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## REFLECTIVITY OF YIG AND YGG: OBSERVATION OF CHARGE TRANSFER AND CRYSTAL FIELD TRANSITIONS

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The reflectivity spectra of yttrium iron garnet (YIG,  $Y_3Fe_5O_{12}$ ) and yttrium gallium garnet (YGG,  $Y_3Ga_5O_{12}$ ) have been measured in the energy range 2–7.5 eV. Structure is observed in YIG which can be attributed to charge-transfer-enhanced crystal field transitions and in YGG to critical point transitions.

Normal incidence reflectivity methods have been extensively used to study critical point transitions in semiconductors and metals.<sup>1,2</sup> Reflectivity allows the use of bulk single-crystal specimens to investigate these very strong absorption regions ( $10^4$ – $10^7$   $cm^{-1}$ ) without the need to produce for transmission measurements thin films whose quality may be difficult to characterize. Reflectivity should also be equally useful for studying other kinds of strongly absorbing electronic systems. In recent years much attention has been given to the optical properties of the garnet class of crystals.<sup>3–8</sup> The best known of this class is yttrium iron garnet (YIG), whose chemical formula is  $Y_3^{3+}Fe_5^{3+}O_{12}^{2-}$ . The space group is  $Ia\bar{3}d$  with 8 chemical formula units per unit cell. Within this unit cell 16  $Fe^{3+}$  ions occupy octahedral sites and 24 tetrahedral sites with respect to nearest neighbor  $O^{2-}$  positions. Of particular interest have been those transitions between the crystal field split terms of the iron ions. However, it has not proved possible to push much beyond 26,000  $cm^{-1}$  because of the onset of strong charge-transfer bands and the difficulty of obtaining extremely thin garnet samples. The presence of charge-transfer at these relatively low energies also has the effect of enhancing the otherwise weak parity and spin forbidden crystal field transitions. Englman<sup>9</sup> has shown that these transitions can become quite strong by borrowing intensity from charge-transfer bands through spin-orbit and vibronic coupling. The strength of the coupling increases with decreasing energy interval between crystal field and charge transfer transitions. In the case of  $Cr^{3+}$  in  $CrCl_3$

and  $CrBr_3$ , the intensity of the  ${}^4T_1$  peak increases by an order of magnitude in the bromide over the chloride as the charge-transfer edge comes 0.36 eV closer.<sup>10</sup> We have observed what also may be such enhanced crystal field transitions superposed on a broad charge-transfer background in the reflectivity spectrum of YIG.

The garnet crystals were grown from PbO-fluxed melts with stoichiometries better than 0.5 mole-percent. Natural crystal facets were used as the reflecting surfaces. No birefringence is to be expected as the garnet unit cell is cubic. A  $\frac{1}{2}$ -m McPherson Seya-Namioka monochromator with a tungsten lamp and a hydrogen discharge tube was used as the light source. Absolute reflectivity was measured by rotating the phototube around the sample and using sample-in-sample-out technique. A liquid nitrogen Dewar in a cold-finger configuration was used for the low temperature work.

The reflection spectrum of YIG and YGG (yttrium gallium garnet) is shown in Fig. 1. The magnitude of the reflectivities can be expected to have absolute errors of up to  $-0.05$  due to irregular crystal surfaces and other alignment difficulties. The rapid drop-off in the uv part of the low temperature curve is due to the gradual deposition of water vapor on the cold sample even when ambient pressures are of the order  $10^{-6}$  torr.<sup>11</sup> The main feature of the YIG spectrum is the presence of numerous peaks superposed on a broad hump in the energy range 2–5 eV. The structure labeled by wave number in Fig. 1 was quite reproducible from run to run and also occurred at nearly the same energy

in the reflection spectrum of GdIG (gadolinium iron garnet). When the sample was cooled to 85°K, the peak structure in this region sharpened and became more distinct with very little shift in energy position. Inasmuch as YGG is devoid of such structure in the same range, these transitions must involve the 3d<sup>5</sup> levels of Fe<sup>3+</sup>. Photoconductivity data<sup>12</sup> indicate that the broad background hump is due to one or more charge-transfer bands formed from O (2p) to empty Fe (3d) transitions. The term "charge-transfer" applies rigorously only to molecular complexes and in solids has merely a descriptive meaning with respect to the degree of initial- and final-state wave function localization. As localization decreases, crystal momentum becomes a good quantum number and the distinction between charge-transfer and interband critical point transitions disappears. For iron oxides trans-

port measurements<sup>13</sup> lead to mobilities of the order 10<sup>-2</sup> cm<sup>2</sup>/V-sec suggesting a localized picture for the 2-5 eV region in iron garnets.

In Fig. 2 the positions of the YIG reflectivity peaks denoted in Fig. 1 are plotted with respect to a recently calculated crystal-field term scheme for YIG by Wood and Remeika.<sup>3</sup> The electrostatic interaction and crystal-field parameters were chosen to provide the best fit to observed absorption peaks in Ga-diluted YIG up to nearly 27,000 cm<sup>-1</sup>. Rather than attempt definite assignments to particular peaks, we only remark that some of the lower energy structures can be correlated with both calculation and transmission data for the tetrahedral Fe<sup>3+</sup> sites. In addition, the peaks at 22,200, 27,000, 35,300, and 44,200 cm<sup>-1</sup> correspond to structure found near these same energies in the transmission spectrum of a thin GdIG film by MacDonald and co-workers.<sup>8</sup> The higher energy peaks could correspond to structure in the charge-transfer band itself or to its perturbing influence on the position of high-energy crystal-field states. It is possible that the strong 27,000 and 35,300 cm<sup>-1</sup> peaks arise from critical point transitions between O (2p) and Fe (3d) bands analogous to those found by Cardona<sup>14</sup> for O (2p)-Ti (3d) in BaTiO<sub>3</sub>.

Absorption intensity determinations from reflectivity data are difficult in the absence of a Kramers-Kronig analysis. However, one can estimate ex-

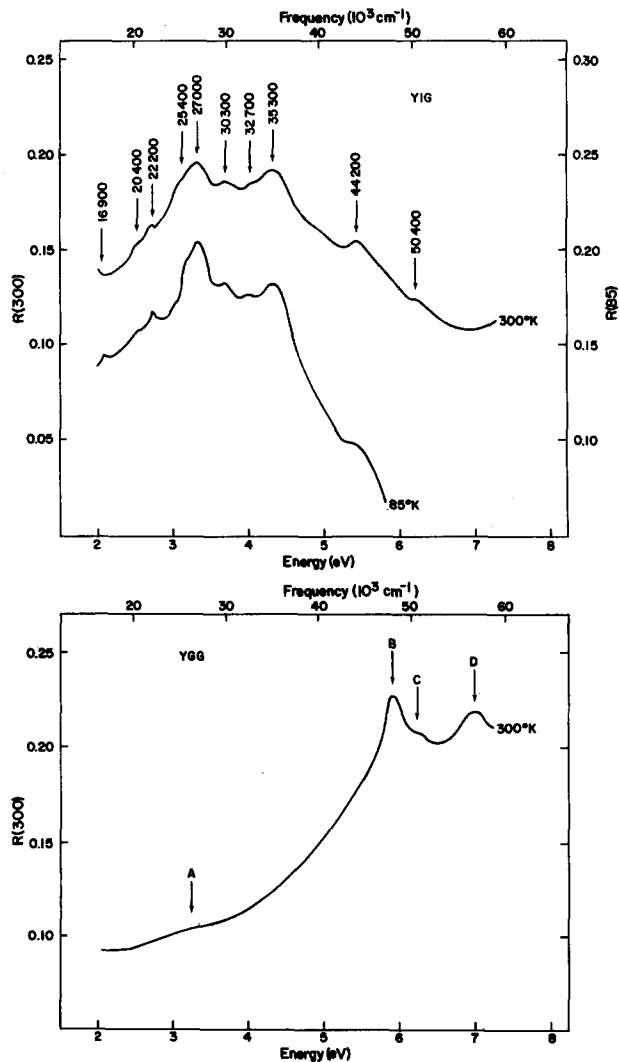


Fig. 1. Reflectivity spectrum of YIG and YGG.

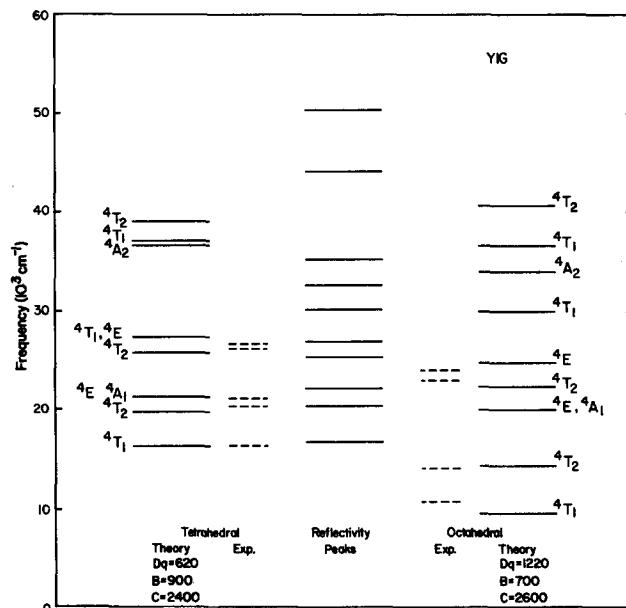


Fig. 2. Calculated crystal-field levels according to Wood and Remeika (ref. 3) for YIG. The dashed lines indicate their experimental results for Y<sub>3</sub>Fe<sub>3-x</sub>Ga<sub>x</sub>O<sub>12</sub> alloys. Where lines were found close together, we have indicated their mean position.

pected changes in reflectivity from transmission data in the following way: The relative change in reflectivity due to small changes in the optical constants  $n$  and  $k$  is given by the total differential of the usual normal-incidence reflectance formula,

$$\frac{\Delta R}{R} = A\Delta n + B\Delta k$$

$$= \frac{4(n^2 - k^2 - 1)\Delta n + 8nk\Delta k}{[(n+1)^2 + k^2][(n-1)^2 + k^2]} \quad (1)$$

In the region of the  $22,200 \text{ cm}^{-1}$  peak, we take  $n \approx 2.3$  as calculated from the reflectivity assuming no absorption and  $k \approx 0.022$  from the data of ref. 8. This gives  $A = 0.93$  and  $B = 2.2 \times 10^{-2}$  indicating changes in refractive index are much more important in this spectral range than changes in extinction coefficient. For weak Lorentzian lines,  $\Delta n \approx \Delta k$ , and taking  $\Delta k = 8.5 \times 10^{-3}$  from ref. 8 and  $R = 16\%$ , Eq. (1) gives  $\Delta R = 0.13\%$  in rough agreement with the observed change of  $0.2\%$ .

As mentioned above, the YGG reflectivity spectrum is entirely different from YIG in the energy range considered. The lack of any similarity in the two spectra suggests that the presence of yttrium is not significant until much higher energies. This is born out by the near identity between the reflectivities of YIG and GdIG. In  $\text{Ga}^{3+}$  the  $3d$  level is completely filled, hence no absorption is to be expected at low energies. The weak shoulder labeled  $A$  is believed to be due to residual impurities and is not an intrinsic effect. The coloration of our YGG samples was faintly yellow whereas very pure crystals are known to be clear. Examination of the  $2\text{--}6 \text{ eV}$  range at  $85^\circ\text{K}$  revealed no further structure. At higher energies, three peaks,  $B$ ,  $C$  and  $D$ , occur at  $5.93$ ,  $6.30$  and  $7.05 \text{ eV}$  respectively. These are probably associated with critical point transitions from  $\text{O}(2p)$  valence bands to a  $\text{Ga}(4s)$  conduction band. No consistent structure could be observed in

the region around  $5 \text{ eV}$  where Tippens<sup>15</sup> finds a transmission edge in  $\beta\text{-Ga}_2\text{O}_3$ . There are several possible explanations for this. One is that the observed transmission edge actually culminates in the  $5.93 \text{ eV}$  reflectivity peak; another is that this edge results from an indirect transition too weak to be noticed in reflectivity. If it is indeed direct, it may be weak from a density-of-states point of view and hence again be difficult to observe. Preliminary YIG reflectivity data in the range  $8\text{--}11 \text{ eV}$  indicates several peaks which may be due to analogous  $\text{O}(2p)\text{--Fe}(4s)$  transitions. More complete results for this energy range will be published soon.

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