the subordinate periodic term as well as harmonics of both terms) appear to be quite different from the asymmetries in the susceptibility oscillations suggesting that the relative strengths of the two periodic terms and their harmonics are probably quite different in the different effects studied.

The magnetoresistance and Hall effect data show reasonable agreement with the data of Kinchin[17] (whose measurements extended up to about 9 kilogauss), although his data were not sufficiently detailed to reveal the presence of oscillations. The magnetic susceptibility data are in excellent agreement with Shoenberg's data even with regard to the finer details. Indeed, it should be emphasized that the fundamental parameters β and E_0 derived from de Haas-van Alphen (susceptibility) measurements show remarkable reproducibility (within a few percent) from crystal to crystal of a given element despite relatively rough physical treatment and in some cases[1,13,18] alloying up to 0.5 atomic percent. Since relatively good agreement is obtained between theory and experiment in the case of magnetic susceptibility, values of these parameters so obtained are probably more reliable than values deduced from Hall effect and magnetoresistance data.

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[18] Croft, Love, and Nix, Phys. Rev. **95**, 1403 (1954).

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Hall Mobility of Optically Excited Carriers in Germanium

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Steady-state Hall coefficient measurements of optically excited carriers have been made for high-resistivity gold-, iron-, cobalt-, and nickel-doped germanium crystals in the temperature range from 200°K to 54°K. In the spectral region of impurity absorption, ($h\nu<0.7$ ev), carriers generated in p-type samples are holes; carriers generated in n-type samples are electrons. In the region of intrinsic absorption, ($h\nu>0.7$ ev), Hall coefficient measurements indicate that photoconduction is due primarily to mobile electrons in both p- and n-type high-resistivity samples. These observations suggest that, in the crystals studied, hole trapping is primarily responsible for the intrinsic photosensitivity in both n- and p-type samples. These results are qualitatively consistent with the double-acceptor model, proposed to account for the two impurity levels introduced into Ge by each of the aforementioned impurities.

I. INTRODUCTION

STUDIES of the properties of Ge crystals doped with Au,[1] Fe,[2,3] Co,[4] and Ni[4] indicate that each of these impurities introduce two deep energy levels, one above and one below the center of the forbidden band of Ge.[5] Thus for each of these doping elements it is possible to prepare both n- and p-type crystals whose extrinsic behavior is dominated by a specific deep impurity level. Resistivity values for such crystals rise to very high values in the region of liquid nitrogen temperature with the resistivity-temperature relationship characteristic of the specific impurity level. The low-temperature photoconductivity spectrum for each of these materials may be resolved into a region of intrinsic photoconduction, ($h\nu>0.7$ ev), and a region of extrinsic or impurity photoconduction, ($h\nu<0.7$ ev). For the intrinsic case the absorption is due to generation of electrons and holes.[6] For the extrinsic photoconduction, the absorption has been presumed to result from the direct excitation of a carrier from the impurity center to the appropriate band. The long-wavelength threshold for impurity photoconduction is related to the ionization energy of the specific impurity level.[7] Primarily because of the much higher value of absorption constant in the region of intrinsic absorption, intrinsic photosensitivity is considerably higher than is impurity photosensitivity. For all of the impurity elements studied, n-type samples show considerably higher intrinsic photosensitivity than p-type samples. They are slower in recovery and demonstrate quenching effects characteristic of hole trapping. Further evidence for hole trapping in n-type Fe-doped Ge has been obtained from studies of injection breakdown[8] and optical absorption of injected carriers.[9]

These observations have been explained by assuming that dissolved impurity atoms (Au, Fe, Co, Ni) each

[1] W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).
[2] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954).
[3] R. Newman and W. W. Tyler, Phys. Rev. **96**, 882 (1954).
[4] Tyler, Newman, and Woodbury, Phys. Rev. **97**, 669 (1955); **98**, 461 (1955).
[5] Recently evidence has been presented indicating that Au also introduces a donor level at about 0.05 ev above the valence band. See Morton, Hahn, and Schulz, Proceedings of the Atlantic City Photoconductivity Conference, November, 1954 (unpublished). Also see W. C. Dunlap, Jr., Phys. Rev. **97**, 614 (1955). Also Bull. Am. Phys. Soc. **30**, No. 2, 12 (1955). We will not be concerned with the 0.05-ev level in this paper.
[6] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).
[7] R. Newman, Phys. Rev. **94**, 278 (1954).
[8] W. W. Tyler, Phys. Rev. **96**, 226 (1954).
[9] R. Newman, Phys. Rev. **96**, 1188 (1954).

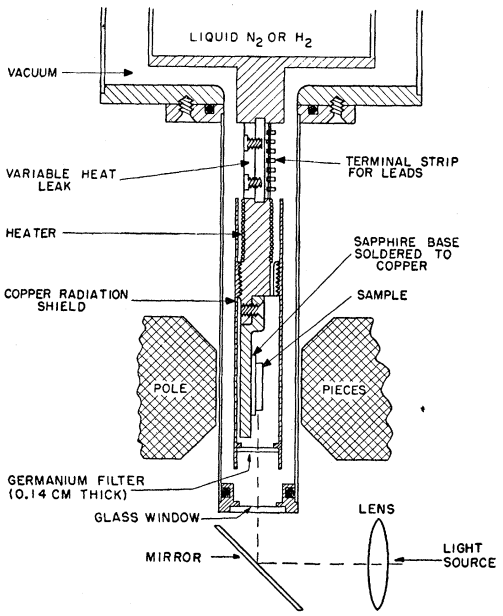

FIG. 1. Sample holder used for Hall measurements, indicating the method of focusing light on the sample.

introduce two acceptor states in Ge.[5] This assumption permits a reasonable model for hole trapping in n-type samples based on charge considerations.[2] If hole trapping is an important photoconductive process, giving rise to the high intrinsic photosensitivity, long decay times, quenching, and breakdown effects in n-type samples, intrinsic photoconduction in such samples should be due primarily to mobile electrons. In order to test this specific hypothesis and to gain general understanding of photoconduction in Ge, it seemed necessary to ascertain the type of carriers responsible for photoconduction in both n- and p-type samples in spectral regions of impurity and intrinsic absorption. To this end studies of steady-state Hall mobility of optically excited carriers were undertaken.

II. EXPERIMENTAL METHOD

Figure 1 shows the experimental arrangement. A cryostat described previously[2] was modified as shown to permit focusing light from the exit slit of a Gaertner spectrometer (crystal quartz optics) on the Ge sample. To excite intrinsic photoconduction light of 1.58 microns (0.78 ev) was used; for impurity photoconduction, light of 2.3 microns (0.54 ev) was used. Slit widths were normally set at 0.5 mm. The light source used was a tungsten ribbon lamp. Some measurements were also performed using a Perkin-Elmer Spectrometer, which provided greater resolution and freedom from stray light. The results were independent of the spectrometer used. For some high-light-level experiments in which spectral resolution was not important, (n-type samples), the W lamp was used directly without the spectrometer. For such experiments, the Ge filter, held at the temperature of the sample under study was particularly important in filtering short-wavelength radiation which would be surface-absorbed in the test sample. With the filter the effects of inhomogeneous absorption of intrinsic radiation were not serious.

Hall mobility measurements were made with the instrumentation which has been described.[2] The magnetic field used for all data to be reported was 4800 gauss. The preparation of samples has also been described. Fused Sn contacts were used for n-type samples and fused In contacts used for p-type samples. Applied voltages during measurement were held at less than one volt to minimize injection effects.

III. EXPERIMENTAL RESULTS

Although p- and n-type high-resistivity samples doped with Au, Fe, Co, and Ni have been studied, detailed data will be shown only for samples designated 55B, Au-doped, p-type; 1476, Au-doped, n-type[10]; 122B, Co-doped, p-type; and 124H, Co-doped, n-type. Qualitatively all high-resistivity samples of the same type behaved in the same manner. The Au- and Co-doped samples were chosen for detailed study because of their relatively high impurity photosensitivity and relatively low photovoltages.

Equilibrium mobility, resistivity and photoconductivity data have been published for Co-doped samples

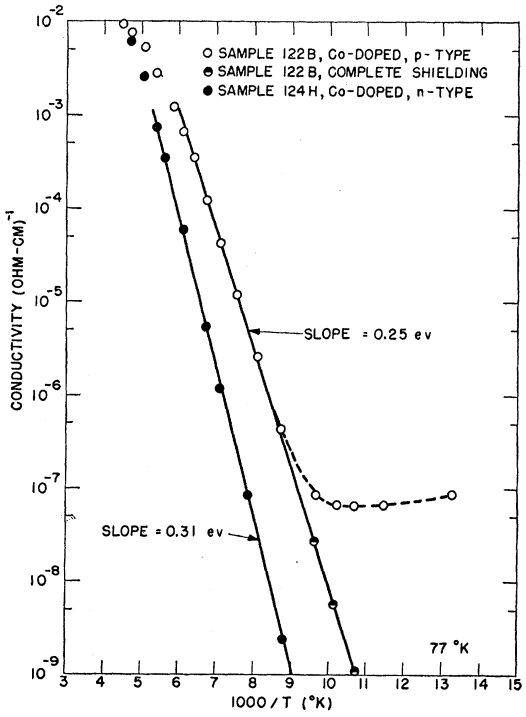

FIG. 2. Dark conductivity data for Co-doped Ge samples 122B and 124H taken with the arrangement shown in Fig. 1. For data indicated by half closed circles, the Ge filter was replaced by copper.

[10] We are indebted to W. C. Dunlap, Jr., for providing us with this sample.

122B and 124H.[4] Samples studied with the arrangement shown in Fig. 1 are continually exposed to the component of 300°K radiation which is not absorbed in the Ge filter. Consequently, values of resistivity and mobility designated as dark values in this paper are not necessarily true equilibrium values. Figure 2 shows the dependence of conductivity on temperature for the Co-doped samples, studied with the arrangement shown in Fig. 1. On replacing the Ge filter with an opaque shield, the conductivity of sample 122B follows the linear relationship to values $<10^{-9}$ (ohm-cm)$^{-1}$. On exchanging the 1.4-mm Ge filter for one five times as thick, the upper curve of Fig. 2 was reproduced exactly, indicating that the sensitivity of sample 122B to 300°K radiation is due almost entirely to the extrinsic component.[11] Figure 2 indicates that sample 122B is more sensitive to 300°K radiation than is 124H, which is consistent with the higher impurity photosensitivity reported for 122B.[4] Figures 3 and 4 show dark values of conductivity and mobility for Au-doped samples 55B and 1476 measured with the arrangement of Fig. 1. For these, the n-type sample is more sensitive to 300°K radiation, again consistent with impurity photoconductivity studies.[6]

Figures 5 and 6 illustrate experimental results characteristic of all high-resistivity n-type samples. Effective Hall mobility values are plotted as a function of conductivity. For a series of fixed temperatures, the

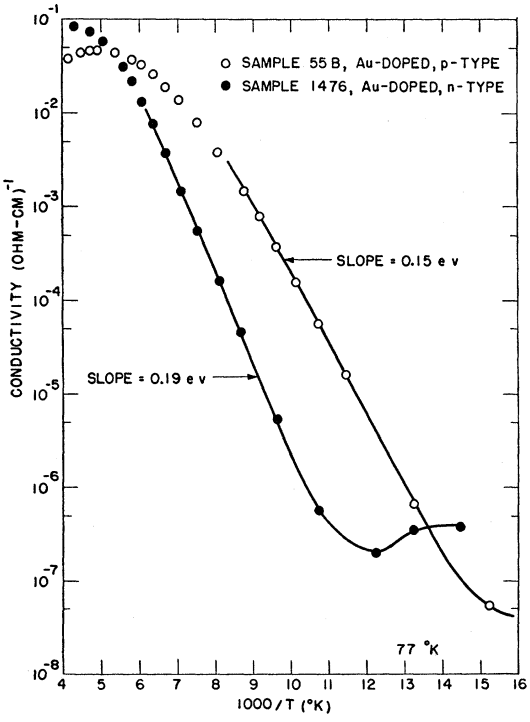

FIG. 3. Dark conductivity data for Au-doped Ge samples 55B and 1476, with the arrangement of Fig. 1.

[11] Similar results were reported for n-type Fe-doped samples in reference 2.

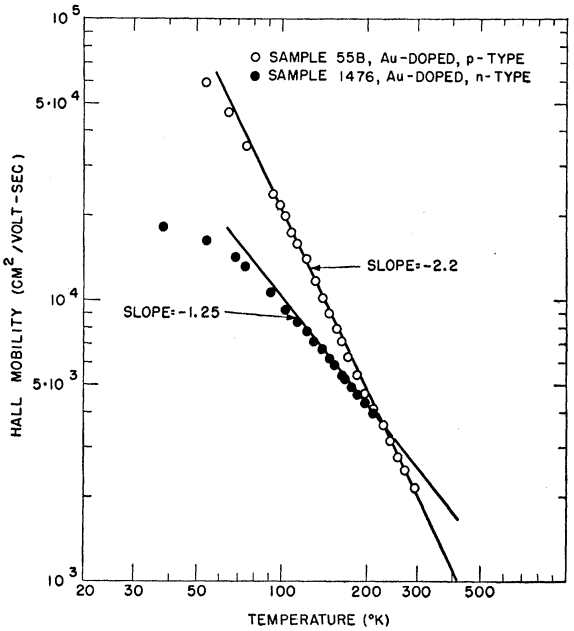

FIG. 4. Dark mobility data for the Au-doped samples 55B and 1476, with the arrangement of Fig. 1.

conductivity was increased from the dark value by increasing the light intensity. As monochromator experiments indicated no significant dependence of behavior (other than sensitivity) on wavelength of the light used, most of these data were taken using the W lamp directly, in order to obtain higher light levels. For both samples some data using monochromatic light are also shown. High-resistivity n-type samples show no appreciable change in effective Hall mobility whether excited by light in the region of intrinsic or impurity absorption. For samples of highest photosensitivity, the conductivity could be changed as much as six or seven factors of ten (primarily intrinsic response) without any appreciable drop in effective mobility. Throughout the temperature range studied, and particularly for the lowest temperatures where the change in conductivity is largest, hole mobility (measured in p-type samples) is higher than electron mobility (measured in n-type samples).[12] Thus the data indicate that holes do not contribute significantly to steady-state photoconduction in high-resistivity n-type samples.

For sample 124H, dark-mobility values at the lowest temperatures tend to fall somewhat below the approximate $\frac{3}{2}$ power temperature dependence observed at higher temperatures. Also at low temperature dark-mobility values show considerable scatter (± 10 percent). With light, effective mobility values rise to saturation values consistent with the $\frac{3}{2}$ power temperature dependence and less scatter is observed. These characteristics of n-type samples were also observed for n-type Fe- and Ni-doped samples. In some cases

[12] See references 2 and 4 for mobility data on Fe-, Co-, and Ni-doped samples and Fig. 4 for Au-doped samples studied.

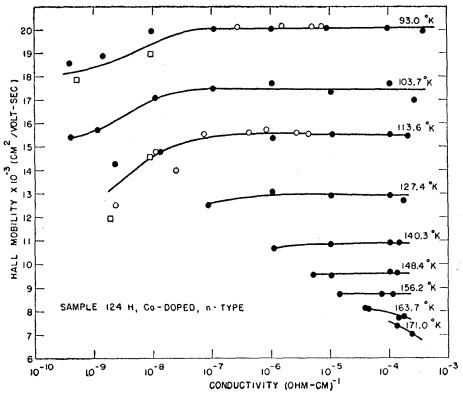

FIG. 5. Effective mobility plotted against optically excited conductivity for Co-doped, *n*-type sample 124H. Closed circles indicate response to radiation from the tungsten lamp. Squares indicate response to extrinsic radiation (2.3 microns), open circles indicate response to intrinsic radiation (1.58 microns). All Hall coefficients are negative.

samples with an anomalous dark mobility-temperature dependence[4] showed a linear $\frac{3}{2}$ power relationship using the photo-saturation values. At the highest temperatures for sample 124H where photosensitivity decreases, effective mobility values fall slightly with increase in conductivity, perhaps indicating that hole conduction is beginning to contribute in determining the Hall coefficient. For sample 1476, effective mobility values initially fall about 5 percent with increasing light level and rise slightly at the highest light levels. For both Figs. 5 and 6, for each temperature, data points to the far left represent dark values of mobility. Data points to the far right were taken at approximately the same light level.

Figures 7 and 8 illustrate behavior typical of high-resistivity *p*-type samples doped with Au, Fe, Co, and Ni. Square data points indicate values of effective mobility as a function of the conductivity change induced by impurity excitation (2.3 microns). Circles represent response to intrinsic excitation (1.58 microns);

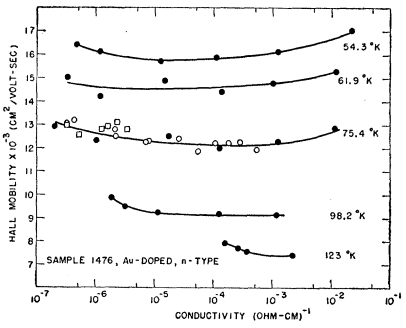

FIG. 6. Effective mobility plotted against optically excited conductivity for Au-doped *n*-type sample 1476. Closed circles indicate response to radiation from the tungsten lamp. Squares indicate response to extrinsic radiation (2.3 microns), open circles indicate response to intrinsic radiation (1.58 microns). All Hall coefficients are negative.

open circles indicate positive values of Hall coefficient, solid circles indicate negative values of Hall coefficient. The Hall inversion which was observed for all high-resistivity *p*-type samples studied, occurs for 122B after the conductivity had been increased by a factor between 3.5 and 4; for 55B the Hall inversion occurs after increasing the conductivity by a factor of about 2.

The data shown in Figs. 7 and 8 indicate that impurity photoconduction in high-resistivity *p*-type samples is due to an increase in the concentration of mobile holes. Conversely, intrinsic photoconduction is due primarily to an increase in the concentration of mobile electrons. Although it is expected that in this temperature range hole mobility is greater than electron mobility,[12] it is not clear exactly what ratio should be used in attempting to analyze the Hall inversion. The curves of Figs. 7 and 8 were repeated at about 10 different temperatures for each sample. The

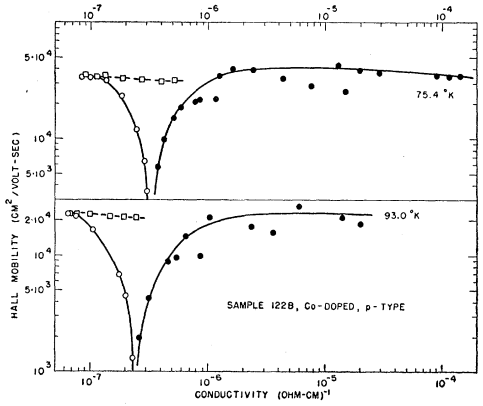

FIG. 7. Effective mobility plotted against optically excited conductivity for Co-doped *p*-type sample 122B. Squares indicate response to extrinsic light (2.3 microns). Both open and closed circles represent response to intrinsic radiation (1.58 microns). For data points indicated by squares and open circles, Hall coefficients are positive. For closed circles Hall coefficients are negative.

effective mobility after inversion saturates at values approximately equal in magnitude to the dark value. There is no evidence for any of the samples studied that the saturation values of mobility after the Hall inversion follow a temperature dependence characteristic of electron mobility.

Photovoltages were observed in many of the *p*-type samples studied but were negligible for all of the *n*-type samples. For sample 55B photovoltages were always less than several percent of the current and Hall potentials. However, for sample 122B photovoltages were in some cases as high as 20 percent of current and Hall potentials. The periodic rise and fall of effective mobility values after inversion shown in Fig. 7 was correlated with factor of 10 scale changes in the current source used in taking data; for the high data points probe potentials due to the current through the sample were appreciably larger than photovoltages, for the

lowest data points photovoltages were as high as 20 percent of probe potential. The spread in data points was considerably greater than shown in Fig. 7 before the potentials used in calculating the conductivity and Hall coefficient were corrected for photovoltages. As the magnitude of photovoltages remained small until the Hall inversion, the inversion point is not affected by photovoltage.

At 75.4°K the dark conductivity value for sample 122B is about 5 factors of ten higher than the true equilibrium value (see Fig. 2). However, the Hall inversion occurs after the same change in conductivity as that observed at 113°K, (not shown in Fig. 7), at which temperature the dark conductivity is approximately equal to the equilibrium value. This is consistent with the observation mentioned above, that the photoresponse of sample 122B to 300°K radiation is due to impurity photoconduction.

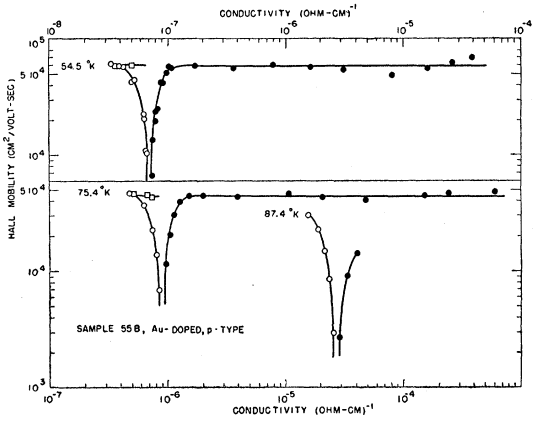

FIG. 8. Effective mobility plotted against optically excited conductivity for Au-doped p-type sample 55B. Squares indicate response to extrinsic light (2.3 microns). Both open and closed circles represent response to intrinsic radiation (1.58 microns). For data points indicated by squares and open circles, Hall coefficients are positive. For closed cirlces Hall coefficients are negative.

Efforts to compare these properties of high-resistivity samples doped with Au, Fe, Co, and Ni with normal Ge samples of high purity, met with little success because of the low photosensitivity of such samples. However, for one n-type sample containing about 2×10^{12}cm^{-3} low ionization energy donor impurities, with a pair lifetime of about 5 milliseconds, the following results were observed. At temperatures from 160°K to about 77°K, when the W lamp was used directly, conductivity increases of about 20 percent resulted in reproducible decreases in effective mobility of about 15 percent. This constitutes some evidence that in normal high-lifetime Ge under intrinsic excitation both electrons and holes contribute to photoconductivity.*

IV. SUMMARY AND DISCUSSION

A. Impurity Photoconduction

Impurity photoconduction in high-resistivity Ge crystals doped with Au, Fe, Co, and Ni is the result of an increase in the concentration of mobile holes in p-type samples and an increase in the concentration of mobile electrons in n-type samples. These results have been assumed heretofore on the basis of the spectral dependence of the impurity photoconduction.[6] The present results demonstrate this directly by Hall coefficient measurements.

In terms of the double-acceptor model which has been proposed to account for the two deep levels introduced in Ge by each of the impurities studied, the explanation of impurity photoconduction is direct. For p-type samples in thermal equilibrium, at least part of the lower acceptor levels are unoccupied. Electrons are excited from the valence bands to these levels, leaving mobile holes. In n-type material, all of the lower levels and at least part of the upper levels are occupied by by electrons. Light excites electrons from these levels directly to the conduction band.

B. Intrinsic Photoconduction

In the region of intrinsic absorption, it is assumed that the production of a free electron and free hole is the initial consequence of the absorption of a photon. To explain our experimental results we assume that, both in n- and p-type samples, the free electron lifetime is significantly larger than the free hole lifetime.[13] Hole trapping seems to be the important photoconductive process in both n- and p-type samples. Because of the higher photosensitivity, longer decay times and quenching effects observed in n-type samples it seems evident that hole trapping is more effective in n-type samples than in p-type samples, giving an appreciably longer free electron lifetime in n-type samples.

A hypothesis for hole trapping in n-type material based on considerations of charge distribution at a double-acceptor site has been proposed to explain high photosensitivity in n-type Fe-doped crystals.[2] It was postulated that hole trapping in such samples was due to the much larger capture cross section for holes by doubly charged negative sites than for electrons by singly charged negative sites. This hypothesis may be extended to explain hole trapping in p-type samples. It is now proposed that the capture cross section for holes by singly charged negative sites is sufficiently larger than the capture cross section for electrons by neutral sites, so that even in p-type material, free-electron lifetimes are appreciably larger than free-hole lifetimes.

* *Note added in proof.*—The cyclotron resonance measurements of optically excited carriers in germanium show that both holes and electrons are mobile in normal high-purity samples at 4°K [see A. F. Kip, Physica **20**, 813 (1955)]. It would be of interest to use the techniques of cyclotron resonance to study the class of phenomena described in this report.

[13] See A. Rose, Phys. Rev. **97**, 322 (1955), for a detailed account of the relationship of carrier lifetime to photoconductive behavior.