TABLE I. Predicted and observed dHvA phases for the lens in cadmium.

	$\frac{1}{2} < gm^*/m_0 < 1$		$1 < gm^*/m_0 < \frac{3}{2}$	
	$p = 1$	$p = 2$	$p = 1$	$p = 2$
Hosack and Taylor ($\gamma = \frac{3}{4}$)	$\frac{7}{8}$	$\frac{5}{8}$	$\frac{3}{8}$	$\frac{5}{8}$
Free electron ($\gamma = \frac{1}{2}$)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{5}{8}$	$\frac{1}{8}$
Experimental result	$0.13_7 \pm 0.02_5$	$0.15_4 \pm 0.05$	···	···

took care to minimize interaction effects by appropriate choice of temperature. The result for $p = 1$ was $\varphi = 1.3_7 \pm 0.02_5$; for $p = 2$, $\varphi = 0.15_4 \pm 0.05$. These results are consistent *only* with the choice $\gamma = \frac{1}{2}$ and $\frac{1}{2} < gm^*/m_0 < 1$, and hence disagree with HT's conclusion.

The requirement $gm^*/m_0 < 1$ was somewhat surprising in that it implies a value of g appreciably less than 2. To check this point we performed a separate experiment in which we observed carefully the amplitude of dHvA signals from the lens with the field rotated in the $(10\bar{1}0)$ plane. Although complicated by the presence of other frequencies, the fundamental appeared to vanish over a fairly narrow angular range about 55° from the hexad axis although the second harmonic was still visible. This behavior, which is entirely consistent with the results of Grassie, is typical of a spin-splitting zero; and, taken in conjunction with the data of Galt *et al.*[5] ($m^* \sim 0.6m_0$ at 55° from $\langle 0001 \rangle$), implies $g \sim 1.6$, in support of our conclusion above.

We wish to thank Professor P. L. Taylor for informing us of his work prior to publication.

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Optical Detection of Site Selectivity for Rare-Earth Ions in Flux-Grown Yttrium Aluminum Garnet

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(Received 15 June 1971)

Linear dichroism of the optical transitions of rare-earth ions in the garnets can be used to determine growth-related site preferences. Site selectivity is detected for Pr^{3+} and Nd^{3+} in yttrium aluminum garnet but not for Eu^{3+}, Tb^{3+}, or Ho^{3+}.

Although the garnet structure is cubic, it has been found that mixed rare-earth iron garnets grown from solution show noncubic magnetocrystalline anisotropy.[1,2] The magnetic axes are related to the orientation of growth facets, and the anisotropy is believed to result from the selective incorporation of rare-earth ions into sites which, while crystallographically equivalent, are inequivalent with respect to growth direction.[3,4] That such site selectivity does indeed occur has recently been demonstrated by spin resonance measurements on Nd^{3+} and Yb^{3+} ions dilutely incorporated into yttrium aluminum garnet (YAlG).[5]

We report here a powerful new technique for measuring the relative site populations through the linear dichroism of the optical transitions of the rare-earth ion. We discuss in particular the linear dichroism of Pr^{3+}-doped YAlG. Dichroism has also been observed in the YAlG:Nd^{3+} spectrum, whereas the spectra of Eu^{3+}, Tb^{3+}, and Ho^{3+} appear to be quite isotropic for the crystals studied.

The rare-earth ions substitute for Y^{3+} on the dodecahedral sites and see a D_2-symmetric crystal field.[6] The wave functions of non-Kramers ions transform as the Γ_1, $\Gamma_2(y)$, $\Gamma_3(z)$, and $\Gamma_4(x)$ representations of D_2.[7] Electric dipole transitions between the states having different representations are polarized along one of the x, y, or z site axes, while transitions between states of the same representation are forbidden. The Pr^{3+} transitions in LaF_3 are known to be strongly electric dipole,[8] and we find from the polarization that this is also the case for Pr^{3+} and Nd^{3+} in YAlG. Consequently, we shall not consider the magnetic dipole transitions here. The wave functions of Kramers ions transform as the Γ_5 representation whatever the state, and electric dipole transitions are allowed in all polarizations. In general, the absorption cross sections will differ for different polarizations, but we do not know *a priori* by how much. While optical dichroism is possible only if sites are unequally occupied, its strength only puts a lower bound on the population difference. In non-Kramers ions, on the other hand, a quantitative determination is possible. Thus the optical method is complementary to and somewhat more general than the paramagnetic resonance technique which applies mainly to Kramers ions.

The orientations of the six magnetically inequivalent dodecahedral sites are shown in the insert in Fig. 1. Following the usual convention the local z axis of a site is chosen to be along a ⟨100⟩ crystal axis. Sites 1 and 2 are related by a 90° rotation about the site z axis. Hence, the labeling of the site x and y axes is arbitrary. We shall take the x, y, and z axes of the sites parallel to the longest, the intermediate, and the shortest dimensions, respectively, of the matchboxes in Fig. 1.

For a (110) growth facet, symmetry requires that sites 3 through 6 be equivalent. However, sites 1 and 2 are not equivalent to each other or to the remaining sites. Let the population of sites 1 and 2 deviate from the average population N by 4δ and 4ϵ, respectively. Then the site populations are

$$N_1 = N(1+4\delta), \tag{1}$$

$$N_2 = N(1+4\epsilon), \tag{2}$$

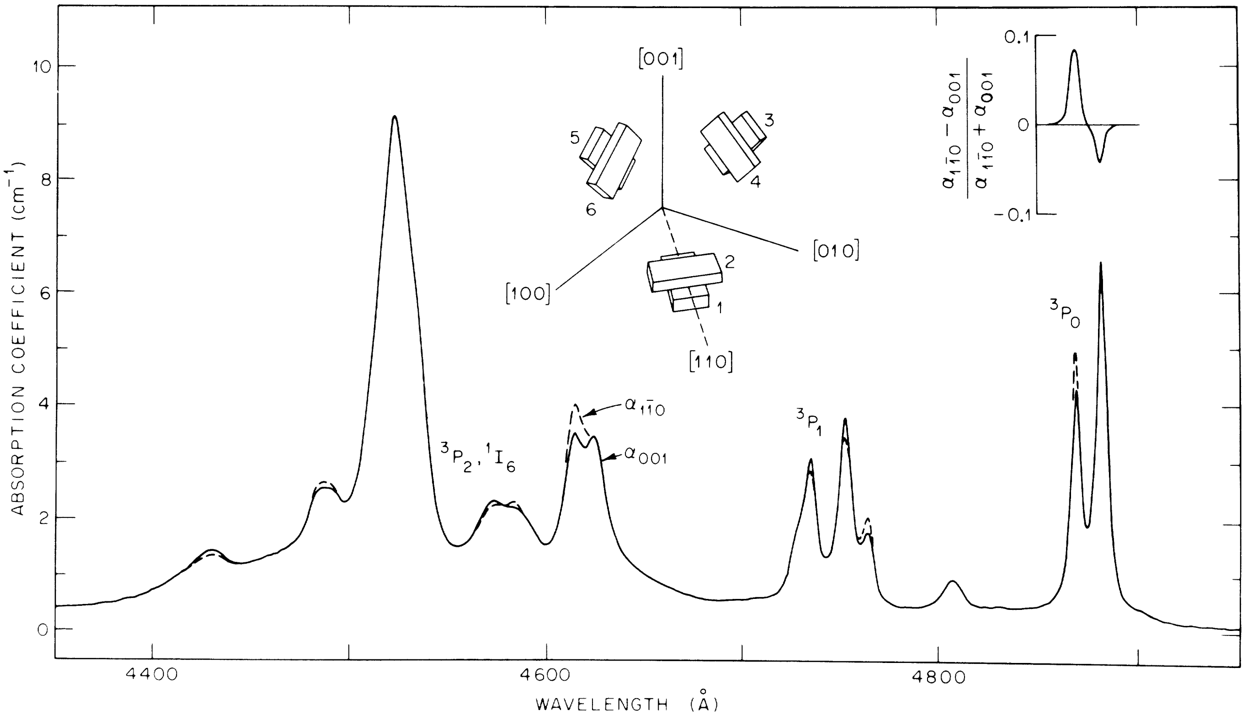

FIG. 1. The absorption coefficient of the $^3H_4$ to $^3P_0$, $^3P_1$, $^1I_6$, and $^3P_2$ transitions for radiation polarized along [001] (solid curve) and [110] (dashed curve) in YAlG:Pr^{3+} at 295°K. The polarization ratio is plotted above two of the transitions to $^3P_0$. The orientation of the six dodecahedral rare-earth sites is also shown [after J. F. Dillon, Jr., and L. R. Walker, Phys. Rev. 124, 1401 (1961)]. Our sites 1 through 6 correspond, respectively, to Z_2, Z_1, X_2, X_1, Y_2, and Y_1 in Refs. 3 and 5.

and

$$N_3 = N_4 = N_5 = N_6 = N(1 - \delta - \epsilon). \tag{3}$$

The symmetry of the second-rank absorption tensor is determined by the relative populations of the sites. When δ or ϵ or both are nonzero the cyrstal is optically biaxial and the principal axes are [110], [$1\bar{1}0$], and [100]. When $\delta = \epsilon \neq 0$, the crystal is unaxial with [001] the unique axis. In the trivial case $\delta = \epsilon = 0$ the crystal is cubic. The absorption coefficients along the principal crystallographic axes are, for a given transition,

$$\alpha_{110} = N[2(\sigma_x + \sigma_y + \sigma_z) - (\delta + \epsilon)(2\sigma_z - \sigma_x - \sigma_y) + 2(\delta - \epsilon)(\sigma_x - \sigma_y)], \tag{4}$$

$$\alpha_{1\bar{1}0} = N[2(\sigma_x + \sigma_y + \sigma_z) - (\delta + \epsilon)(2\sigma_z - \sigma_x - \sigma_y) - 2(\delta - \epsilon)(\sigma_x - \sigma_y)], \tag{5}$$

$$\alpha_{001} = N[2(\sigma_x + \sigma_y + \sigma_z) + 2(\delta + \epsilon)(2\sigma_z - \sigma_x - \sigma_y)], \tag{6}$$

where σ_x, σ_y, and σ_z are the absorption cross sections in the site coordinate frame. The significant experimental quantities are the polarization ratios

$$R = (\alpha_{1\bar{1}0} - \alpha_{001})/(\alpha_{1\bar{1}0} + \alpha_{001})$$

and

$$R' = (\alpha_{1\bar{1}0} - \alpha_{110})/(\alpha_{1\bar{1}0} + \alpha_{110}).$$

For any one transition of a non-Kramers ion, at most only one of σ_x, σ_y, and σ_z is nonzero and the polarization ratios depend on which. If $\sigma_z \neq 0$ (i.e., the transition is z polarized),

$$R_z = -3(\delta + \epsilon)/(2 + \delta + \epsilon),$$

$$R_z' = 0. \tag{7a}$$

If $\sigma_x \neq 0$,

$$R_x = (\delta + 5\epsilon)/(4 - 3\delta + \epsilon),$$

$$R_x' = 2(\epsilon - \delta)/(2 - \delta - \epsilon). \tag{7b}$$

The polarization for $\sigma_y \neq 0$ is obtained by interchanging ϵ and δ in Eq. (7b). Transitions with $\sigma_z \neq 0$ can be identified unambiguously, since if $\delta \neq \epsilon$ only they have $R_z' = 0$, while for small $\delta = \epsilon$, $|R_z|$ is twice as large as $|R_x|$ or $|R_y|$. Thus $\delta + \epsilon$ and $|\delta - \epsilon|$ can be determined from observations on three nonoverlapping transitions. The ambiguity in the sign of $\delta - \epsilon$ corresponds to the arbitrary labeling of x and y axes.

For a (112) growth facet, Eq. (3) no longer holds by symmetry since sites 3 and 5 are distinct from sites 4 and 6. The magnitude of the additional parameter, which yields the difference in the average population of sites 3 and 4, can in principle be determined from the examination of the [112], [$1\bar{1}0$], and [$11\bar{1}$] polarized spectra. Our method should therefore give useful results on (112) as well as (110) facets; however, we have confined our attention to the latter.

Samples in the form of small polished rectangular parallelepipeds were obtained from the center of exposed {110} growth facets from flux-grown YAlG doped with nominally 2% Pr^{3+} concentration.[9,10] The polished faces were, respectively, parallel to (110) (the growth plane), ($1\bar{1}0$), and (001). The polarized absorption spectra were obtained using a Cary 14 spectrophotometer. Identical polarizing sheets were used in the signal and reference beams in order to eliminate the wavelength-dependent polarizer absorption. As an instrumental check, similar anisotropic absorption spectra were obtained using a Jarrell-Ash 1-m Czerny-Turner spectrometer.

The absorption spectrum for [$1\bar{1}0$] and [001] polarization of several of the Pr^{3+} transitions in the range from 4400 to 4900 Å at 295°K is shown in Fig. 1. While some transitions overlap, and are only weakly polarized, the isolated transitions in Fig. 1 and other transitions are found to have polarization ratios of either $+0.088 \pm 0.005$ or -0.046 ± 0.007. The polarization ratios plotted above the 4868- and 4882-Å transitions are typical of the two classes. High-resolution spectra taken at 1.6°K indicate that ion pairs and clusters are not important in producing the dichroism. The ratios are substantially reduced after annealing the crystal at 1300°C for 60 h in an oxygen atmosphere. To within the experimental error of about 1%, the absorption coefficients for [110] and [$1\bar{1}0$] polarization are equal, implying that sites 1 and 2 are equally populated. From Eq. (7) we then obtain $\delta = \epsilon = -0.030 \pm 0.005$. Thus sites 1 and 2 are depopulated relative to the other sites. This result is consistent with the paramagnetic resonance investigation of 3% Nd^{3+} in YAlG by Wolfe *et al.*[5] in which, in our notation, $\epsilon = -0.064$ and $\delta = -0.078$ were found.

In addition to determining the relative site populations, the optical data allow us to distinguish Γ_3 (z-polarized) transitions from Γ_2 or Γ_4 transitions, and hence partially to determine the symmetry of the crystal field states. For example, $^3P_0$ has Γ_1 symmetry and the transitions at 4808, 4868, and 4882 Å are (x,y), z, and (x,y) polarized, respectively. Thus the 4868-Å line originates on a Γ_3 substate of $^3H_4$, while the other two originate on Γ_2 or Γ_4 substates. The above analysis can be extended to identify the transformation properties of many of the excited states. The additional information provided by the site preference results, together with the forbiddenness of transition between states of the same symmetry,[11] imposes stringent limitations in the calculations of the crystal field parameters which have not been considered heretofore.

Our sensitivity was low compared with what can be obtained using well-known modulation techniques by which polarization ratios of 10^{-5} can be measured.[12,13] Hence, the optical dichroism of the crystal can be used, in principle, to determine differences in the site population distributions as small as a few parts in 10^5. The results presented here and in Ref. 5 indicate that the largest site selectivity is obtained for ions whose radii differ most from Y^{3+}.[14] The measurement of the site selectivity may provide a detailed probe for studying the dynamics of the flux crystal growth process.

We are grateful to L. Kopf for technical assistance, and to R. C. Miller and R. Wolfe for comments on the manuscript.

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Nonmagnetic 4f Shell in the High-Pressure Phase of SmS†

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(Received 19 May 1971)

The magnetic susceptibility of SmS indicates a discontinuous and hysteretic magnetic transition at 6 kbar. The ground state of the $4f$ shell in the metallic high-pressure "collapsed" phase is nonmagnetic, contrary to Hund's rules. Nonmagnetic behavior of the $4f$ shell is correlated with an intermediate valence in SmS, SmB$_6$, and α-Ce. It is suggested that in such intermediate-valence phases at $T = 0$ the $4f$ shell is demagnetized in the sense of the Friedel-Anderson model as modified by Hirst.

Recently, pressure-induced semiconductor-metal transitions were discovered in SmTe, SmSe, and SmS.[1,2] A large volume decrease (~ 10–20%) in the transitions without change of crystal structure indicates an electronic valence change of the Sm ions which should have a profound influence on their magnetic behavior. By susceptibility measurements under pressure we have found a first-order magnetic phase transtion in SmS, as expected from the resistivity measurements of Jayaraman *et al.*[2] Quite unexpectedly, however, the Sm ions do not carry localized magnetic moments after the pressure-induced valence change. This finding, taken