d\to p} = +1.6\times 10^{27}\ \text{sec}^{-2},$$

$$\langle\sigma_{xy}^{(2)}\rangle_{f\to d} = +1.3\times 10^{29}\ \text{sec}^{-2}.$$

The weight associated with the two peaks in $\omega\sigma_{xy}^{(2)}$ at 2.5 and 4.5 eV corresponds to the calculated weight for $p \to d$ transitions, and, based on this, the magneto-optical absorption below 6 eV is attributed primarily to interband transitions from occupied p-character conduction-band states to empty d-character states. The model calculations predict that $4f$ transitions will produce magneto-optical absorption having about 3 times the total weight of the $p \to d$ transitions and with the same initial positive sign. The initial sign of the first peak and the weight of the two peaks above 6 eV are consistent with this prediction. The occurrence of two peaks is discussed later.

Recent optical absorption measurements predict a $4f$ excitation threshold in Gd metal at 6.1 eV.[7] The dashed curve in Fig. 2 illustrates this edge as it appears in the optical conductivity $\sigma_{xx}^{(1)}(\omega)$. The sum rule for the integrated number of electrons corresponding to this curve exceeds the complement (3) of Gd conduction-band electrons at about 10 eV, far below the $5p$ threshold that occurs at about 20 eV. This confirms contribution to the optical absorption in Gd by $4f$ excitations below 10 eV; the magneto-optical structure verifies the assignment of the $4f$ edge at 6.1 eV.

Previous attempts to observe $4f$ excitations in metals using optical methods have yielded inconclusive results, the primary reason being attributed to delayed oscillator strength of $4f$ transitions. The behavior of atomic oscillator strengths has been studied extensively[8] and in particular, for transitions initiating from $4f$ cores, $f \to g$ matrix elements are expected to exceed $f \to d$ matrix elements by about a factor of 5. In addition, a sharp and quickly exhausted $f \to d$ threshold is predicted, whereas the $f \to g$ transitions are delayed in energy and yield a broad threshold.[9] The same features should exist in the metal, and the experimental results basically support these predictions: The integrated number of $4f$ electrons from the optical absorption threshold ($4f^7 \to 4f^6 5d$) appears to saturate at about 1 electron rather quickly after threshold. Contributions from the six remaining $4f$ electrons presumably require exciting g-symmetry final states and hence excitation energies 20–30 eV above threshold. The reason that $4f$ electrons appear so strikingly in the magneto-optical spectrum in Gd is that they are essentially 100% spin polarized and this greatly enhances their magneto-optical properties relative to the weakly polarized conduction-band states.

Additional evidence supporting assignment of the two peaks in $\omega\sigma_{xy}^{(2)}(\omega)$ to $4f$ excitations is weak structure observed on the peaks. At high beam currents (just after injection of the ring) a series of weak bumps was resolved on both peaks using the slowest available monochromator scan rate. The structure was resolved at a signal-to-noise ratio of about 3, and checked by repeated scans at the same angle. A tracing of $\Delta I/I$ *data* at 50° angle of incidence for the 8-eV peak is shown as an inset in Fig. 2. Time limitations precluded a careful study of the fine structure, and improvements in the apparatus will be helpful in obtaining an accurate quantitative experimental description. No attempt was made to include the fine structure in the reduced data. $\omega\sigma_{xy}^{(2)}(\omega)$, because reliable fine-structure data at all angles were not obtained. No evidence of fine structure was observed in the Fe, Ni, and Co data out to 12 eV. The sequence of bumps are attributed to the $4f^{n-1}$ hole multiplet. In the case of Gd (and Eu) the initial $^8S_{7/2}$ $4f$ configuration produces a ^7F_J, $J = 0, 1, 2, \ldots, 6$ core hole, and the single peak observed in XPS studies of Gd and Eu corresponds to this unresolved multiplet. The other rare-earth metals having initially nonsymmetric (neither filled nor half filled) $4f$ shells produce final-state splittings of several eV which are easily studied with XPS. The higher-energy peak in $\omega\sigma_{xy}^{(2)}$ (8 eV) exhibits seven bumps that appear to be equally spaced in energy and have a total width of just under 1 eV. This is consistant with the expected ^7F_J-state structure assuming a breakdown of LS coupling.[10] The lower-energy peak is more complicated, indicating that several final states are involved in the excitation process near the 6.1-eV threshold. This is also apparent from the weak shoulder on the high-energy side of the main peak centered around 6 eV. The groups of arrows in Fig. 2 are placed to represent the energies associated with

the two primary and one secondary excitation energies.

XPS experiments measure a $4f$ binding energy for Gd metal of about -8 eV relative to the Fermi level.[1] The $4f$ threshold from both the optical and magneto-optical experiments is 6.1 eV, although the magneto-optical spectrum also exhibits sharp structure at 8 eV, and the shape of the optical absorption suggests that strong $f \rightarrow d$ oscillator strength extends out to about 9.5 eV. Modulation experiments typically enhance the structure of optical spectra, and the two peaks in the magneto-optical spectrum can be regarded as a more sensitive definition of the behavior of $\sigma_{xx}^{(1)}(\omega)$.

These features of the XPS and optical spectra illustrate an important difference in the two methods which can be accounted for qualitatively within the framework of a discussion of core excitations given by Combescot and Nozières.[11] If the $4f$ hole potential is sufficiently strong to form a bound state with a conduction electron, two optical thresholds are possible depending on whether the bound state is filled or empty. In the optical experiments, at threshold, the electron needed to fill the bound state is created by the threshold-energy photon, and the absolute threshold, E_{4f}, is observed. At higher energies, the photoelectron is not localized near the hole, but escapes into the crystal. If one assumes that on a short time scale (i.e., the time required for the photoelectron to escape the atom from which it is ejected) a bound state is not formed from conduction-band states, then the empty bound-state configuration is the final state sampled by XPS; and a secondary edge in the optical absorption is also seen at $E_{4f}+E_B$, where E_B is the bound-state binding energy. For the $4f$ core potential in Gd, E_B can be judged to be about 2 eV based on this model. It is interesting to note that Herbst, Watson, and Wilkins[2] have shown that the difference in binding energy of Gd $4f$ electrons assuming a fully screened core hole (neutral atom) and unscreened core hole is approximately 6 eV. The bound-state model is basically a specific way to describe two different screening configurations reached by XPS and optical excitations, and the threshold difference could be regarded as pointing to a partial rather than complete screening of the final-state XPS core hole.

In summary, the first magneto-optical study of metals above the quartz cut-off is reported. The experimental results for Gd confirm both the $4f$ optical threshold at 6.1 eV predicted by recent optical absorption studies and earlier predictions of the strength of $4f$ magneto-optical absorption. The correct strength and *sign* for predicted magneto-optical effects associated with $4f$ levels (which are known to have majority spin polarization) supports previous conclusions regarding the spin polarization of state near the Fermi level in nickel that were based on the same model.[3] Observed fine structure in the magneto-optical spectrum is consistant with the ^7F core-hole splitting, although additional work is needed to clarify the features. The magneto-optical method enhances structure seen in the optical absorption, exhibiting a secondary threshold that can be explained along with the shifted XPS edge in terms of different screening configurations around the core hole. These results suggest numerous applications of magneto-optical spectroscopy to the other rare-earth-metal ferromagnets as well as to core-state studies of other ferromagnetic metals.[12]

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Dynamic Central Peaks in a Crystalline Solid: $KTaO_3$

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Use of a computer-assisted normalization procedure and a resonant reabsorption technique has permitted frequency resolution of two central peaks in the quasielastic-light-scattering spectrum of $KTaO_3$ in the 0 to 3 cm^{-1} range. The intensities, and the polarization, temperature, electric field, and angular dependences of the linewidths indicate that the narrow component (2.3 ± 0.3 GHz at 300 K in right-angle scattering) is due to entropy fluctuations. A tentative identification of the broader component with two-phonon processes is made.

Over the past five years the existence and nature of quasielastic features (central peaks) in neutron- and light-scattering spectra of solids has generated considerable interest. Most attention has been paid to the possible role of central peaks in structural phase transitions.[1] To date such features in neutron experiments[2] and optical studies[3] have defied unambiguous spectral resolution or have been obscured by elastic-scattering or stray-light effects. The theoretical difficulty in accounting for dynamic processes in solids of sufficiently low frequency to escape spectral linewidth measurement has left open the possibility that central peaks in solids may be neither dynamic nor intrinsic to the crystal lattice. In this paper we report the first observation and spectral resolution of two kinds of central peaks in the quasielastic spectra of light scattered from crystalline solids in the frequency regime of interest in structural phase transitions. Our experimental technique permits detailed examination of weak spectral features beyond ± 500 MHz from the exciting laser frequency. Although both the linewidth and intensities of the central peaks exhibit considerable temperature dependence between 20 and 300 K, we find no evidence of divergent behavior for either feature upon approaching the ferroelectric or antiferroelectric structural transitions in the perovskites $KTaO_3$ and $SrTiO_3$. The observed results are essentially identical in the two materials. Because it remains in the simple perovskite structure (O_h^1) throughout the temperature range studied, and therefore has simpler lattice dynamics, the results in $KTaO_3$ will be emphasized here.

The spectra were excited by 150 mW of 5145-Å radiation from a single-mode Ar^+ laser. The data were obtained using a tandem Fabry-Perot interferometer with a resolution of 2 GHz and an effective free spectral range of 690 GHz (30 GHz = 1 cm^{-1}). The 5145-Å radiation allowed the use of a molecular-iodine resonant absorption cell to remove light elastically scattered by sample imperfections. The apparatus is described elsewhere[4] as is the digital normalization technique[5] employed to remove the structure introduced into the spectrum by I_2 absorptions in the vicinity of the 5145-Å line. For the present purposes the important feature of this technique is that quantitative line-shape information may be obtained despite the strong subsidiary structure introduced by the use of the I_2 cell when operated at high peak attenuation ($> 10^7$).

Typical normalized spectra are shown in Fig. 1,