Photoconductivity in Gadolinium Garnets

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Photoconductivity has been observed in gadolinium iron garnet (GdIG) commencing near 2.5 eV and in gadolinium gallium garnet (GdGaG) near 4.0 eV. For each garnet type, the onset of both photocurrent under applied voltage and short-circuit steady state photocurrent is associated with the high absorption region. The photocurrents are small, leading for GdIG to a mobility-lifetime product $\mu\tau = 2 \times 10^{-10}$ cm^2/volt and about one order less for GdGaG. For GdIG, the photocurrents decrease with decreasing temperature, whereas for GdGaG the photocurrent remains essentially constant down to -60°C. The photoconductivity in GdIG is attributed to charge transfer-like transitions from a filled s-p valence band to empty Fe 3d levels resulting in an Fe^{2+} — s-p hole pair. The observation of roughly the same activation energy for photoconductivity as for dark conductivity indicates dissociation of this pair. While the Fe^{2+} centers form negative polaron charge carriers, self-trapping of the s-p hole with the aid of neighboring Fe^{3+} ions leads to positive polaron conduction. This is confirmed by the relative temperature independence of photoconductivity in GdGaG suggesting that here photocarriers move in s-p bands with negligible self-trapping, consistent with the absence of empty d-levels.

* On leave from Technische Hochschule, Karlsruhe.

(48.5)

bulletin

OF THE AMERICAN PHYSICAL SOCIETY

INCLUDING THE PROGRAMME OF THE
1967 "MARCH" MEETING AT CHICAGO
27-30 MARCH 1967

measured in the energy range 5.5 to 7.5 eV. The concentration and the orientation of the films (on KCl substrates) have been determined by x-ray and electron diffraction. Peaks associated with the iodine ions are observed in the bromine-rich solutions below the bromine peaks. The position of both, bromine and iodine peaks shifts with composition. The energy of the iodine peaks shifts linearly with composition at both sides the miscibility gap but this variation cannot be linearly extrapolated through the miscibility gap. This is in contrast with systems without a miscibility gap (KCl–KBr): the peaks associated with one halogen ion vary linearly in these systems throughout the whole composition range. Results for the CsCl–CsBr system will also be presented.

BM6. Intrinsic Luminescence of RbCl, CsBr, and CsI at 10°K. J. Ramamurti (introduced by K. J. Teegarden) and K. J. Teegarden, *University of Rochester.*—Previously reported studies of the emission spectra of the alkali halides[1,2] under irradiation with ultraviolet radiation at 10°K have been extended to RbCl, CsBr, and CsI. Irradiation in the fundamental absorption region gives rise to both the intrinsic emission bands and those due to unintentional impurities. RbCl shows bands with peaks at 3.18 and 2.34 eV for excitation with 10- or 8-eV photons. The band at 2.34 eV is identified as an intrinsic emission band. CsBr gives rise to emission bands at 4.60, 3.81, and 3.18 eV, of these the band at 3.18 eV is identified as intrinsic. The nature of the 3.81 eV band is not known at present; the 3rd band is due to an impurity. The 2 intrinsic emission bands of CsI are at 3.62 and 4.27 eV. The excitation spectra of some of these bands will be presented and the origin of the luminescence discussed.

[1] J. Ramamurti and K. J. Teegarden, Phys. Rev. 145, 698 (1966).
[2] J. Ramamurti and K. J. Teegarden, Bull. Am. Phys. Soc. 11, 246 (1966).

BM7. EPR Investigations of Electroluminescence in ZnS:Mn, Cl.* L. Leopold and J. P. Sattler, *Georgetown University.*—EPR signals obtained from the $^6S_{5/2}$ ground state of Mn^{++} ions introduced into a ZnS lattice decrease on application of a time varying voltage by an amount which is given by $S = S_0 (1-KfV^3)$. Here S and S_0 are the spin signals with and without applied voltage, V is the voltage, f is the frequency, and K is a constant. The effect is only observed in the presence of Cu impurities. This result is interpreted as being due to transfer of electrons from the Mn^{++} to the Cu^+ ions with a trapping time at the Cu sites of about 45 μsec. A model for the V^3 law is presented.

BM8. Self-Trapped Exciton States in Alkali Halide Crystals. Milton N. Kabler and David A. Patterson, *U. S. Naval Research Laboratory.*—The spectra, lifetimes and polarizations of luminescent self-trapped exciton transitions in several alkali halide crystals at 4°K have been measured. For 9 different alkali halides, the Stokes shifts from crystal to crystal for both the allowed (when present) and forbidden transitions vary monotonically with the relative displacements which 2 adjacent halide ions undergo when they trap the exciton. The displacements, which are simply estimated from known ionic and atomic size parameters, thus serve as an adequate configuration coordinate. Furthermore, *departures* from a strict proportionality between the forbidden band transition probability and the square of the appropriate spin–orbit coupling parameter of the anion are also related

to the anion displacements. These results are consistent with a multiplicity-forbidden transition whose probability depends primarily upon the anion spin–orbit coupling and secondarily upon the relative anion displacements for self-trapping. This latter dependence implies an asymmetric broadening and peak shift of the emission band with temperature which has been observed qualitatively in KBr.

BM9. Theory of Trapped Electron-Phonon Interaction in Realistic Crystals. John T. Ritter* (introduced by Jordan J. Markham) and Jordan J. Markham, *Illinois Institute of Technology.*—A scalar interaction potential between an electron and a host ionic lattice, has been derived. This interaction potential is related to the Fröhlich model interaction, but considers the lattice in a more realistic manner. This interaction potential was employed in the theory of trapped electron optical absorption and a "per mode Huang Rhys" or "S_j" has been obtained. S_j is a product of 2 quantities: 1 depends on the details of the lattice vibrations and the other is related to details of the electron trap geometry. The 1st part we call the per mode lattice factor L_j and it was calculated for a representative set of modes from various available lattice vibration calculations. The 2nd part is not calculable from currently available information. L_j itself, however indicates which phonons are expected to be prominent in vibronic spectra. A comparison of our theoretical predications with observed vibronic spectra for 3 alkali halides indicated agreement.

BM10. Trapping Levels in Rare-Earth-Doped CaF_2.* M. Schlesinger and P. W. Whippey, *University of Western Ontario.*—The nature of electron and hole trapping levels in rare-earth-doped CaF_2 is being studied. Emphasis is put on the possibility of developing a new lasing system. Conductivity, glow re-excitation,[1] and other experimental techniques are being used. The temperature range studied is 4° to about 400°K. Preliminary results pertaining to thermoluminescence re-excitation in 2 of the crystals show marked differences between CaF_2:Ho and CaF_2:Eu. In the first it is found that light absorbed in color centers does not re-excite; while thermal re-excitation [i.e., keeping the room-temperature (R.T.) x-rayed crystal at liquid-N_2 temperature (LNT) in the dark for an extended period of time] re-excites practically all of the glow peaks between RT and LNT. In the case of CaF_2:Eu, the opposite is the case. The spectral distribution of the glow which is different for different activators has been studied in detail. Laser light is found to be a very useful tool in our studies; it stimulates the luminescence emission of x-rayed crystals and is also employed to achieve high population of excited defect states.

BM11. Photoconductivity in Gadolinium Garnets. Paul M. Grant and Wolfgang Ruppel,* *IBM Research Laboratory, San Jose.* Photoconductivity has been observed in gadolinium iron garnet (GdIG) commencing near 2.5 eV and in gadolinium gallium garnet (GdGaG) near 4.0 eV. For each garnet type, the onset of both photocurrent under applied voltage and short-circuit steady-state photocurrent is associated with the high absorption region. The photocurrents are small, leading for GdIG to a mobility-lifetime product $\mu\tau = 2 \times 10^{-10}$ cm^2/V and about 1 order less for GdGaG. For GdIG, the photocurrents decrease with decreasing temperature, whereas for GdGaG the photocurrent remains essentially constant to $-60°$C. The photoconductivity in GdIG is attributed to charge-transferlike transitions from

a filled $s-p$ valence band to empty Fe $3d$ levels resulting in an $Fe^{2+}/s-p$ hole pair. The observation of roughly the same activation energy for photoconductivity as for dark conductivity indicates dissociation of this pair. While the Fe^{2+} centers form negative polaron charge carriers, self-trapping of the $s-p$ hole with the aid of neighboring Fe^{3+} ions leads to positive polaron conduction. This is confirmed by the relative temperature independence of photoconductivity in GdGaG, suggesting that here photocarriers move in $s-p$ bands with negligible self-trapping, consistent with the absence of empty d levels.

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BM12. Photoconductivity in Thin, Polycrystalline, Zinc Oxide Film.* M. L. McDaniel (introduced by H. J. Watson), H. J. Watson, and R. R. Mitchell, *Brown Engineering Company, Inc., Huntsville.*— Thin films of polycrystalline zinc oxide exhibit a "fast" and "slow" photoconductivity. Measurement of this photoresponse (conducted in high vacuum) shows that there is a dependence of the "fast" electronic photoresponse upon the degree to which the "slow" photoresponse, due to photodesorption of oxygen, has progressed. Hall measurements of the film in vacuum have also been performed indicating the behavior of charge carrier density and effective mobility of the film under irradiation.

*Work supported by the Research Projects Laboratory, George C. Marshall Space Flight Center, Huntsville, Alabama.

BM13. Electrical Conductivity of Rubidium Chloride. Robert G. Fuller* (introduced by Clifford C. Klick), *U. S. Naval Research Laboratory.*— The electrical conductivity (σ) of "pure" rubidium chloride single crystals has been measured in the temperature (T) range from $773°$ to $973°$ K. Log (σT) plotted vs $(1/T)$ shows a positive curvature, suggesting that, as in KCl, the current is being carried by both anions and cations. Using this model the activation energies for the anion and cation contributions to the conductivity of RbCl have been obtained.

*NRC–NAS Postdoctoral Research Associate.

BM14. Magnetoconductivity and Band Symmetry of Several Alkali Halides.* Jonathon W. Hodby and J. A. Borders, *University of Illinois.*— A new technique which avoids significant space-charge polarization has been developed for the measurement of photocurrents in insulating crystals. Electrons are repetitively excited from F centers by a xenon flash tube and the resulting charge pulses are averaged by a boxcar integrator. Depolarization is accomplished by illumination between exciting pulses in the absence of an applied field. Measurements have been made of transverse magnetoconductivity and hot electron phenomena at $4°$K in 6 alkali halides. Any angular anisotropy of the effective mass of the conduction band of NaI, KCl, KBr, KI, RbCl, and CsBr is less than 1%. The experimental technique will be briefly discussed and the results interpreted in terms of the present understanding of the polaron problem and the band structures of these materials. The experimental techniques are being extended to observe cyclotron resonance in the above materials at 140 GHz using the electron heating method previously described.[1]

*Work supported in part by U.S. Army Research Office (Durham).
[1] M. Mikkor, K. Kanazawa, and F. C. Brown, Phys. Rev. Letters 15, 489 (1965).

BM15. Photoionization of Aromatic Molecules in Solution.* L. I. Grossweiner and Karl J. Youtsey, *Illinois Institute of Technology.*— Flash photolysis experiments have shown that ultraviolet-light irradiation of some aromatics in aqueous solution (particularly those with electron-donating substituents, aryl acids, and certain heterocyclics) generates the solvated electron and the radical product of 1-electron oxidation.[1-3] Measurements of relative electron and phenoxyl radical quantum yields obtained from p-cresol in water and alcoholic solvents indicate that the photochemical step involves competition between electron release and rupture of OH bond. It is postulated that the extent of these respective processes is controlled by the activation energy for escape of the electron and the H atom from the radical in the solvent cage. Relative yield measurements in mixed water–ethanol solvents suggest that H bonding favors the photoionization path. Previous spectral and photochemical studies on phenolate have indicated that the electron is not released in the $\pi-\pi^*$ transition.[4] The nature of the intermediate, possibly the triplet or a complex of the excited molecule with the solvent, has not been established.

*Work supported by a Public Health Service Grant from the National Institutes of General Medical Sciences.
[1] L. I. Grossweiner, G. W. Swenson, and E. F. Zwicker, Science 141, 805 (1963).
[2] L. I. Grossweiner and H. I. Joschek, Advances in Chemistry Series No. 50 *Solvated Electron* (American Chemical Society, Washington, D. C., 1965), p. 279.
[3] H. I. Joschek and L. I. Grossweiner, J. Am. Chem. Soc. 88, 3261 (1966).
[4] J. Jortner, M. Ottolenghi, and G. Stein, J. Am. Chem. Soc. 85, 2712 (1963).

1967 Chicago APS Meeting Talk

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Introduction

Both optical and transport properties of several ferrimagnetic garnets and the closely related $\alpha-Fe_2O_3$ have been reported, but apparently photoconductivity techniques have not been applied to these materials. However, there is a good chance that such measurements may aid in differentiating inter- and intraconfigurational transitions and charge transfer-like transitions in materials where the cations have open shells. That is, one intuitively expects that charge transfer transitions are more likely to lead ultimately to mobile carriers and hence photoconductivity than d-d transitions.

In this talk I would like to discuss our observations of steady-state photoconductivity in Gd I G and GdGaG with this point of view in mind.

Slide 1.   Summary of Crystal and Transport Data

Here we have summarized the crystal and transport data for our samples. The specimens were high purity single crystals grown from PbO - fluxed melts with stoichiometries better than 0.5 mole-percent. The garnet crystals were p-type at room temperature as determined from the sign of the thermoelectric power (GdIG only) and the direction of the I_{SSPC}. Maximum I_{AVPC} appearing when the anode was illuminated also, implied p-type material. For GdIG, ρ_{dark} is roughly 3×10^{10} $\Omega \cdot cm$ and for GdGaG 2×10^{15} $\Omega \cdot cm$. The E_a for GdIG was about $0.3\ eV$ ($-100°C < T < 100°C$); no attempt being made to measure this parameter for GdGaG. The GdIG results compare well with those obtained by others for p-type YIG.

The mobility - lifetime product for GdIG was found to be about 10^{-10} $cm^2/volt$ and about an order less for GdGaG. The $\mu\tau$ - product is a figure of merit of photoconductive efficiency, being around unity for CdS and 10^{-6} for Se; obviously garnets are not very good photoconductors.

Slide 2. Photoresponse of GdIG and GdGaG

This slide shows the energy dependence of the absorption and photocurrent for GdIG and GdGaG (explain each curve). Note that the onset of the photocurrents for both garnets is associated with their high absorption regions. The sample thickness was always enough to absorb all incident light even at low energies. The photocurrents in GdIG could no longer be detected when the temperature was lowered to $-60°C$ and the exponential temperature dependence in this range ...d to a photocurrent activation energy of $0.3 eV$, the same as for ρ_{dark}. On the other hand, I_{AVPC} for GdGaG remained essentially constant with temperature, a small I_{SSPC} appearing at about $-50°C$.

As is well known, the two low energy absorption peaks at $1.0 eV$ (not shown) and $2.1 eV$ are due to $A_1 \rightarrow T_1$, $A_1 - T_2$ transitions of the ferric octahedral coordination; the charge transfer region beginning at $2.4 eV$. This optical structure is almost the same for YIG and $\alpha - Fe_2O_3$.

Slide 3. Proposed Models for Photoconductivity

This slide summarizes what we believe to be the photo-conductivity mechanism in GdIG.

(1) First of all, the absorbed light creates charge transfer transitions from oxygen s-p valence bands to empty Fe 3d levels resulting in a possibly bound Fe^{2+} - s-p valence hole pair. It is not clear whether the optical excitation is directly to the continuum of this polaritonic pair or whether spontaneous dissociation into an Fe^{2+} center and a self-trapped hole occurs.

(2) Secondly, the separated Fe^{2+} center and self-trapped hole constitute small negative and positive polarons. Both carrier types must be present to explain the existence of short-circuit photocurrent. The p-type dark conductivity suggests that the photo-conductive activation energy (0.3 eV) may be the jumping activation energy of the positive polaron.

(3) Next, the absence of detectable photocurrent below −60°C for incident photon energies up to 4.5 eV indicates that the valence - conduction band gap is above 4.5 eV or that, if it is not, hole-electron lifetime is being shortened possibly via Fe^{3+} centers.

(4) The absence of detectable photocurrent up to 80°C at the $3d^5$ peaks can be interpreted by picturing the $A_1 - T_1, T_2$ transitions as Frenkel excitons whose binding energies are large enough to inhibit thermal dissociation.

(5) Finally, for GdGaG, in which Ga^{3+} has a closed shell configuration, the absorption spectrum is very similar to YGaG, suggesting that Gd only plays a passive role in this part of the spectrum. The persistence of photoconductivity to low temperatures implies that here carriers are excited to and move in s-p bands with little self-trapping, consistent with the absence of empty d-levels.