

of such group seems to be rather general in view of measurements done at this laboratory on the copper (II) and silver (II) derivatives of the pyridine-monocarboxylic and -dicarboxylic acids. Strong differences in the spin-lattice relaxation time of different compounds have been observed.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† On leave of absence from Instituto Venezolano de Investigaciones Cientificas, Caracas.

¹ D. Kivelson and R. Neiman, *J. Chem. Phys.* **35**, 149 (1961).

² A. H. Maki and B. R. McGarvey, *J. Chem. Phys.* **29**, 35 (1958).

E13. Electrochromism (Stark Effect) in Solids Due to Isolated Absorbing Centers. J. KUMAMOTO, J. C. POWERS, AND W. R. HELLER, *IBM Thomas J. Watson Research Center, Yorktown Heights.*—A study has been made of the effect of applied electric fields upon the absorption spectrum of a dye molecule (methyl red) dissolved in a relatively inert, transparent matrix of high dielectric strength (polystyrene). Theory indicates that the existence of a large dipole moment in either ground or excited state (or in both, if the moment differs in the two states) should lead to a broadening of the absorption band. In contrast, the existence of excited states of appropriate type lying close to that involved in the transition should produce a shift to the red. In the present instance, the second effect dominates, and one observes, with a field of about 1 million v/cm, a shift of around 10 Å of the principal band which is

centered near 5000 Å. Possible uses of this technique are in evaluating the local field at an absorbing molecule and in estimating dipole moments of various states.

E14. Preparation and Electrical Conductivity of Cu-tetra-2,3-pyridino-porphyrazine and Cu-tetra-2,3-pyrazino-porphyrazine. M. J. DANZIG AND C. Y. LIANG, *American Viscose Corporation.*—In order to relate semiconduction of organic substances to structure, copper tetra-2,3-porphyrazines were made containing pyridine and pyrazine rings. These were prepared from the corresponding dinitriles and copper. The electrical conductivity of the samples in pressed disks was measured with a vibrating-reed electrometer. Conducting glass was used as front electrode of the sandwich cell. The cell was placed in a metal container which could be evacuated and heated to a higher temperature. At room temperature, the resistance is in the order of 10^9 ohms for Cu-tetra-2,3-pyridino-porphyrazine and 10^5 ohms for Cu-tetra-2,3-pyrazino-porphyrazine mono-hydrate. Similar measurement for a sample of Cu-phthalocyanine is in the order of 10^{11} ohms. The resistance for each sample was found to follow the equation $R=R_0 \exp(\Delta E/2KT)$ with activation energy ΔE being 1.17 eV for Cu-tetra-2,3-pyridino porphyrazine and 0.69 for Cu-tetra-2,3-pyrazino-porphyrazine. With tungsten-lamp illumination, the photocurrents were found to be proportional to the applied voltage across the samples at various temperatures.

MONDAY AFTERNOON AT 2:00

Lord Baltimore, Calvert Room

(F. HERMAN presiding)

Invited Papers

EA1. Free-Carrier Magneto-Optic Phenomena in Semiconductors. E. BURSTEIN, *The University of Pennsylvania.* (30 min.)

EA2. Cyclotron Resonance in Diamond. C. ROUCH, *Lincoln Laboratory MIT.* (30 min.)

Band Structure and Excitons in Diamond-Type Crystals

EA3. Faraday Rotation in *p*-Type GaSb. H. PILLER AND V. PATTON, *U. S. Naval Ordnance Laboratory, Corona* (introduced by R. F. Potter).—The Faraday rotation in *p*-type GaSb has been measured in the wavelength region 1.5 to 5 μ . Magnetic fields up to 20 kgauss were obtained by a Varian 4-in. magnet. The Faraday effect corresponding to direct transitions takes on negative values for wavelengths shorter than 1.9 μ and has positive values corresponding to indirect transitions for larger wavelengths. The Faraday effect was measured at 297° and 77°K. The Verdet coefficients have values between -1.7×10^{-4} at 1.7 μ , 1.7×10^{-5} at 2.2 μ , and 3×10^{-6} at 3.6 μ in units of radian/centimeter gauss. The shift of the rotation with temperature is $4.5 \times 10^{-3} \text{ deg}^{-1}$ at 1.7 μ . No rotation was observed in the free-carrier range.

EA4. Polarized-Radiation Studies of Magnetoplasma Reflection in InSb. E. D. PALIK, B. W. HENVIS, AND S. TEITLER, *U. S. Naval Research Laboratory.*—Magnetoplasma reflection at room temperature was measured on a sample of *n*-type InSb with 10^{18} carriers/cm³ using left and right, circularly polarized, infrared radiation propagating parallel to the magnetic field (Faraday orientation). The plasma edge shifts to higher or lower frequency as given by $\omega_{\pm} \approx \omega_p \pm (1/2)\omega_c \pm (1/8)\omega_c^2/\omega_p$. The Kerr effect was measured when plane-polarized radiation incident in the Faraday orientation exhibited rotation due to the differential phase shifts on reflection for the left and right circular components and an ellipticity due to the differential-reflectivity amplitudes. The

frequency dependence of the ellipticity was characterized by two extrema separated by ω_c . Similarly, rotation and ellipticity measurements were made for incident plane-polarized radiation with electric vector oriented at 45° with respect to the magnetic field and propagating perpendicular to it (Voigt orientation). The rotation is due to the differential-reflectivity amplitudes of radiation with electric vector parallel and perpendicular to the magnetic field, and the ellipticity is due to the differential phase shifts upon reflection. All experimental results were in reasonable agreement with theoretical results obtained using a Drude-Zener model for carrier motion.

EA5. Resistivity of Gray Tin as a Function of Pressure. STEVEN H. GROVES AND WILLIAM PAUL, *Harvard University.*—The variation of resistance of *n*-type gray tin with hydrostatic pressure has been measured between 77° and 233°K. Near 233°K, the increase in intrinsic resistivity with pressure, if left uncorrected for (small) dimensional changes and mobility changes, gives a pressure coefficient of the energy gap of $+5 \times 10^{-6}$ eV/kg/cm², identical with the coefficient for the L_1-F_{25}' gap in Ge. Between 173° and 77°K, we observe very large changes of resistivity (60% decrease in 2800 kg/cm² at 125°K) that are inexplicable in terms of changes of the parameters of a single band, when Ge and Si are used as typical examples. These results, however, are qualitatively reasonable if the electron scattering depends upon the hole population (which decreases rapidly as the application of pressure increases the energy gap). If, at these temperatures, the energy

gap is of the order of phonon energies, electron scattering may be predominantly from conduction band(s) to valence band. Electron scattering by holes would also show this strong pressure dependence.

EA6. Pressure Dependence of Reflectivity Peaks in Germanium and Related Materials. R. ZALLEN, WILLIAM PAUL, AND J. TAUC,* *Harvard University*.—The identification of the electronic transitions responsible for the reflectivity peaks in Ge and related semiconductors provides a method for investigating the shift with hydrostatic pressure of energy-band extrema lying in the deeper regions of the band structure. The suggestion that corresponding transitions have about the same pressure dependence in the cubic group 4, group 3-5, and group 2-6 semiconductors may be tested. Measurements have been made to 9000 kg/cm² using an arrangement involving four successive reflections from etched surfaces. In Ge, the spin-orbit split peaks due to L_3' to L_1 transitions occur at energies of $(2.11 + 7.5 \times 10^{-6}P)$ eV and $(2.31 + 8.3 \times 10^{-6}P)$ eV; in GaSb the corresponding peaks occur at $(2.03 + 6.5 \times 10^{-6}P)$ eV and $(2.48 + 8.2 \times 10^{-6}P)$ eV, where P is the pressure in kg/cm². A small increase of the L_3' spin-orbit splitting with pressure is indicated. The accuracy of the pressure coefficients is about 5%. For Ge we can deduce, from these data and other information, the following pressure shifts (in units of 10^{-6} eV/kg/cm²): Γ_{25}' , -3.6; L_1 , +1.4; L_3' , -6.1 and -6.9.

*UNESCO fellow, on leave from Institute of Technical Physics, Czechoslovakian Academy of Sciences, Prague.

EA7. Exciton and Impurity Absorption in GaSb,* E. J. JOHNSON AND H. Y. FAN, *Purdue University*.—The absorption edge in GaSb shows a sloping tail due to impurity excitation as is indicated by photoconductivity studies of Habegger. In the purest samples (p -type), the tail is very weak at helium temperature. Three sharp exciton peaks have been observed on the steep edge by using high resolution. At 1.7°K, the peak α is at the top of the absorption edge at 0.8100 eV and corresponds to the first peak observed previously¹ under applied magnetic field. The other peaks, β (0.8049 eV) and γ (0.7960 eV), are apparently excitons bound to impurities. Under magnetic field, the α peak shifts to higher energy, about linearly (~ 0.12 MeV/kg) above 10 kg. The peak is broadened by the presence of more than one component, the positions differing for $E||H$ and $E \perp H$. A number of oscillations in absorption was observed at higher energies which agree substantially with the results of Zwerdling *et al.* The β and γ peaks split into doublets under magnetic field and shift to higher energies. The shift appears to be quadratic in H up to 20 kg. Both components are little affected by the polarization of the radiation. These results are useful for the understanding of exciton formation and energy-band structure.

*Work supported by a U. S. Signal Corps contract and by a General Telephone fellowship.

¹S. Zwerdling, B. Lax, K. Button, and L. M. Roth, *J. Phys. Chem. Solids* **9**, 320 (1959).

EA8. Recombination Radiation in GaSb.* I. FILINSKI AND H. Y. FAN, *Purdue University*.—Recombination radiation in GaSb has been studied using electrical and optical injections.

Electron-hole recombination emission has a peak close to the energy gap: 0.72 eV at 300°K and 0.798 eV at 77°K, the shift being associated with the increase of energy gap. At 300°K a second peak was observed at ~ 0.67 eV, and at 77°K a second peak was seen at 0.778 eV. These peaks were apparently produced by electron recombination with impurity levels which are estimated to be ~ 0.05 and ~ 0.025 eV above the valence band. At liquid-He temperature, two peaks were observed at 0.778 and 0.796 eV. The 0.779-eV peak corresponds to the 0.778-eV peak at 77°K. The 0.796-eV peak does not, however, correspond to the hole-electron recombination emission which peaks at 0.798 eV at 77°K. It is interpreted as exciton recombination at some impurity; a sharp peak at 0.796 eV has been observed also in infrared absorption as reported in the companion paper. Degenerate p -type, compensated p -type, and n -type samples have been studied also, in which emissions involving various impurity levels are observed.

*Work supported by the U. S. Army Signal Corps.

EA9. Exciton-Recombination Radiation and Phonon Spectrum of 15R SiC. W. J. CHOYKE, D. R. HAMILTON, AND LYLE PATRICK, *Westinghouse Research Laboratories*.—The optical transitions in 15R SiC are indirect,¹ and the low-temperature exciton-energy gap is about 2.99 eV (1% less than that of the more-common polytype, 6H). We have observed a photoluminescence spectrum in 15R SiC consisting of about 50 resolvable narrow lines with photon energies falling between 2.85 and 2.98 eV. The lines can all be attributed to exciton recombination at un-ionized nitrogen (donors), both with and without phonon emission. The complexity of the spectrum is due to the large unit cell of 15R SiC, which has two significant effects. (1) There are five inequivalent carbon sites on which nitrogen may substitute, thus giving rise to five series of emission lines. (2) The large unit cell generates a complex phonon spectrum which makes each series of lines complex. Examination of a single series of lines yields a phonon spectrum. The binding energies of excitons to the different nitrogen centers have been determined. The largest binding energy is about twice the smallest.

¹Lyle Patrick, W. J. Choyke, and D. R. Hamilton, *Bull. Am. Phys. Soc.* **6**, 148 (1961).

EA10. Comparison of 6H SiC and 15R SiC Exciton-Recombination Radiation. LYLE PATRICK, D. R. HAMILTON, AND W. J. CHOYKE, *Westinghouse Research Laboratories*.—At the New York meeting,¹ we reported observation of an exciton-recombination radiation spectrum for 6H SiC. In many respects it is similar to the 15R SiC spectrum described in the previous abstract. One obvious difference is that there are only three series of lines in the 6H SiC spectrum instead of the five in 15R SiC. (There are three crystallographically inequivalent sites available to nitrogen in 6H SiC.) It is now possible to compare the two polytypes with respect to energy gaps, phonon energies, and binding energies of the exciton-to-nitrogen donors. Extended k -space plots are used to classify the phonons.

¹W. J. Choyke and Lyle Patrick, *Bull. Am. Phys. Soc.* **7**, 77 (1962).

MONDAY AFTERNOON AT 2:00

Emerson, Grand Ballroom

(G. D. WATKINS presiding)

Radiation Damage in Semiconductors and Insulators

F1. Distribution of Electron-Bombardment-Induced Radiation Defects with Depth in Silicon. H. FLICKER AND J. J. LOFERSKI,* *RCA Laboratories*.—The density of recombination

centers introduced into silicon by 0.50-MeV electron bombardment has been measured as a function of penetration distance by monitoring the decrease of short-circuit electron-