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PHOTOCONDUCTIVITY IN GARNETS

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Photoconductivity in gadolinium iron garnet and gadolinium gallium garnet has been detected. The photoconductivity is associated with empty d-levels in the former and sp bands in the latter.

ALTHOUGH both optical[1-4] and transport[5-7] properties of several ferrimagnetic garnets, as well as for the closely related α - Fe_2O_3,[7] have been reported, photoconductivity techniques have not been applied to these materials. Such measurements should aid in differentiating inter- and intraconfigurational transitions from charge transfer-like transitions in compounds, e.g. transition metal oxides, where the cations have open shells.

In this letter we wish to report the observation of steady-state photoconductivity in gadolinium iron garnet (GdIG) and gadolinium gallium garnet (GdGaG). The specimens were high purity single crystals grown from PbO-fluxed melts[8] with a stoichiometry better than 0.5 mole percent.[9] Gold contacts 0.5 mm apart were evaporated onto a crystal facet and the incident light focused in the region of one of the contacts. All measurements were made in a vacuum of 5×10^{-6} torr; however, no influence of ambient between this value and atmospheric pressure was observed on the dark or photocurrents. The GdIG single crystals were p-type at room temperature as determined from the sign of the thermoelectric power. The room temperature dark resistivity was 3×10 Ω-cm with an activation energy ($-100°C < T < 100°C$) of roughly 0.3 eV. For GdGaG, the room temperature resistivity was 2×10^{15} Ω-cm.

Maximum photoconductivity under applied voltage occured when the area adjacent to the anode was illuminated. In addition, a short-circuit steady-state photocurrent was observed in the absence of an applied voltage. Assuming a layer depleted of positive charge to exist at the illuminated electrode, the sign of the short-circuit photocurrent indicated p-type conductivity for both GdIG (agreeing with the thermoelectric power) and GdGaG. The photocurrent under applied voltage in GdIG depended linearly on light intensity up to 80 $\mu W/cm^2$ (λ = 460 nm) beyond which saturation began. Assuming unit quantum efficiency for carrier production by 2.7 eV photons, one obtains for the mobility-lifetime product $\mu\tau = 2 \times 10^{-10}$ cm^2/V for GdIG and about one order less for GdGaG.

The photocurrent dependence on incident photon energy is shown in Fig. 1. The onset of photocurrent under applied voltage and short-circuit photocurrent for both GdIG and GdGaG occurs at energies associated with high absorption regions. We wish to emphasize that the light penetration depth was small compared to the sample thickness even for energies in the low absorption region. Hence, all incident photons were always absorbed within the current path regardless of their energy. The photocurrent under applied voltage in GdIG, as well as the short-circuit photocurrent, became immeasurably small as the temperature approached -60°C. An activation energy of 0.3 eV was determined from the exponential dependence on T^{-1} in this range. However, the photocurrent under applied voltage for GdGaG remained essentially constant down to -60°C. A small short-circuit photocurrent appeared at this temperature which did not occur at room temperature.

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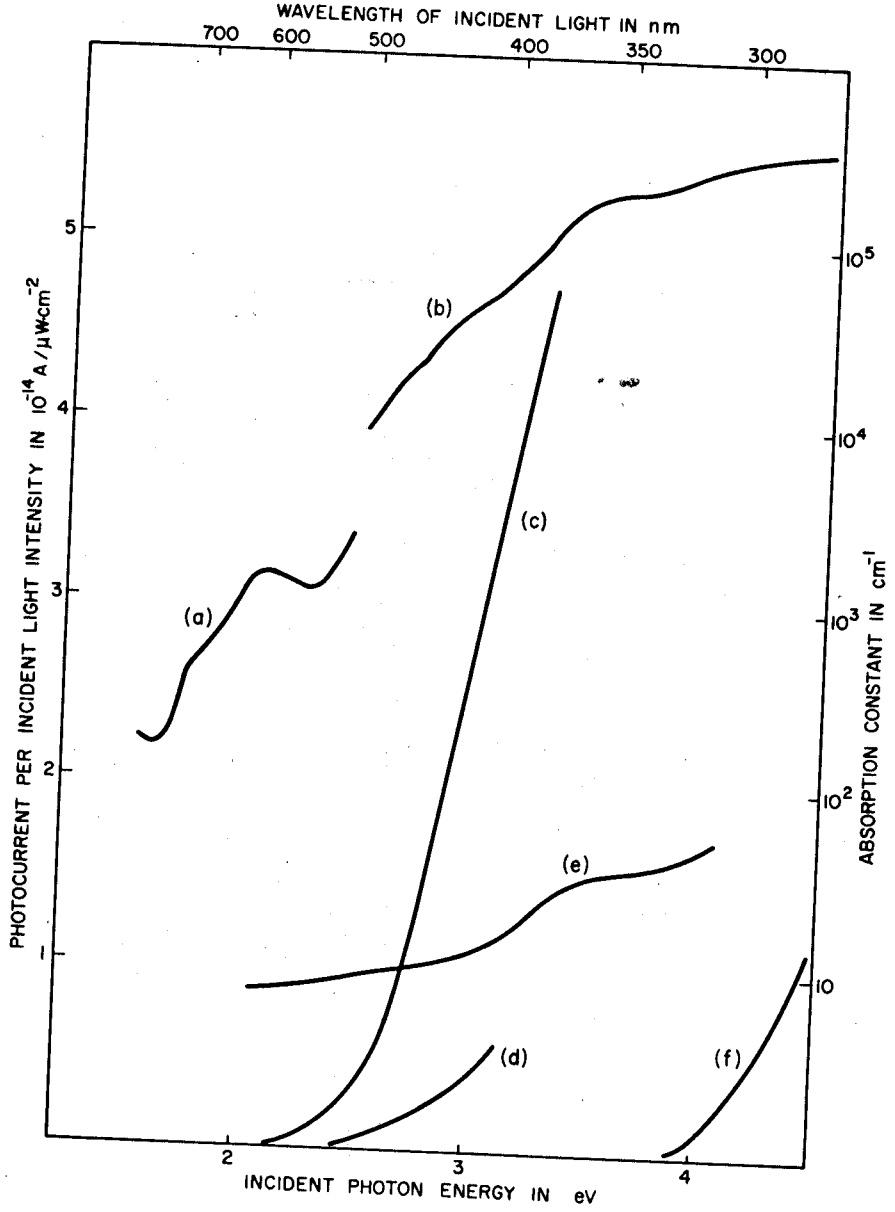

FIG. 1

Absorption and photoconductivity for GdIG and GdGaG at room temperature. (a) Absorption of GdIG according to Dillon[1]; (b) Absorption of GdIG according to MacDonald, et al.[10]; (c) Photocurrent under 20 volts applied for GdIG; (d) Short-circuit photocurrent for GdIG; (e) Absorption of GdGaG; (f) Photocurrent under 200 V applied for GdGaG.

For GdIG, two weak absorption peaks occur near 1.0 eV and 2.1 eV with strong absorptions beginning near 2.4 eV.[1] This behavior is typical of all of the ferrimagnetic garnets and α - Fe_2O_3 with only slight energy shifts involved to distinguish among them. The two peaks are associated with $3d^5\ {}^6A_1\ ({}^6S_{5/2}) \rightarrow 3d^5\ {}^4T_1\ ({}^4G)$ and $3d^5\ {}^6A_1\ ({}^6S_{5/2}) \rightarrow 3_d{}^6\ {}^4T_2\ ({}^4G)$ of the ferric octahedral coordination with the 2.4 eV absorption edge due to a charge transfer transition.[3,4] The presence of photoconductivity near 2.4 eV can be explained according to the following model.

Electronic transitions (charge transfer) occur from oxygen sp (bonding) valence band states to empty Fe 3d levels via photon absorption: $Fe^{3+} + h\nu \rightarrow Fe^{2+} +$ sp valence hole. This reaction may result in a bound Fe^{2+} —— sp hole pair. It is not clear at this point whether the optical excitation is directly to the continuum of this excitonic pair (note that the photoconductive threshold lies somewhat higher in energy than the absorption edge) or whether spontaneous dissociation into an Fe^{2+} center and a self-trapped hole occurs. The observation of roughly the same activation energy for photoconductivity as for dark conductivity is in accord with either description. Photoconductivity arising from initially non-conducting excitations has been discussed for alkali halides.[11] The separated Fe^{2+} center and self-trapped hole constitute small negative and positive polarons which are the carriers of photocurrent under both applied voltage and short-circuit conditions. The p-type dark conductivity suggests that the photoconductive activation energy ($\sim$ 0.3 eV) is the jumping activation energy of the positive polaron. This value is within the range for mobility activation in α - Fe_2O_3.[7] The absence of detectable photocurrent below -60°C for incident photon energies up to 4.5 eV indicates that either the valence-conduction band gap is above this range or that trapping of the sp hole-electron pair occurs at Fe^{3+} sites. The absence of detectable photocurrent up to 80°C at the $3d^5$ peaks can be interpreted as the creation of Frenkel excitons whose binding energy is large enough to inhibit extensive thermal dissociation.

Figure 1 shows that absorption in GdGaG begins 0.5 - 1.5 eV higher than in GdIG, and, in fact, is very similar to YGaG,[3] suggesting that the role of Gd in this part of the spectrum is passive. This result, in addition to the persistence of photoconductivity to low temperatures, implies that here carriers are excited to and move in sp bands with little self-trapping, consistent with the absence of empty d-levels.

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Photoleitfaehigkeit wurde in Gadolinium-Eisengarnet und Gadolinium-Galliumgarnet festgestellt. Die Photoleitfaehigkeit des Ersteren ist mit unbesetzten d-Niveaus, die des letzteren mit sp-Banden verbunden.