Optical Constants of Single-Crystal Gray Tin in the Infrared*

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Reflectance measurements were made on grown, gray tin single crystals by the Avery method. The measurements were done at 300°K and in the 1- to 25-μ region of the spectrum. An analysis of the data yielded the index of refraction, extinction coefficient, and other related constants. The absorption coefficient was characterized by two regions of strong absorption separated by an absorption minimum at 0.075 eV and a weaker minimum at 0.14 eV. The long-wave absorption was shown to be due to free carriers as evidenced by the behavior of $n^2 - k^2$ versus λ^2 according to the Drude-Zener theory of the free-carrier electrical susceptibility. Correlation of information from the $(n^2 - k^2)$ curves with Hall effect data then led to estimates of the hole effective mass.

I. INTRODUCTION

THIS paper reports on a part of a continuing program of study of the properties of gray tin single crystals that began when the growing techniques were devised in 1958.[1] Some of the electrical properties have previously been reported.[2-5] The work reported here was undertaken to discover some of the properties of gray tin by optical techniques. Due to the failure of several attempts to observe infrared transmission, a reflectance method was adopted. Measurements were made in the 1- to 25-μ region of the spectrum and at a sample temperature of 300°K. Reflectance measurements at shorter wavelengths, within the fundamental absorption region, have recently been reported by Cardona and Greenaway.[6]

Analysis of our data led to a complete determination of the phenomenological optical constants for the spectral region investigated. By correlating some of the results of these measurements with information obtained from Hall measurements on the same samples, estimates of the hole effective mass were obtained.

II. EXPERIMENTAL

Single crystals of gray tin were grown from a mercury solution by a method that has been described by Ewald and Tufte.[1] Optical samples were cut from these crystals in such a way that a natural grown face was always the surface on which the reflectance measurements were made. Even though gray tin is not the thermodynamically stable phase at temperatures above 13.2°C,[7] it was found that a properly prepared sample could be kept at room temperature for the duration of an experiment lasting several hours without a sign of conversion to the white phase.

A Perkin-Elmer infrared spectrometer with an added reflectometer arm, similar to a design that has been described by Simon,[8] was used for the measurements. To permit measurements at the long wavelengths at which the fundamental absorption edge was expected to occur, the spectrometer was equipped with cesium iodide optics. Infrared radiation from a Globar was mechanically chopped before reflection at the sample surface so that the signal from the radiation thermo-couple detector could be amplified by the use of a 10-cycle amplifier. An infrared polarizer was constructed essentially according to the directions given by Elliott, Ambrose, and Temple[9] and used in front of the entrance slit of the spectrometer. This type of polarizer consists of a set of six self-supporting, evaporated films of selenium set at the polarizing angle and used in transmission. Such a polarizer produces a negligible lateral displacement of the beam of radiation as the polarizer is rotated about an axis parallel to the radiation.

The method of Avery[10] was used in this work. In this method one measures the ratio of reflection coefficients for incident intensities polarized respectively parallel and perpendicular to the plane of incidence. When this ratio is measured for two angles of incidence at any particular wavelength, it is possible to obtain both the real and the imaginary parts of the complex dielectric constant. For greatest accuracy, it is desirable to make measurements in the vicinity of the principal angle of incidence,[11,12] which for gray tin was found to be near

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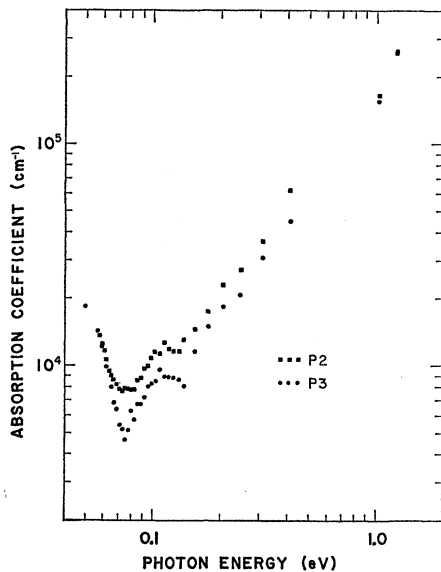[12] J. R. Beattie and G. K. T. Conn, Phil. Mag. **46**, 222 (1955).

FIG. 1. Absorption coefficient vs energy for two samples of gray tin at 300°K.

TABLE I. Electrical and optical parameters of the specimens studied. The quantity ΔN is the excess of acceptor over donor concentrations; A and ϵ_0' are defined in the text.

Sample	ΔN (cm^{-3})	A (cm^{-3})	ϵ_0'
P1	8.7×10^{19}	(see text)	20
P2	1.7×10^{18}	6.0×10^{19}	23
P3	2.3×10^{18}	6.7×10^{19}	26
N1	-3.7×10^{16}	5.8×10^{19}	22

n-type impurity concentration of sample N1 is just that of the tin used to supply the growers.

III. RESULTS AND DISCUSSION

The absorption coefficient $\alpha = 4\pi k/\lambda$ as a function of energy for two of the samples, is shown in Fig. 1. The minima at 0.075 eV and at about 0.14 eV and the relatively high level of absorption even in the vicinity of the minima may be noted. The data points for sample N1 which are not included in the figure would fall between the curves shown. This sample also showed a sharp minimum at 0.075 eV similar to that of sample P3 and a secondary minimum at 0.14 eV.

Recently, a new model for the band structure of gray tin has been proposed by Groves and Paul[15] on the basis of several items of experimental evidence. This model postulates that the forbidden energy gap is fixed at zero at $\mathbf{k}=0$ for all temperatures and pressures. The interpretation of the 0.075-eV absorption minimum within this framework is that it is simply due to the summation of two absorption processes, one increasing with energy (direct interband transitions) and the other decreasing with energy (free carrier absorption). The similarity of this value with the observed value of[16] 0.082 eV for the activation energy of the electrical conductivity then becomes quite accidental.

In support of the Groves and Paul model are the recent photoconductivity measurements made in this laboratory[17] that exhibit neither the peak in spectral response at 16 μ nor the fall off at longer wavelengths that were observed by Becker[18] in his measurements on transformed samples. Additional support for the idea of a vanishing energy gap comes from the failure of all workers to observe infrared transmission. Presumably, if the gap is zero, there are always enough free carriers present to prevent transmission.

The structure observed in the absorption curves for energies greater than 0.075 eV is then perhaps analogous to the similar structure seen in the absorption of p-type germanium,[19,20] both being caused by transitions

77°. Therefore, the following three angles of incidence were used for most of the work: 60°, 77.5°, and 80°. The third, redundant angle provided a convenient check on the consistency of the data.

The optical constants were obtained from the experimental data by a method devised by the authors.[13] By this method one obtains an exact solution of the system of modified Fresnel equations by means of a geometric construction. The raw data were, of course, corrected for apparatus polarization before being processed.

Following the reflectance measurements, Hall specimens were cut from each of the optical samples and Hall measurements were made at 77°K. Except in the case of a heavily doped p-type sample, the Hall coefficients showed a strong field dependence and did not saturate within the field range available. The high-field coefficients were obtained by fitting the curves with the formula given by Jan[14] for the field-dependent Hall coefficient which is based on a classical two carrier model. These coefficients were equated to $1/ec(N_h-N_e)$, where N_h and N_e are, respectively, the hole and electron concentrations in cm^{-3} and e is the magnitude of the electronic charge in esu. Then, by electrical neutrality and assuming complete impurity ionization, N_h-N_e was equated to $N_a-N_d=\Delta N$, the excess of acceptor over donor concentration. The values of ΔN for the four samples on which extensive optical measurements were made are given in Table I. Sample P1 was doped with gallium in the growing process. The p-type conductivity of samples P2 and P3 resulted from diffusion of mercury into the crystals at room temperature. The

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between the various valence bands.[21,22] In the case of gray tin, the transitions to the conduction band are included in the analogy because, in the Groves and Paul model, the conduction band is degenerate with the valence band at $\mathbf{k}=0$ and has $\Gamma_{25'}$ symmetry. Groves and Paul assume that the usual conduction state at $\mathbf{k}=0$, the $\Gamma_{2'}$ state, is depressed by the antisymmetric potential in the lattice to a position 0.3 eV below the $\Gamma_{25'}$ state. The $\mathbf{k}\cdot\mathbf{p}$ interaction between the $\Gamma_{2'}$ state and one of the $\Gamma_{25'}$ states then causes the corresponding valence band to invert and assume a positive curvature so that it then plays the rôle of a conduction band. That such a depression of the $\Gamma_{2'}$ state below the $\Gamma_{25'}$ state can occur is corroborated by some recent calculations. By taking the eigenvalues $\Gamma_{2'}=-8.67$ eV and $\Gamma_{25'}=-9.08$ eV calculated by Bassani and Liu[23] neglecting relativistic corrections, and applying the relativistic (spin-orbit, mass-velocity, and s-shift) corrections, $\delta E_s=-2.16$ eV and $\delta E_p=-0.34$ eV, estimated by Herman *et al.*,[24] one obtains a negative energy gap of 1.41 eV.

Figure 2 shows the index of refraction n and the extinction coefficient k for the two samples used for Fig. 1.

The real part ϵ' of the complex dielectric constant is plotted against wavelength squared in Fig. 3. The decrease with increasing wavelength is attributed to the effect of free carriers. According to the Drude-Zener theory as modified to include the effects of both electrons and holes:

$$\epsilon'=n^2-k^2=\epsilon_0'-(10^{-8}e^2/\pi mc^2)A\lambda^2, \qquad (1)$$
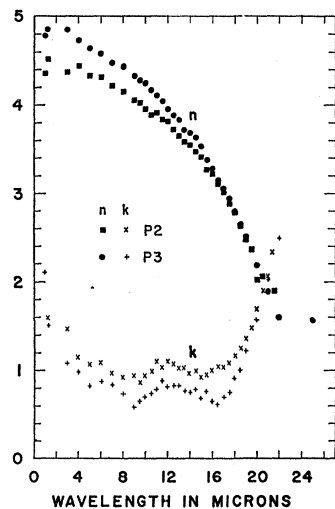
FIG. 2. Index of refraction n and extinction coefficient k versus wavelength for two samples of gray tin at 300°K.
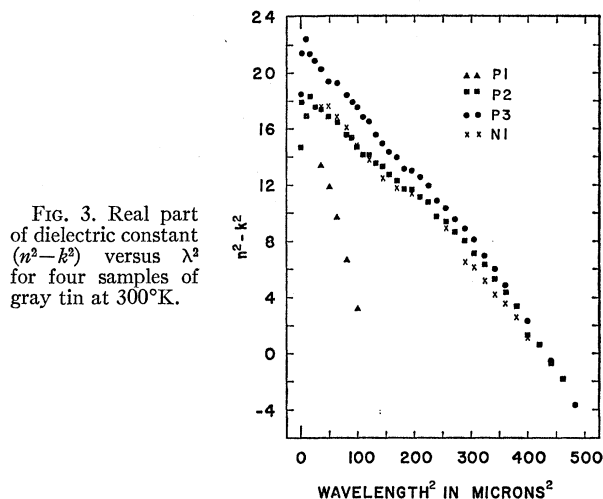
FIG. 3. Real part of dielectric constant (n^2-k^2) versus λ^2 for four samples of gray tin at 300°K.

where we have defined

$$A\equiv N_e m/m_e+N_h m/m_h \qquad (2)$$

and assumed parabolic energy bands (see Spitzer and Fan[20]). The quantities m_e and m_h are the effective masses of electrons and holes, respectively, m is the free electron mass and λ the wavelength in microns. The quantity ϵ_0' is the portion of the dielectric constant that is due to all contributions to the electrical susceptibility other than the free carrier contribution. The jog in the curves for samples N1, P2, and P3 at about 200 μ^2 appears to be due to a change in ϵ_0' because of band to band transitions. At longer wavelengths ϵ_0' should remain constant assuming that the lattice vibrational bands are not sufficiently strong to appreciably affect the dielectric constant. To evaluate ϵ_0' and the parameter A, straight lines were fitted to the long wavelength portions ($\lambda\geqq15$ μ) of the curves for the above three samples. The values found from the intercepts and slopes are given in Table I. The average value of ϵ_0' is 24 and, therefore, the infinite wavelength index of refraction is $n_0=(24)^{1/2}=4.9$.

Because of the stronger free carrier effect in sample P1 and the consequent limited wavelength range of the curve, the data were treated somewhat differently. First, a least-squares fit was made using all data points. This yielded $\epsilon_0'=20$ and $A=1.8\times10^{20}$ cm^{-3}. In view of the rather low value of ϵ_0' obtained in this way, a second evaluation of A was made using as intercept the average evaluated from the other three samples together with only the last three data points for this sample. This yielded $A=2.3\times10^{20}$ cm^{-3}. Both values of A were used to evaluate the hole mass ratio by Eq. (2). This could be done directly for this sample because, due to the heavy p-type doping, the electron contribution could be neglected. The resulting two values of the hole mass ratio are 0.49 and 0.38. These are in reasonably close agreement with the value 0.46 found from

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Hall, conductivity and thermoelectric power data.[25] Other published estimates[6,26] of the hole mass ratio in gray tin range from 0.2 to 3.0.

The electron mass ratio could not be deduced directly from the parameters of sample N1 because of the small value of ΔN. While heavily doped n-type crystals have been grown, they do not show the high quality optical surfaces required for reflectance measurements. Attempts to extract the electron mass ratio using the tabulated electrical and optical parameters of several samples simultaneously were not successful due to the similarity of three of the samples.

It was found that the imaginary part $2nk$ of the complex dielectric constant did not show a simple λ^3 dependence. Spitzer and Fan[20] have pointed out that

the expression for the wavelength dependence of the conductivity involves the relaxation time τ when $(\omega\tau)^2 \gg 1$, which is not the case for the susceptibility. Therefore, if τ is energy-dependent, $2nk$ can have a complicated λ dependence even when $n^2 - k^2$ is linearly dependent on λ^2. An extreme example of this type of behavior is shown by the results of Spitzer and Fan[20] for p-type indium antimonide where the absorption coefficient α is almost independent of wavelength, but nevertheless the free-carrier susceptibility shows a good λ^2 dependence.

ACKNOWLEDGMENTS

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Optical Bleaching of V_3 Centers in KCl†*

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Bleaching of V_3 centers by uv light absorbed in the V_3 band was studied in Harshaw KCl crystals which had been x-ray irradiated at room temperature. The bleaching measurements were made in the temperature range from 75 to 110°C, where the uv bleaching rate was appreciable but purely thermal bleaching (in the dark) was not significant. The V_3 band decay was approximately exponential in time. Furthermore, the decay constant was approximately an exponential function of inverse temperature, with an activation energy of 0.6 eV. The calculated quantum efficiency for the bleaching was small throughout this temperature range, being given by $\eta \approx 10^6 \exp(-0.6 \text{ eV}/kT)$. Some interaction between V_3 centers and F centers was observed, since bleaching of either band by light absorbed in the band led to partial bleaching of the other band. The results are interpreted in terms of a model for the V_3 center consisting of a Cl_3^- molecular ion at a cation vacancy. The V_3-band bleaching differs from U-band bleaching in its strong temperature dependence and the lack of any accompanying F-band production.

I. INTRODUCTION

RADIATION damage in the alkali halides produces, in addition to the F band in the visible, various optical absorption bands in the uv region.[1] Electron-spin resonance measurements have conclusively established that some of the uv bands formed by irradiation at low temperature are electron-deficit halogen-molecule centers, which complement the F center (an electron trapped at an anion vacancy) in one way or another. The radiation damage mechanism at higher temperature is less clear, however, since the V_3 center, the principal uv companion of the F center in "pure" crystals irradiated at room temperature, has a structure which

is not yet definitely understood. Beside the molecular halogen centers, various impurities also give rise to absorption bands in the uv, and some of these may be modified by irradiation. In particular, the absorption due to H^- (U band) and OH^- ions located on an anion site should be noted. In KCl, these absorption bands peak at 215 and 204 nm, respectively.

The V_3 band in KCl, which also peaks at 215 nm, has been attributed to a Cl_3^- center that contains a cation vacancy, on the basis of its production by x rays[2] and its effect on electrical conductivity.[3] The Cl_3^- ion is observed in solution to have a linear, symmetrical configuration, with the charge concentrated at the ends,[4] and its optical absorption peaks at roughly the same

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