perature-dependent position of the lower-field line, the g factor of the upper field line was independent of temperature. It showed a shift of 0.2% to lower field with respect to a saturated solution of $Sc(NO_3)_3$.

Both Sc^{45} resonances were very broad. The higher field line had a full width between derivative extrema of ≈ 44 G. Assuming a Lorentzian line shape this corresponds to $T_2 \approx 4.5\times10^{-6}$ sec. While the displaced line was broadened by anisotropic shifts it approached a high-temperature linewidth of ≈ 35 G or $T_2 \approx 5.6\times10^{-6}$ sec. The lines might be broadened by quadrupolar interactions.

At 77°K, there was a singificant difference between the saturation behavior of the two lines. The higher field line could be saturated with the result that we determined $T_1 \approx 0.5$ sec. On the other hand the lower field line could not be saturated, so that for this line $T_1 < 0.05$ sec. In contrast to these results at 77°K, at 300°K it was not possible to saturate either resonance. Although it appears from these results that the temperature dependence of T_1 for the higher field line is more rapid than $1/T$ (although in that direction) still we feel that the accuracy of the measurements is not sufficient to eliminate a metal-like $1/T$ dependence for this resonance.

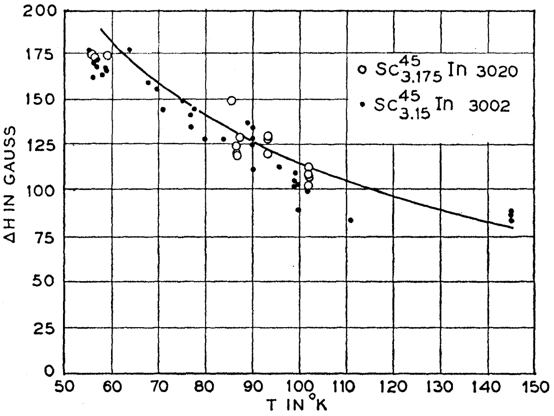

FIG. 2. Shift of lower field Sc^{45} line from (ω/γ) as a function of temperature. The solid line shows the previously measured susceptibility normalized to fit the shifts at 90°K. These measurements were made at 15.5 Mc/sec.

Attempts were made to correlate these two resonances with the two different phases of the alloys. A DO_{19} superstructure phase has been shown[2] to exist near the $Sc_{3.0}In_{1.0}$ composition and our general impression, based upon a number of different heat treatments of these samples, is that this phase is responsible for the displaced nmr signal as well as the paramagnetism (and hence the low-temperature ferromagnetism) of these alloys. However, more work on the correlation between the crystallographic state and the magnetic properties including the nmr is indicated.

We would like to thank Mrs. Vera B. Compton, H. J. Williams, and R. C. Sherwood for their help in trying to understand these alloys.

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Franz-Keldysh Effect in the Space-Charge Region of a Germanium *p-n* Junction*

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By use of the carrier-depleted region of a reverse-biased *p-n* junction, it has been possible to study the effect of large electric fields on the optical absorption coefficient of germanium at room temperature. In the energy range below the edge of the direct interband transitions, the absorption coefficient increases very strongly with field, and the experimental results are in fairly good agreement with the theoretical predictions of Franz, Keldysh, and others. In the region of the indirect transitions, the changes in the absorption coefficient with field oscillate between positive and negative values as a function of energy. This behavior can be related to the phonon-assisted processes first observed by Macfarlane *et al.*

I. INTRODUCTION

THE shift of the optical absorption edge to lower energies under the influence of electric fields has been predicted for insulators and semiconductors by Keldysh[1] and Franz.[2] More recently the problem has been treated by Bulyanitsa,[3] Callaway,[4] and Tharmalingam.[5] The effect has been observed in a number of different solids: silicon,[6,7] cadmium sulfide,[8] gallium

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[7] V. S. Vavilov and K. I. Britsyn, Fiz. Tverd. Tela **2**, 1936

arsenide,[9] and others,[10] and the results are in rough agreement with the theoretical predictions. However, in many of the experiments, the optical absorption edge in the material used was already exponential in the absence of an external field, so that the transition from a sharp direct interband absorption edge to an exponential edge, to be expected from theory, was not explicitly demonstrated. In addition, the materials investigated were limited to those which were or could be made highly insulating. In this paper, a technique for the measurement of the change of the absorption edge in the depleted space-charge region of conducting crystals will be described, and the results of room-temperature measurements on germanium *p-n* junctions will be reported. The authors have already shown[11] that the reverse biased germanium *p-n* junction has great possibilities for use as an electronic light modulator.

II. EXPERIMENTAL TECHNIQUE

A schematic representation of the experimental method is shown in Fig. 1 (a). A monochromatic light beam impinges normally upon the [111] plane of a wide area *p-n* junction. The light traverses both the p and the n regions, and is then detected by a lead sulfide photocell. The planes denoted by the points x_n and x_p are those where the junction region begins to have properties different from the adjacent volume. Both x_p and x_n are functions of the applied voltage, moving away from each other for increasing reverse bias. If all the effects associated with free carrier absorption are neglected, the absorption of light near the band edge should be similar to that of the intrinsic crystal, except for the presence of the large electric field in the region between x_p and x_n. Previous experiments[6–10] have shown that large electric fields increase the absorption coefficient and decrease transmission through the crystal. Since both the electric field and the width of the junction increase with increasing reverse bias voltage, a very large change in the light-transmission properties of a *p-n* junction can be effected. Figure 1(b) shows the relative transmitted light versus light energy for zero and 150 V reverse bias. The maximum field in the junction is close to the breakdown value. Notice that near the direct edge the application of the reverse bias has reduced the transmission by almost a whole decade. Since no effort was made to optimize the effect, this result plus others presented in the latter part of the paper suggest that *p-n* junctions have very great promise for use as electronic light modulators. Although the results of Fig. 1(b) are fairly straightforward in terms of practical applications, a number of difficulties arise in attempting to compare such results with theory, since the observed change in transmission is the average result of all the electric field values in the junction. In order to obtain the effect associated with just one particular value of the electric field, the following technique was used. The junction was reverse biased to a voltage V_{rev} and in addition a much smaller ac voltage, V_{mod}, of frequency 1000 cps was imposed on the dc bias. This results in a weak modulation of the transmitted light that can be easily detected with the aid of a phase-sensitive tuned amplifier. It will be shown that the ratio of the 1000 cps signal ΔI to the total transmitted light I is directly related to the change in absorption coefficient corresponding to the maximum field in the junction.

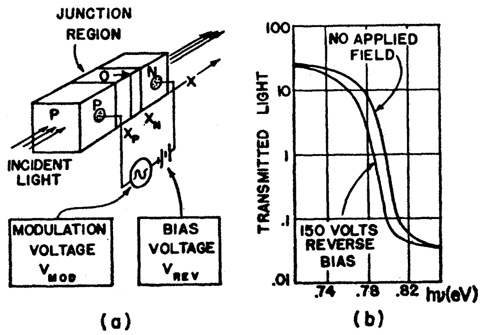

FIG. 1. (a) Schematic representation of the sample arrangement. (b) Transmitted light through the junction for zero and 150 V reverse bias ($F_{\max} \simeq 10^5$ eV/cm).

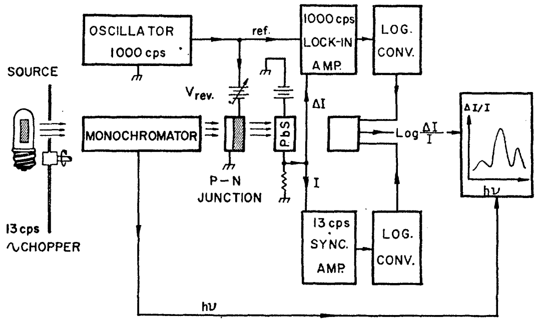

FIG. 2. Block diagram of the experimental apparatus.

The transmitted light I was determined simultaneously with ΔI by putting a chopper in the path of the beam: the two periodic signals induced in the lead sulfide detector were separated by filtering networks and independently amplified through phase-sensitive circuits (Fig. 2). The 13 cps chopped signal was made approximately sinusoidal in order to avoid generation of high-frequency harmonics. Two logarithmic converters enabled the direct recording of the ratio of the two signals. An example of experimental recording is shown in Fig. 3. The sensitivity of the apparatus was such that ratios as small as $\Delta I/I \approx 10^{-6}$ could be easily

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detected. In some cases, at very low signal levels, it helped to perform the measurements of ΔI and I in succession rather than simultaneously: using dc light and recording the signal immediately after the lock-in detection gave an additional improvement in signal-to-noise ratio. For energies higher than the gap, however, the major source of error came from the measurement of the total transmitted light, due to the presence of long-wavelength scattered light. In the range $h\nu > 0.81$ eV, the experimental values of $\Delta I/I$, whenever different from zero, are to be considered uncertain.

Measurements were carried out on a number of samples, but only the data from two of them were extensively studied. The samples were p type, 7 Ωcm square slices, approximately 100–150 μ thick, 0.5–1 cm^2 area, on top of which a thin n-type layer had been created by diffusion of arsenic. Ohmic gold-plated contacts were placed on both sides of the junction, except in the path of the light beam. All samples were etched by CP4. This etch, under proper stirring, enabled us to obtain a rather smooth and specular surface. The over-all final etching was necessary to achieve good reverse breakdown characteristics.

The capacitance of the junction versus reverse voltage was measured by a Boonton 1 Mcps capacitance bridge. This function was used to evaluate both the maximum electric field in the junction and the depletion region depth as a function of reverse voltage.[12]

All data were taken at room temperature. The samples were water-cooled to prevent heating due to the reverse current in the junction: even close to breakdown no appreciable temperature variation was observed. The Joule heat dissipated in the junction during a half-cycle by the ac component of the current was at most 5×10^{-6} J and excludes the possibility that the measured effect is due to temperature fluctuations. As an additional experimental check, the rise-time of the effect was measured by applying a square-wave electric field across the junction, and detecting the transmitted light change by another p-n junction of the same type. The results showed that the signal has a rise-time less than 4 μsec, which was the limit of the external circuit used in the experiment.

III. RESULTS

A. The Direct Edge

The experimentally measured quantity $\Delta I/I$ can be derived analytically from Lambert's law neglecting all effects due to free carriers and reflection. Considering only the p side of the junction, the fractional change in transmitted light occurring when the reverse bias V is changed by a small amount ΔV is given, in the limit $\Delta I/I \ll 1$, by

$$\Delta I/I=\int_{x_p}^{0}\Delta\alpha dx=\int_{x_p}^{0}\frac{d\alpha}{dF}\frac{\partial F}{\partial V}\Delta V dx, \qquad (1)$$

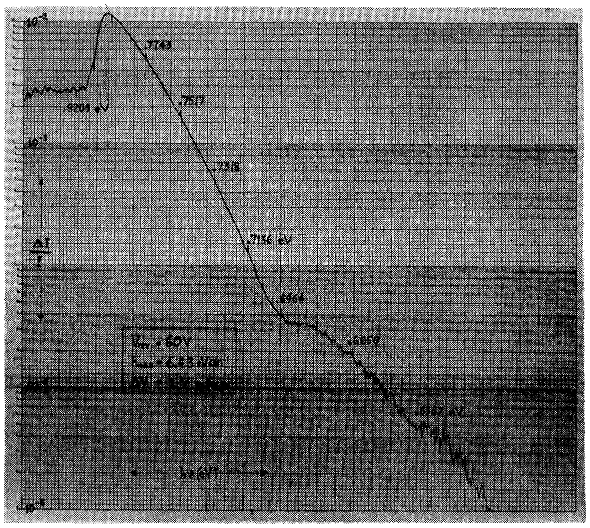

FIG. 3. Typical experimental recording for $F_{\max}=6.43\times10^4$ V/cm.

where α is the absorption coefficient, F/q is the electric field (q = electron charge), and x_p is the effective boundary of the space-charge region. Both F and x_p are functions of the applied voltage V. For a depletion layer of the type encountered in p-n junctions, $\partial F/\partial V$ is independent of x and can be replaced by $\partial F_{\max}/\partial V$, where $F_{\max}/q$ is the value of the electric field at the center of the junction ($x=0$).[12] We have neglected the contribution from the n side of the junction, since this is much more highly doped than the p side ($x_n \ll x_p$). Also, it will be assumed that the potential drop ΔV can be considered as occurring almost entirely on the p side.

The integral in Eq. (1) can be easily evaluated in the simple case of an abrupt junction (density of charge ρ = constant). Then

$$\frac{\Delta I}{I}\frac{1}{\Delta V}=\frac{\partial F_{\max}}{\partial V}\int_{x_p}^{0}\frac{d\alpha}{\partial F/\partial x}=\frac{q}{F_{\max}}[\alpha(F_{\max})-\alpha(0)], \qquad (2)$$

since in this particular case $F_{\max}/q=[2\rho V/\epsilon]^{1/2}$ and $\partial F/\partial x=(\rho q/\epsilon)$, where ϵ is the permittivity. Unfortunately, this was not the case for our samples. The capacitance measurements indicated that ρ varied approximately as x^n, where $n=0.42$. In this case, the integration has to be performed numerically. An expression for $d\alpha/dF$ can be obtained from the theory. According to Refs. 1–5, the change in absorption coefficient upon application of an electric field is given asymptotically (i.e., for $B/F \gg 1$) by

$$\Delta\alpha(F)=\alpha(F)-\alpha(0)=AF\exp(-B/F), \qquad (3)$$

where

$$A=[K\mu/8\pi\nu(E_G-h\nu)],$$

and

$$B=[8\pi(2\mu)^{1/2}/3h](E_G-h\nu)^{3/2},$$

(μ = reduced effective mass, E_G = energy gap, and

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[12] L. B. Valdes, *The Physical Theory of Transistors* (McGraw-Hill Book Company, Inc., New York, 1961).

K = constant related to the interband optical matrix element). Equation (1) becomes

$$\frac{\Delta I}{I}\frac{1}{\Delta V}=A\frac{\partial F_{\max}}{\partial V}\int_{x_p}^{0}(1+B/F)\exp(-B/F)dx$$

$$=A\frac{q}{x_p}\int_{x_p}^{0}\left[1+\frac{B}{F_{\max}}\frac{1}{1-(x/x_p)^{n+1}}\right]\times\exp\left(-\frac{B}{F_{\max}}\frac{1}{1-(x/x_p)^{n+1}}\right)dx$$

$$=Aq\exp(-B/F_{\max})\left\{\frac{1}{\exp(-B/F_{\max})}\times\int_{1}^{0}\left[1+\frac{B}{F_{\max}}\frac{1}{1-(x/x_p)^{n+1}}\right]\times\exp\left(-\frac{B}{F_{\max}}\frac{1}{1-(x/x_p)^{n+1}}\right)d(x/x_p)\right\}.$$

Calling $1/\Phi$ the bracketed term we finally obtain

$$\frac{\Delta I}{I}\frac{1}{\Delta V}=\frac{Aq}{\Phi}\exp\left(-\frac{B}{F_{\max}}\right)=\Delta\alpha(F_{\max})\frac{1}{F_{\max}}\frac{q}{\Phi}. \qquad (4)$$

Φ has been evaluated numerically and tabulated as a function of $B/F_{\max}$. Taking the logarithm of Eq. (4) and extracting from A its frequency-dependent term we have:

$$\ln\left[\frac{\Delta I}{I}\frac{1}{\Delta V}\Phi(E_G-h\nu)h\nu\right]=\ln\left[\frac{\mu hKq}{8\pi}\right]-\frac{B}{F_{\max}}. \qquad (5)$$

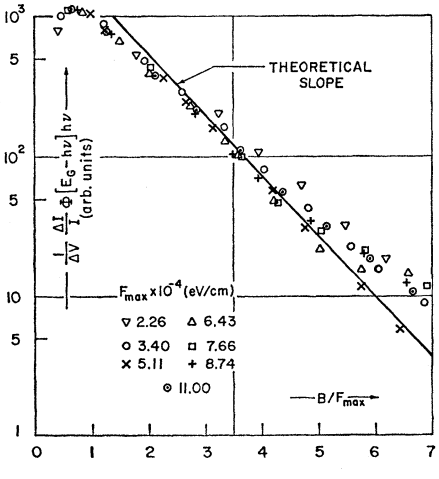

FIG. 4. Plot of the left side of Eq. (5) versus $B/F_{\max}$ for a number of values of the electric field (sample No. 1).

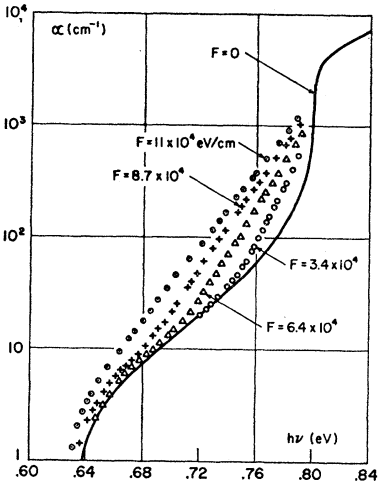

FIG. 5. Absorption coefficient as a function of photon energy for various values of the electric field.

The right side of Eq. (5) is a linear function of B, provided K is independent of energy and field, the slope being given by the reciprocal of the maximum field in the junction. A plot of the left side of Eq. (5) versus $B/F_{\max}$ should result in a single straight line of unit slope independent of the magnitude of the applied field. In calculating B, E_G was taken equal to 0.805 eV and the reduced mass was obtained from the electron effective mass at $k=0$, $m_e=0.036m_0$,[13] and the light hole effective mass at $k=0$, $m_l=0.0426m_0$.[14] The results for the direct optical transitions are shown in Fig. 4 (sample No. 1). The experimental points fit rather well on the expected line, the error being within the uncertainty in the determination of the field ($\sim$10%). The deviation occurring for $B/F_{\max}$ very small is due to the failure of Eq. (3) in this range. For $B/F_{\max}$ large, contributions from the indirect absorption process are present and cause a spread of the data above the theoretical line. It should be noted that the indirect edge for the various fields is located at different values of the abscissa. The good agreement between theory and experiment suggests that the light holes rather than the heavy holes play a dominant role in this process. The ratio of the electron-heavy hole effective mass to the electron-light hole effective mass is equal to 1.7. Thus, the heavy holes should contribute more at small values of $B/F_{\max}$ while the light holes processes should dominate for $B/F_{\max}$ large.

From Eq. (4) the change in α for a given value of $F_{\max}$ can be evaluated. Addition of this term to the absorption coefficient in the absence of the electric field has made it possible to obtain the curves of Fig. 5 [data in the proximity of the edge have been omitted since Eq. (4) is not valid in this region]. Figure 5 shows that the steep direct edge at zero-field shifts gradually to a more slowly rising exponential-type edge with increasing electric field. The effect is remarkably large: at $\approx$0.78 eV the change in α at $F=1.1\times10^5$ eV/cm is

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[13] S. Zwerdling, B. Lax, and L. M. Roth, Phys. Rev. 108, 1402 (1957).

[14] R. N. Dexter, H. J. Zeiger, and B. Lax, Phys. Rev. 104, 637 (1956).

$\approx 500\ \text{cm}^{-1}$, four times the zero value. At $\alpha = 100\ \text{cm}^{-1}$ the shift to longer wavelengths for the same field is approximately 1000 Å. We should point out here that these figures differ from those given in Ref. 11, where a few preliminary results had been reported. In those papers, the $\Delta\alpha$'s were evaluated through Eq. (2) assuming that the junction was not far from being abrupt. Equation (2) differs from Eq. (4) only by the presence of the factor Φ. For $B/F_{\max} \geqslant 3$, Φ is approximately a constant equal to 0.6. The simple treatment reported in Ref. 11 is therefore qualitatively correct, but leads to an overestimation of the effect, the error being almost equal at all energies.

B. The Indirect Edge

Figure 5 shows that for large values of the electric field the tail of the direct absorption process extends to very low energies, so that it is not possible to differentiate the indirect from the direct absorption. For low electric fields, however, it is possible to observe effects related to the indirect absorption process. Figure 6 shows the changes of $\Delta I/I$ for sample No. 2 on a linear scale in the energy region about the indirect edge: the observed $(\Delta I/I)$'s are positive as well as negative and have magnitude of the order of $10^{-6} - 10^{-5}$. Notice that the existence of negative values is a further argument against possible temperature effects.

In Fig. 6 the energies E_0 and E_1 for optical transitions with phonon absorption and E_2, E_3 for optical transitions with phonon emission have been indicated. The values were obtained from Macfarlane *et al.*,[15,16] and correspond to a temperature of 291°K. If one takes into account that the central oscillations are somewhat affected by the positive tail both of the direct edge and of the 0.687-eV peak (they eventually disappear for higher fields, as shown by the dotted curve in Fig. 6), it can be said that each of the four phonon lines lies approximately at an inflection point of the spectrum. Although this behavior may be explained in terms of the Franz-Keldysh effect, the overlapping of the various processes involved makes this quite difficult to analyze. At approximately 0.71 eV there is another inflection which may be associated with the optical absorption of a photon and the emission of two phonons, one tranverse optical and one tranverse acoustical. A tunneling transition of this type has been observed by Chynoweth[17] in tunnel diodes at low temperatures.

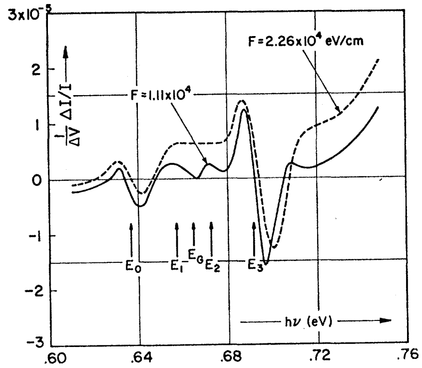

FIG. 6. Measured $\Delta I/I$ in the region about the indirect energy gap (sample No. 2).

The importance of these results is that they show how the Franz-Keldysh effect may be used as a tool for the observation of the indirect phonon processes. We want to mention also that silicon demonstrates a similar behavior at the indirect edge, while showing no presence of direct edge.[18,19] No phonon peaks have been observed in gallium arsenide.[20] Both results were to be expected if our interpretation of the nature of the observed oscillations is correct.

ACKNOWLEDGMENTS

We would like to thank Robert Pfeifer for his assistance with the experimental work, and Dr. Carl Meyer and E. Paskell of the Delco Radio Division of General Motors for providing the diffused germanium junctions. We are much indebted to Claude Penchina for many helpful suggestions.

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[18] Data to be published.

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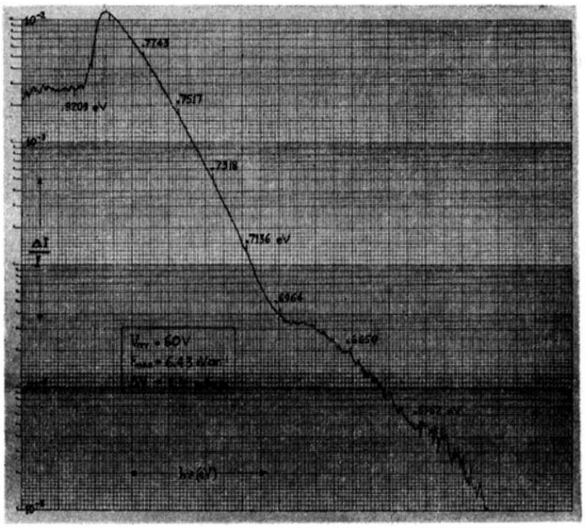

FIG. 3. Typical experimental recording for $F_{\max} = 6.43 \times 10^4$ V/cm.