Temperature Dependence of Photo-Hall Effects in High-Resistivity Gallium Arsenide. I. One-Carrier Effects*

RICHARD H. BUBE† AND HAROLD E. MACDONALD‡
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

(Received June 14, 1962; revised manuscript received September 10, 1962)

The new opportunities for investigating imperfections in high-resistivity photoconductors through temperature-dependent photo-Hall effects have been utilized for a number of problems in gallium arsenide crystals in which one-carrier conductivity dominates. Such problems include (1) the type of trapping centers in "pure" GaAs, (2) the identity of the carriers in "pure" crystals which exhibit an exponentially increasing photosensitivity with increasing reciprocal temperature, and (3) the nature of variations of Hall mobility with photoexcitation, indicating strong scattering effects.

INTRODUCTION

THE interpretation of photoelectronic phenomena in high-resistivity photoconductors has been generally limited up to the present time by the ability of the experimenter to measure only the conductivity. He has thus been ignorant of the sign of the charge carriers contributing to the conductivity and of the mobility of these charge carriers. Initial experiments at room temperature have shown how important it is to make measurements of the photo-Hall effect in conjunction with photoconductivity, if one is to evaluate rightly the nature of the processes involved.[1–4] It has been demonstrated, for example, that the mobility may vary considerably with light intensity even in cases where the conductivity is associated with carriers of only one sign, and that the presence of two-carrier conductivity may come and go as a function of light intensity without any evidence being shown in the monotonic variation of measured photoconductivity. The importance of measuring the Hall effect is all the more emphasized when photoelectronic analysis is carried out through measurement of the temperature dependence of photoconductivity.

Although the literature contains scattered references to the measurement of photo-Hall effects,[5–15] no detailed investigation of the temperature dependence of the photo-Hall effect in high-resistivity photoconductors has been undertaken. Such an investigation is the purpose of the present work.

This paper is concerned primarily with photo-Hall effects in which the conductivity is exclusively by, or dominated by, carriers of one type; an associated paper[16] discusses the investigation of photo-Hall effects in which both types of carrier play an important role in the conductivity. It is not always possible to make a complete separation of measured effects into these two categories and there may well be some overlap. In the discussion of each effect, due consideration has been taken of the possibility of both one-carrier and two-carrier phenomena. Those observations classified here as one-carrier effects may be described as (1) the determination of carrier type under conditions in which a nearly constant Hall mobility is measured with changes in light intensity or temperature; (2) the measurement of an increase in Hall mobility with increasing light intensity at fixed temperature, when the dark conductivity is too large for the lower mobility to be attributed to a two-carrier effect,[2] and (3) the measurement of a variation of Hall mobility with light intensity or temperature, under any circumstances when the effect is inexplicable in terms of a two-carrier analysis.

The material chosen for these initial experiments is gallium arsenide. This choice has been motivated by the fact that gallium arsenide is typical of many other III-V and II-VI high-resistivity photoconductors, that both n-type and p-type conductivity and photoconductivity are easily obtained and commonly observed in gallium arsenide, and that a considerable body of basic information on the properties of the crystals to be examined by photo-Hall techniques had already been established by photoelectronic analysis.[2,17,18] The study of the temperature dependence of photo-Hall effects in

* The research reported in this paper was sponsored by the Electronics Research Directorate, Air Force Cambridge Research Laboratories, Office of Aerospace Research, United States Air Force, under Contract AF 19(604)8353.

† Present address: Stanford University, Stanford, California.
‡ Present address: California Institute of Technology, Pasadena, California.

1 R. H. Bube and H. E. MacDonald, Phys. Rev. **121**, 473 (1961).
2 J. Blanc, R. H. Bube, and H. E. MacDonald, J. Appl. Phys. **32**, 1666 (1961).
3 R. H. Bube, H. E. MacDonald, and J. Blanc, J. Phys. Chem. Solids **22**, 173 (1961).
4 A. B. Fowler, J. Phys. Chem. Solids **22**, 181 (1961)
5 C. C. Klick and R. J. Maurer, Phys. Rev. **81**, 124 (1951).
6 F. C. Brown, Phys. Rev. **92**, 502 (1953).
7 H. Diedrich, Ann. Physik **13**, 349 (1953).
8 J. R. MacDonald and J. E. Robinson, Phys. Rev. **95**, 44 (1954).
9 A. G. Redfield, Phys. Rev. **91**, 753 (1953); **94**, 526, 537 (1954).
10 F. A. Kroeger, H. J. Vink, and J. Volger, Philips Research Repts. **10**, 39 (1955).
11 W. W. Tyler and R. Newman, Phys. Rev. **98**, 961 (1955).
12 W. W. Tyler and H. H. Woodbury, Phys. Rev. **102**, 647 (1956).
13 E. Yamaka and K. Sawamoto, Phys. Rev. **101**, 565 (1956); J. Phys. Soc. Japan **11**, 176 (1956).
14 K. Kobayashi and F. C. Brown, Phys. Rev. **113**, 507 (1959).
15 T. Masumi and F. C. Brown, Bull. Am. Phys. Soc. **6**, 131 (1961).
16 R. H. Bube and H. E. MacDonald, following paper [Phys. Rev. **128**, 2071 (1962)].
17 R. H. Bube, J. Appl. Phys. **31**, 315 (1960).
18 J. Blanc, R. H. Bube, and L. R. Weisberg, Phys. Rev. Letters **9**, 252 (1962).

high-resistivity photoconductors has been made possible by the construction of apparatus described in a separate publication.[19]

The following measurements are now possible on a single crystal: (1) temperature dependence of Hall effect in the dark; (2) temperature dependence of photo-Hall effect under constant photoexcitation intensity; (3) photo-Hall effect as a function of photoexcitation intensity at various temperatures; and (4) thermally stimulated Hall effect, i.e., the Hall effect of carriers freed from traps by thermal stimulation. It is possible also to measure optically stimulated Hall effect, optically quenched Hall effect, and all the other Hall-effect analogs of normal photoconductivity measurements. The limitations imposed by the present apparatus are a minimum mobility of about 0.1 cm^2/V-sec, a maximum resistivity of about 10^{10} Ω-cm, and a temperature range from 77 to 450°K.

The rich pattern of phenomena revealed by a detailed study of photo-Hall effects in conjunction with photoconductivity analysis, can be indicated only in part by the presentation of this paper on one-carrier effects and its accompanying related paper on two-carrier effects. We have attempted to sample a number of basic effects; in doing this we have naturally been led to the conception of many other types of measurement which could and should be done. The results described here, therefore, should really be considered as illustrative rather than exhaustive. Although we have been able to answer a number of questions about imperfections in GaAs which were previously unanswerable, the very techniques which have led to these answers have provided us with certain other questions which the reader will perceive for himself.

The following problems are the ones to which the present paper is addressed:

(1) What carriers are involved in trapping effects in "pure" high-resistivity GaAs?

(2) What carriers are involved in the photoconductivity of "pure" GaAs crystals which have exhibited a photosensitivity increasing exponentially with increasing reciprocal temperature?

(3) In GaAs:Si:Cu crystals which show high photosensitivity at low temperature: (a) What carriers are involved in the low-temperature photoconductivity? (b) How does the carrier mobility behave in the region of temperature quenching of photoconductivity? (c) How does the mobility vary with light intensity at low temperatures?

(4) How do the stepwise variations of Hall mobility with light intensity previously observed in "pure" GaAs at room temperature, vary with temperature?

(5) How do the anomalously large variations of Hall mobility with light intensity previously observed at room temperature in certain GaAs crystals vary with temperature?

EXPERIMENTAL

The GaAs crystals used in this investigation were of two types: (1) "pure" as-grown GaAs crystals without intentionally added impurities, grown either by the Bridgman method or by floating-zone techniques,[20] and (2) initially high-conductivity GaAs:Si crystals compensated by diffused Cu to produce high-resistivity highly photosensitive crystals. Many of the crystals used are the very same crystals for which the photoelectronic properties have been described in previous publications.[2,17,18]

The apparatus used is described elsewhere.[19] It essentially consists of a dc method, using two Cary 31V vibrating-reed electrometers for detection of voltage drop in the crystal and of the Hall voltage. The crystal to be measured is equipped with six melted-indium ohmic contacts, only five of which are used at any one time; two of these are large-area contacts applied to the ends of the crystal (typical crystal dimensions: $6\times2\times1$ mm^3), and the others are point contacts applied two each to either edge of the crystal, at about the $\frac{1}{3}$ points of the crystal length. The Hall voltage is read directly, for either polarity of applied electric field or of magnetic field, and bucking circuits are provided to cancel out the misalignment potential existing between the Hall probes in the absence of a magnetic field. The crystal with its attached leads is mounted on a Teflon block in a cryostat in which it is surrounded by dry helium gas, which acts both as an inert atmosphere and as a medium for heat transfer. The magnetic field is supplied by a 4-in. Varian magnet and was 6×10^3 Oe for the gap used.

It is important for the experiments undertaken here that the crystal be photoexcited homogeneously throughout its volume. Since the spectral response of photoconductivity in these crystals of GaAs[2,17] is limited almost entirely to volume-absorbed light, i.e., to light with wavelengths greater than the absorption edge, because of the high surface-recombination velocity associated with the sand-blasted surface used, the measurements described in this paper were made with a broad band of excitation derived from a No. 1497 microscope lamp operated at 6 V. The crystal itself provided the effective short-wavelength cutoff of this band, and a water filter was normally used to give a long-wavelength cutoff at 1 μ to exclude possible optical quenching effects present in some crystals.[2] The use of this source provided a much higher photoexcitation intensity than could be obtained from a monochromator; past checks on a comparison between the effects obtained with the broad-band source and monochromatic radiation with weakly absorbed radiation have indicated no significant

[19] H. E. MacDonald and R. H. Bube, Rev. Sci. Instr. 33, 721 (1962)

[20] Samples of floating-zone grown GaAs were obtained from the Bell Telephone Laboratories and from the Services Electronics Research Laboratories.

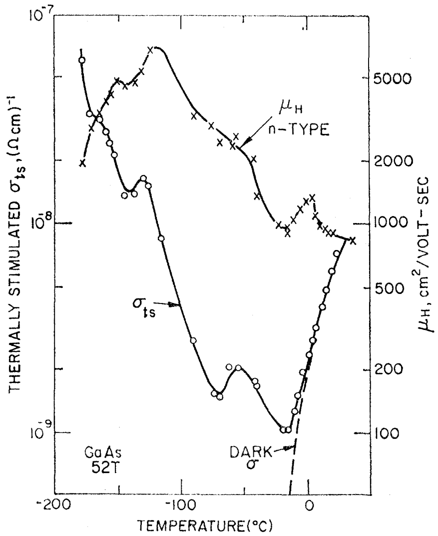

FIG. 1. Thermally stimulated conductivity and Hall effect as a function of temperature for "pure" GaAs crystal 52T.

differences. The intensity of excitation was varied by means of a set of neutral wire-mesh filters.

RESULTS

Trapping in "Pure" High-Resistivity GaAs

Trap densities in "pure" as-grown high-resistivity GaAs crystals are generally fairly low. As a result, the conductivity of such crystals in the measurement of thermally stimulated conductivity[21] usually does not exceed 10^{-10} $(\Omega\text{-cm})^{-1}$ over any appreciable temperature range. The thermally stimulated conductivity at a given temperature is proportional to the rate of trap emptying multiplied by the lifetime of a freed electron. In a few crystals, therefore, in which a reasonably high trap density is combined with a fairly high free electron lifetime at the temperature of trap emptying, it becomes possible to measure the Hall effect of the thermally stimulated conductivity.

One of the first successful reported attempts to make a measurement of this type is shown in Fig. 1. The crystal was cooled to 77°K, photoexcited for a period of minutes to steady state, and then heated in the dark at a heating rate sufficiently slow to permit meaningful Hall effect measurements. Figure 1 shows the temperature dependence of the thermally stimulated conductivity, contributed by the thermal emptying of traps; at all temperatures below -10°C the dark conductivity of the crystal is negligible compared to the thermally stimulated conductivity. Figure 1 also shows the measured Hall mobility corresponding to each thermally stimulated conductivity point. The indicated result, that only electron traps contribute significantly to the trapping in "pure" high-resistivity GaAs crystals, is typical. Such a finding is to be contrasted with the importance of hole traps in crystals subjected to annealing.[16]

High Photosensitivity in "Pure" GaAs at Low Temperatures

In "pure" as-grown high-resistivity GaAs crystals, whether grown by the Bridgman or the floating-zone method, it is commonly found that the photoconductivity increases exponentially with increasing reciprocal-temperature. Apparently a certain minimum purity is required before this effect is observed. In early preparations of high-resistivity crystals by the Bridgman method,[17] the effect was seen only very occasionally. As the technique of growth of "pure" crystals by the Bridgman method was gradually improved, the appearance of the effect has become more and more common. Every crystal grown by the floating-zone method, which has been measured, has shown this effect. A summary of some 11 crystals exhibiting the effect is given in Table I. The activation energy for this process appears to be about 0.09 eV.

Photo-Hall effect measurements were made on three of the crystals in Table I to determine the sign of the carriers involved, and to obtain the activation energy more accurately. Typical results for two of these crystals are shown in Figs. 2(a) and 2(b), using an excitation intensity of about 10^3 ft-c. It was found that the conductivity was due to electron conduction; the temperature dependence of the Hall mobility corresponding to these measurements is given in Figs. 6 and 8. A plot of the density of photoexcited electrons, corrected for the temperature dependence of the density of states, as a function of $1/T$ yields in each case a region

TABLE I. Photosensitivity activation energies in "pure" GaAs

Crystal	Dark σ 300°K $(\Omega\text{-cm})^{-1}$	$E_{\Delta\sigma}$ (eV)[a]	$E_{\Delta n}$ (eV)[b]	E_a (eV)[c]
Bridgman				
10	5×10^{-5}	0.072		
52T	2×10^{-8}	0.077	0.090	0.45
52–2	2×10^{-8}	0.080		
58	8×10^{-9}	0.100	0.095	0.38
57–2	10^{-7}	0.088	0.083	0.46
52–5	10^{-8}	0.091		
52–5′ (52–5 annealed in KCN at 700°C)	7×10^{-9}	0.084		
Floating Zone				
102–A[d]	10^{-8}	0.095		
102[d]	10^{-8}	0.105		
FZP[e]	10^{-8}	0.105		
FZP–2[e]	10^{-8}	0.096		
FZI[e]	3×10^{-8}	0.105		

[a] $\Delta\sigma \propto \exp(E_{\Delta\sigma}/kT)$.
[b] $\Delta n(T/300)^{-3/2} \propto \exp(E_{\Delta n}/kT)$.
[c] Energy of sensitizing center calculated from sharp departure from exponential variation of Δn with $1/T$ with increasing T.
[d] Bell Telephone Laboratories sample.
[e] Service Electronics Research Laboratory sample.

[21] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), pp. 292–299.

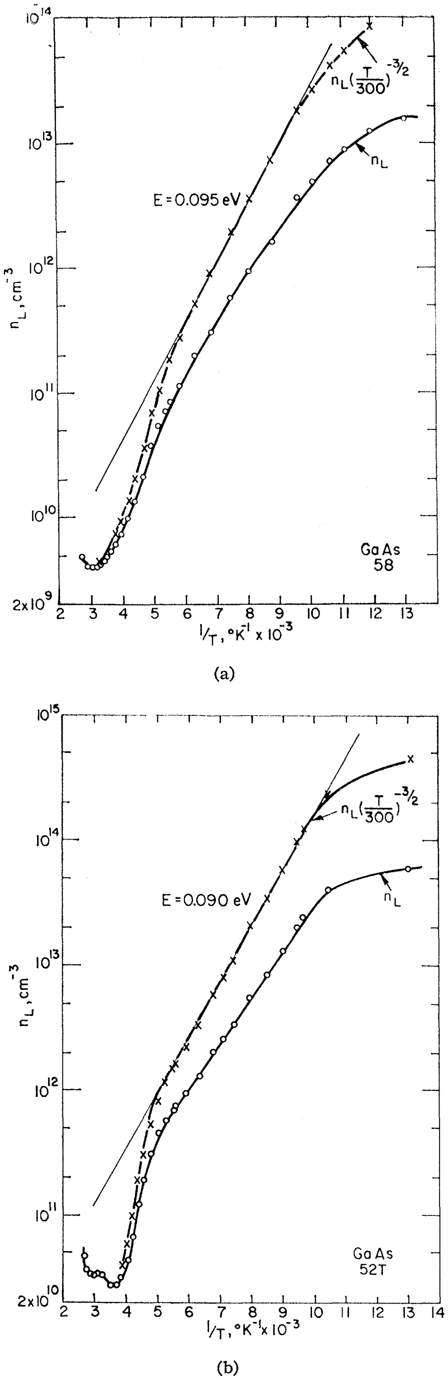

FIG. 2. (a) Temperature dependence of density of photoexcited electrons in "pure" GaAs crystal 58. (b) Temperature dependence of density of photoexcited electrons in "pure" GaAs crystal 52T.

extending over several orders of magnitude with an activation energy of 0.09 eV. The simplest interpretation calls for the existence of centers lying 0.09 eV above the valence band which act as sensitizing centers for electron conductivity to the extent that photoexcited holes may be stably held in them. This level at 0.09 eV above the valence band may well be the same as the level measured in GaAs:Si:Cu crystals[2] which were p type and with room temperature dark conductivity in excess of 5×10^{-6} (Ω-cm)$^{-1}$. The temperature dependence of photoconductivity (probably p type) in five such crystals showed that the photosensitivity *decreases* exponentially with increasing reciprocal temperature with an activation energy of 0.09 ± 0.01 eV. That the same center which acts as a sensitizing center for n-type photoconductivity should act as a recombination center for p-type photoconductivity is consistent.

Evidence for another level common to these "pure" high-resistivity GaAs crystals and to the high-resistivity GaAs:Si:Cu crystals[2] is indicated by the sharp departure from an exponential variation of free electron density with $1/T$ as T increases in Fig. 2(a) and (b). From the location of the electron Fermi level at the point of this departure, the location of the level involved, E_a eV above the valence band, can be calculated [22] using a value of $S_p/S_n=4\times10^4$ previously determined for sensitizing centers.[23] Here S_p is the capture cross section of these centers for holes and S_n is the subsequent capture cross section for electrons.

$$E_a=E_{fn}+kT\ln(S_p/S_n), \tag{1}$$

where E_{fn} is the depth of the electron Fermi level below the conduction band. The values of E_a determined in this way for three crystals are given in the last column of Table I. The behavior and the energy agree well with the presence of sensitizing centers lying 0.45 eV above the valence band, responsible for high photosensitivity in GaAs:Si:Cu crystals[2] with room temperature p-type dark conductivity less than 5×10^{-6} (Ω-cm)$^{-1}$. The similarity is enhanced by the observation that GaAs:Si:Cu crystals sometimes showed an exponential region with activation energy of 0.09 eV at low temperatures beyond the 0.45-eV break (e.g., see crystal ES 41, Fig. 3 of reference 2).

The occurrence of the 0.45 and 0.09-eV levels in both "pure" as-grown GaAs and GaAs:Si:Cu crystals indicates that they are associated with (a) impurities other than Si or Cu, common to all GaAs crystals, (b) residual traces of Si or Cu in the "pure" crystals, or (c) crystal defects. The last of these seems the most probable and is discussed further in the associated paper.[16]

GaAs:Si:Cu Crystals with High Photosensitivity at Low Temperature

The crystals investigated here are those with high photosensitivity associated with sensitizing centers lying 0.45 eV above the valence band, as described above.

The temperature dependence of the photo-Hall effect in two crystals of this type is shown in Fig. 3(a) and

[22] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957).
[23] R. H. Bube, J. Appl. Phys. **32**, 1707 (1961).

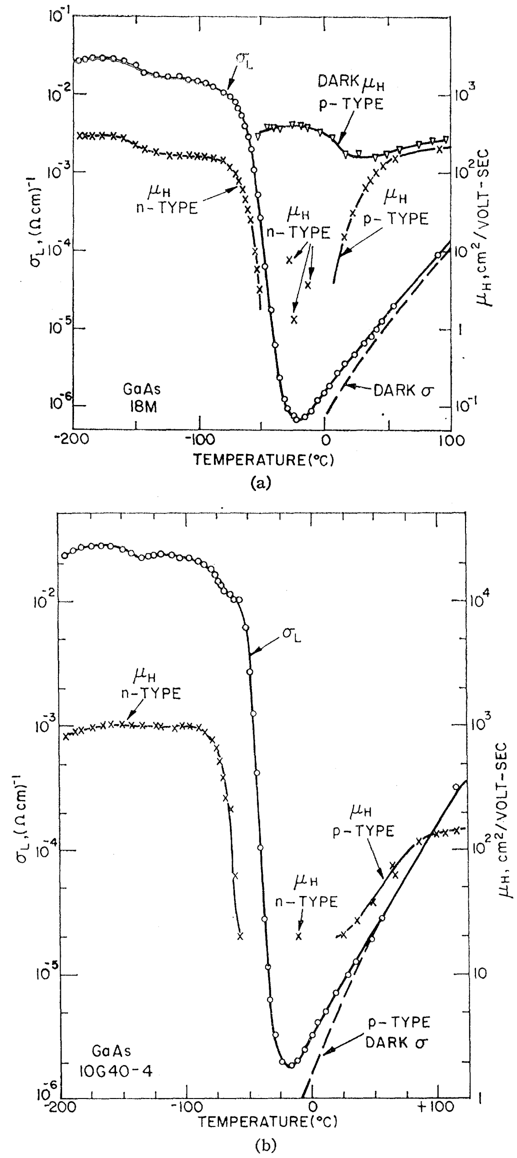

FIG. 3. (a) Temperature dependence of photoconductivity, photo-Hall mobility, and dark Hall mobility for GaAs:Si:Cu crystal 18M. (b) Temperature dependence of photoconductivity and photo-Hall mobility for GaAs:Si:Cu crystal 10G40-4.

(b) using an excitation intensity of about 10^3 ft-c. Both crystals show a high photosensitivity, relatively insensitive to temperature at low temperatures, with an abrupt thermal quenching of this photosensitivity by about four orders of magnitude when the temperature exceeds about -60°C at the light levels used.

The photoconductivity which is p type at room temperature and above, changes to n type when the crystal is cooled below the minimum conductivity point at about -20°C. At this point photoexcited holes begin to become stably held in the 0.45 eV sensitizing centers in appreciable densities, and as a result the electron lifetime and the photosensitivity rise rapidly.

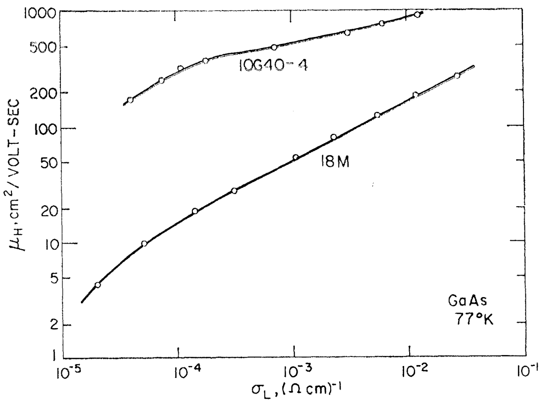

FIG. 4. Dependence of Hall mobility on photoconductivity, as varied by changing light intensity, at 77°K for GaAs:Si:Cu crystals.

The Hall mobility measured in this range, however, is very low, of the order of 1 to 20 cm²/V-sec. The Hall mobility reaches its maximum low-temperature value (note that it is still relatively low, of the order of 100 to 1000 cm²/V-sec) only after the photoconductivity has risen to its high low-temperature value.

For both samples of Fig. 3(a) and (b), it was not possible to make continuous measurements of Hall mobility between about -50 and 0°C. This difficulty was not caused by the increased resistance of the crystals, but was rather associated with a high noise background in the Hall-voltage circuit in this particular temperature range only.

The low-temperature n-type Hall mobilities of these crystals under photoexcitation are rather low, as mentioned previously. The mobility is also found to be a strong function of the photoexcitation intensity. Crystal 10G40-4, which had the higher mobility, decreases in mobility from 1000 to 150 cm²/V-sec when the photoconductivity is decreased by about three orders of magnitude by decreasing the light intensity, as shown in Fig. 4. A still larger effect is shown by crystal 18M, for which the mobility decreases from 200 to 4 cm²/V-sec,

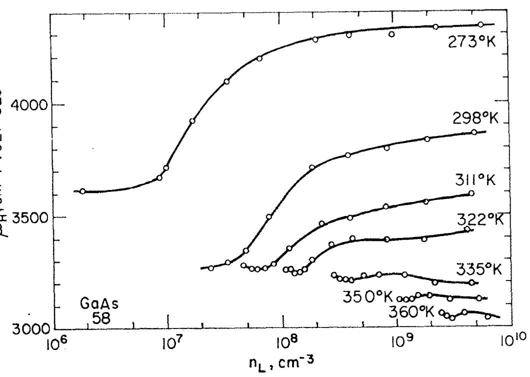

FIG. 5. Dependence of Hall mobility on density of photo-excited electrons, as varied by changing light intensity, at various temperatures. For "pure" GaAs crystal 58.

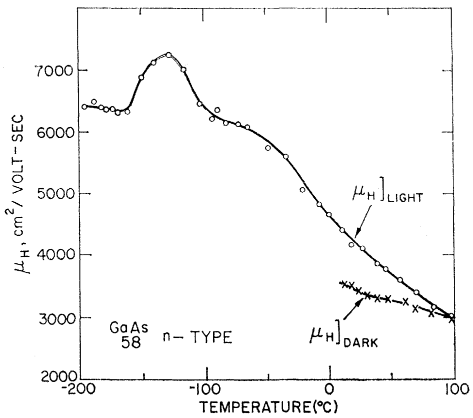

FIG. 6. Temperature dependence of photo-Hall mobility and dark Hall mobility for "pure" GaAs crystal 58.

with decreasing light intensity. The lower limits to which these measurements were taken were dictated by practical considerations of light leakage, rather than any intrinsic property of the material or the phenomenon being investigated. There is every expectation that the Hall mobility would approach arbitrarily close to zero with continued reduction in photoexcitation intensity.

Stepwise Variations of Mobility with Photoexcitation

A variation of mobility with photoexcitation at fixed temperature is often observed with "pure" as-grown high-resistivity GaAs crystals.[2,3] It is the purpose of the current investigation to see how this variation of mobility with photoexcitation depends on the temperature.

The behavior of a crystal showing a well-defined single step of mobility with light intensity is shown in Fig. 5. The temperature dependence of mobility for photoexcitation of the highest intensity used in Fig. 5 and for the absence of photoexcitation, is shown in Fig. 6. Above -50°C the mobility in the light varies as $T^{-1.37}$ and the mobility in the dark varies as $T^{-0.65}$. The dark conductivity has an activation energy of 0.63 eV as determined by Hall-effect measurements. The independently measured thermally stimulated current shows 6.5×10^{14} cm^{-3} traps with depth of 0.54 eV and 5.2×10^{14} cm^{-3} traps with depth of 0.63 eV. As the temperature is increased, the effect of photoexcitation on the mobility decreases, until above 340°K no detectable effect remains.

Similar effects for a crystal of GaAs exhibiting a double step are shown in Fig. 7. The temperature dependence of mobility is given in Fig. 8. The effects are qualitatively similar to those of the previous crystal.

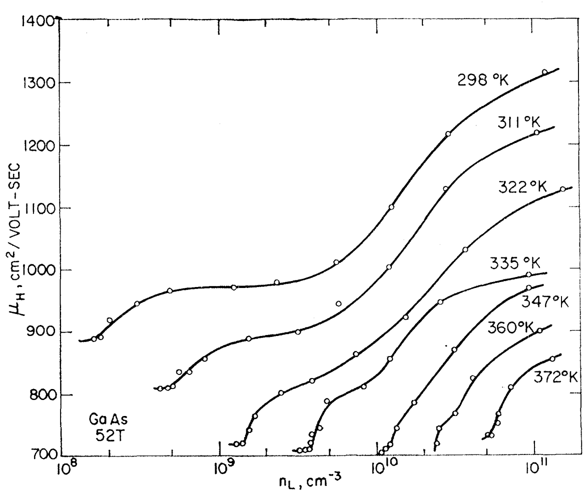

FIG. 7. Dependence of Hall mobility on density of photoexcited electrons, as varied by changing light intensity, at various temperatures. For "pure" GaAs crystal 52T.

Anomalous Variation of Mobility with Photoexcitation

There have been a number of cases in which a very large variation of mobility with photoexcitation has been observed at fixed temperature, the Hall voltage in the dark decreasing to immeasurably small values.[1–3] Such effects are usually observed in highly photosensitive crystals with diffused impurities, such as the GaAs:Si:Cu crystals of Fig. 4, or in highly photosensitive defect-sensitized crystals, such as CdSe, particularly when operated in a range where thermal quenching of photoconductivity is significant. Occasionally anomalous variations of mobility are observed in less sensitive crystals with diffused impurities, with very low near-intrinsic dark conductivity. Typical curves for such a crystal, showing the dependence of Hall mobility on photoconductivity, are plotted in Fig. 9, as the photoconductivity is varied by varying the light intensity. The results show that the anomalously low mobilities are removed by raising the temperature sufficiently, as well as by photoexcitation at lower fixed temperature. Figure 10 gives the temperature dependence of photoconductivity and Hall mobility for this crystal, using the highest value of light intensity used in Fig. 9.

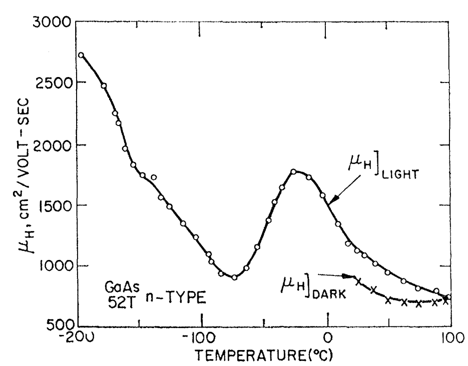

FIG. 8. Temperature dependence of photo-Hall mobility and dark Hall mobility for "pure" GaAs crystal 52T.

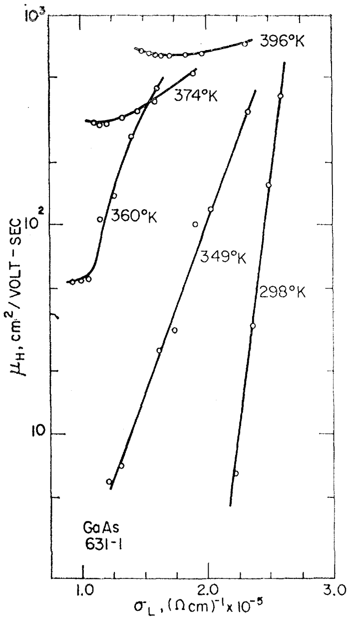

FIG. 9. Dependence of Hall mobility on photoconductivity, as varied by changing light intensity, for GaAs:Si:Cu crystal 631-1.

DISCUSSION

Dependence of Hall Mobility on Imperfections

There are several ways in which the presence of imperfections in a crystal can affect the measured Hall mobility.

(1) An increase in Hall mobility, corresponding to an increase in microscopic mobility, can be caused by photoexcitation if the charge on ionized scattering centers is removed as a result of the capture of photoexcited carriers. If $\Delta(1/\mu)$ is the magnitude of the mobility change, m_e^* is the effective carrier mass involved in the conductivity process, N is the density of scattering centers, and ΔS is the change in scattering cross section caused by photoexcitation,[3]

$$\Delta(1/\mu)=10^4 m_e^{*\frac{1}{2}} T^{\frac{1}{2}} N \Delta S. \qquad (2)$$

If the scattering centers involved are point defects with Coulombic scattering cross section, then ΔS is given to within a factor of order unity by

$$\Delta S=(10^{-10}/K^2)\ \text{cm}^2 \qquad (3)$$

at room temperature, for the change from a singly charged to a neutral center, where K is the dielectric constant.

(2) An increase in Hall mobility, corresponding to an increase in microscopic mobility, can be caused by photoexcitation if the charge on inhomogeneously distributed ionized centers is removed as the result of the capture of photoexcited carriers. This case is similar to the first except that here the scattering is associated with space-charge regions surrounding volumes in the crystal with differing Fermi level. Weisberg[24] has shown how such an inhomogeneous distribution of charged imperfections can lead to apparently huge scattering cross sections if the observations are interpreted in terms of point-defect scatterers.

(3) An increase in Hall mobility, corresponding to the decrease in various effects causing a "spuriously" low measured value of Hall mobility, can be caused by photoexcitation if the degree of inhomogeneity in the crystal is decreased. These effects are to be distinguished from the previous two in that the measured Hall mobility in very inhomogeneous samples does *not* represent the behavior of the microscopic mobility. It would be expected that the electric field might become sufficiently distorted in very inhomogeneous samples so as to result in an apparently much smaller value of the Hall voltage than actually corresponds to the conductivity process. Alternatively, the effect of high-resistivity regions limiting the current flow while the Hall measurement is made in a relatively low-resistivity region, is also to decrease the value of the measured Hall voltage. If, to take a simple example, a high-resistivity region ρ_h extends over a fraction f of the crystal length (assumed uniform across the cross section), whereas the Hall probes are in a region with low-resistivity ρ_l, the relationship between Hall mobility μ_H and microscopic mobility μ is given by

$$\mu_H=\frac{\mu}{1+f(\rho_h/\rho_l-1)}. \qquad (4)$$

The effect of photoexcitation on such a system is to

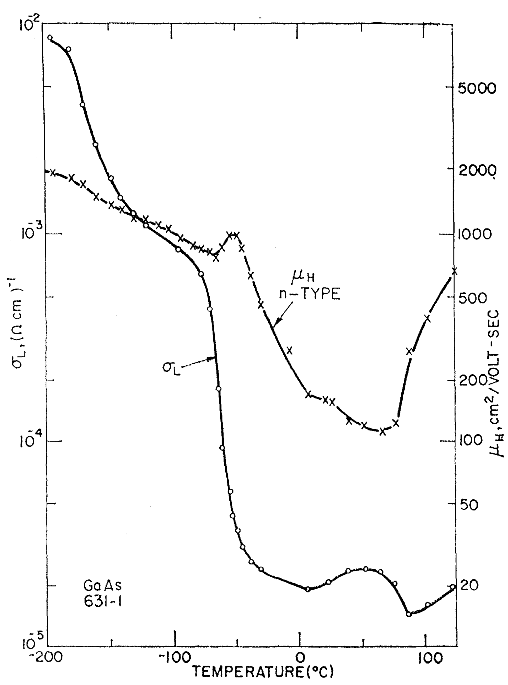

FIG. 10. Temperature dependence of photoconductivity and photo-Hall mobility for GaAs:Si:Cu crystal 631.1.

[24] L. R. Weisberg, J. Appl. Phys. 33, 1817 (1962).

decrease ρ_h down toward ρ_l. If photoexcitation does not change ρ_l, then the apparent effect will be a change in Hall mobility but no change in carrier density with photoexcitation; this is a common characteristic of many of the anomalous variations of Hall mobility with photoexcitation observed to date.[1–3]

Stepwise Variations of Mobility with Photoexcitation

When Eq. (2) is applied to measured crystals in which a stepwise variation of mobility with photoexcitation is found, scattering cross sections one to two orders of magnitude larger than the Coulomb cross section of Eq. (3) are calculated, using a center density derived from thermally stimulated currents. The fact that the mobility is insensitive to photoexcitation at both very low and very high intensities suggests that we are dealing with a real scattering effect of the second type described in the previous section, or that the density of traps determined from thermally stimulated current measurements is too low for one of several possible reasons[25] and we are dealing with a real scattering of the first type.

For the case of the crystal shown in Figs. 5 and 6, it seems likely that the deeper 0.63-eV traps correspond to compensated centers of the same type which give rise to the dark conductivity when uncompensated.[17] It is presumably the 0.54-eV traps with which the scattering is associated. A summary of the analysis of the curves of Fig. 5 is given in Table II.[26] At lower temperatures the scattering cross section calculated from Eq. (2), using a trap density of 6.5×10^{14} cm^{-3}, is approximately constant at a value of 5.3×10^{-11} cm^2, some fifty times larger than a Coulomb cross section. As the temperature is increased, the apparent cross section decreases until above 330°K the observed effect is compatible with a normal Coulomb scattering cross section. The data show that an increase in temperature is able to remove the scattering effect associated with the large calculated values of ΔS.

TABLE II. Analysis of variation of mobility with photoexcitation[a] (crystal 58).

T (°K)	T_t (eV)[b]	$\Delta(1/\mu)$ (volt-sec/cm^2)	ΔS (cm^2)
273	0.53	4.6×10^{-5}	5.3×10^{-11}
298	0.54	4.8×10^{-5}	5.3×10^{-11}
311	0.55	2.8×10^{-5}	3.0×10^{-11}
322	0.57	1.4×10^{-5}	1.5×10^{-11}
335	···	$\sim2\times10^{-6}$	$\sim2\times10^{-12}$

[a] Using Eq. (2) with $m_e^*=0.072\ m_0$ and $N=6.5\times10^{14}$ cm^{-3}, as measured by thermally stimulated currents.
[b] As determined from the $\Delta(1/\mu)/3$ value of the electron Fermi level (reference 1). To be compared with a value of 0.54 eV from thermally stimulated current.

It is possible to interpret these data in a number of ways. The apparent decrease in scattering cross section with temperature can be argued away as unreal by proposing, for example, that the photoexcitation becomes less effective in removing the scattering at elevated temperatures, either because (1) the capture cross section of scattering centers for holes increases with temperature, thus keeping them charged even when they lie below the steady-state quasi-Fermi level, or (2) there is another photo-induced scattering process which increases with temperature, like that caused by the capture of photoexcited holes by deep donors lying below the Fermi level. On the basis of the least number of specialized assumptions required, however, the authors prefer the interpretation that a real decrease in scattering cross section is being measured. Scattering is due to an inhomogeneous distribution of imperfections with the resultant development of space-charge regions surrounding volumes with differing Fermi level.[24] Photoexcitation removes the charge on these imperfections and therefore the space-charge regions as well. Increasing the temperature drives the conductivity toward intrinsic and by this means also removes the effect of these scattering regions. On this view it is supposed that the dark Hall mobility would have decreased much more rapidly with increasing temperature than actually observed, if increasing temperature did not act to reduce the space-charge scattering, and that the coalescence of dark Hall mobility and light Hall mobility at elevated temperatures results from an increase in the dark Hall mobility. Since the mobility under photoexcitation is still considerably less than the lattice mobility (12,500 cm^2/V-sec at 300°K[27]), it must be assumed that scattering from imperfections with still shallower levels is also present.

Regardless of this portion of the interpretation, however, the possible contention that the scattering cross sections are indeed normal Coulomb cross sections and that the error lies in the determination of the density of scattering centers, seems ruled out by the large departure of the scattering from a T^{-2} variation with increasing temperature.

[25] Trap densities measured by thermally stimulated currents may be too low for one of the following reasons: (a) The free carrier lifetime may be smaller during the thermally stimulated current (TSC) measurement than for the same location of the steady-state Fermi level under steady-state excitation; (b) the TSC may be associated with the escape of one type of carriers from traps with a shorter free lifetime than the other type of carriers which dominate during steady-state photoconductivity; (c) if compensated donors and acceptors are present in roughly comparable densities, the donors behaving as electron traps and the acceptors as hole traps, TSC will indicate the density of imperfections with the lower activation energy, but only a very much reduced density, if any, of those with the higher activation energy; this effect results from the recombination of carriers freed from the shallower traps with carriers trapped in the deeper traps. Data on the crystals of this investigation do not suggest the applicability of any of these limitations.

[26] Since the values of ΔS are determined from a rather small mobility change, it is appropriate to indicate that limits of error on relative values of mobility, as indicated by the points at low light intensities in Figs. 5 and 7, are less than 1%.

[27] L. R. Weisberg, F. D. Rosi, and P. G. Herkart, Metallurgical Society Conferences 5, 25 (1959).

TABLE III. Analysis of variation of mobility with photoexcitation[a] (crystal 52T).

	Shallow trap			Deep trap		
T (°K)	E_t (eV)[b]	$\Delta(1/\mu)$	ΔS (cm^2)	E_t (eV)[c]	$\Delta(1/\mu)$	ΔS (cm^2)
298	0.41	2.8×10^{-5}	1.5×10^{-11}	0.52	9.5×10^{-6}	5.7×10^{-13}
311	0.43	3.0×10^{-5}	1.6×10^{-11}	0.52	1.1×10^{-5}	6.4×10^{-13}
322	0.44	3.5×10^{-5}	1.9×10^{-11}	0.52	1.5×10^{-5}	8.6×10^{-13}
335	0.47	2.5×10^{-5}	1.3×10^{-11}	0.51	1.6×10^{-5}	9.0×10^{-13}
347	0.47	3.2×10^{-5}	1.6×10^{-11}			
360	0.48	2.2×10^{-5}	1.1×10^{-11}			
372	0.48	1.5×10^{-5}	7.4×10^{-12}			

[a] Using Eq. (2) with $m_e^*=0.072\ m_0$, and $N=1.3\times10^{15}\ cm^{-3}$ for the shallow trap, and $N=1.2\times10^{16}\ cm^{-3}$ for the deep trap, as measured by thermally stimulated currents.
[b] As determined from the $\Delta(1/\mu)/3$ value of the electron Fermi level (reference 1). To be compared with a value of 0.49 eV from thermally stimulated current.
[c] As determined from the $\Delta(1/\mu)/3$ value of the electron Fermi level (reference 1). To be compared with a value of 0.56 eV from thermally stimulated current.

The analysis for the crystal of Figs. 7 and 8 is summarized in Table III. It is interesting to note than in this crystal the scattering due to the deeper trap is within the range attributable to normal Coulomb scattering, whereas the scattering due to the shallower trap reaches this range only at elevated temperatures.

Anomalous Variation of Mobility with Photoexcitation

The anomalously large variations of Hall mobility with photoexcitation which have been reported[1–3] and which are described in this paper must be attributed to gross imperfection inhomogeneity resulting in "spurious" Hall voltage readings. The magnitude of the conductivity, for the crystal of Figs. 9 and 10, for example, is such that the phenomenon cannot be simply interpreted as a two-carrier phenomenon. At 300°K, the simultaneous conditions $p\mu_p^2=n\mu_n^2$, required for the Hall mobility to approach zero, and $np=n_i^2$, limit the conductivity to a value of about 4×10^{-10} (Ω-cm)$^{-1}$. The removal of the inhomogeneities by raising the temperature is consistent with an approach to intrinsic conductivity with elevated temperature.

Likewise the behavior of the GaAs:Si:Cu crystals of Figs. 3 and 4 cannot be described in terms of two-carrier conductivity. Even if the electron and hole mobilities were equal, a mechanism would be required which would reduce *both* electron and hole densities by four orders of magnitude during the temperature quenching. The following observations also suggest that a true measure of the microscopic mobility is not being obtained by Hall measurements: (1) in Fig. 3(b), the Hall mobility drops by a factor of 50 while the photoconductivity drops by no more than a factor of 2; (2) the measurements from which the data for crystal 18*M* in Fig. 4 are derived show an approximately linear variation of photoconductivity with light intensity, but an extremely slow apparent variation of free carrier density with light intensity.

The method of preparation of these GaAs:Si:Cu crystals is one which makes the hypothesis of gross inhomogeneities a reasonable one. High-conductivity GaAs:Si crystals were compensated by diffused Cu. It is well known in Ge, for example, that Cu diffuses in an inhomogeneous manner as determined by dislocations and similar lattice imperfections.[28]

Although the decrease in n-type Hall mobility with thermal quenching cannot be associated with two-carrier conductivity, it seems likely that the behavior of the Hall mobility above -50°C is at least partially associated with two-carrier conductivity. The effect is included here rather than in the associated two-carrier effect paper[16] in the interest of continuity. This conclusion is supported by the data shown in Fig. 3(a), where the p-type dark Hall mobility is compared with the measured Hall mobility in the light. Above 0°C, the p-type Hall mobility under photoexcitation is less than in the dark, and between -50 and 0°C, the p-type Hall mobility in the dark is actually changed to an n-type Hall mobility in the light. The sporadic nature of the measurements of the Hall effect in this intermediate range are probably associated with the formation of local p-type regions in the otherwise n-type crystal under photoexcitation.

CONCLUSIONS

Techniques of temperature-dependent photo-Hall effects have been applied to gain information about one-carrier photoelectronic effects in GaAs.

Thermally stimulated Hall effect indicates that electron trapping dominates in "pure" high-resistivity GaAs crystals.

The exponential increase in photosensitivity with increasing reciprocal-temperature observed in "pure" high-resistivity GaAs crystals, is associated with electron conductivity. The free-electron lifetime is dependent upon the concentration of photoexcited holes stably held at sensitizing centers located 0.09 and 0.45 eV above the valence band.[29] Similar levels have previously been identified in GaAs:Si:Cu crystals.

Stepwise increases in Hall mobility as a result of photoexcitation in "pure" GaAs crystals are removed by increasing temperature and are attributed to scattering by space-charge regions in the crystal associated with inhomogeneous imperfection distributions. When such effects are analyzed in terms of point-defect scattering, effective cross sections are calculated which are some fifty times larger than Coulomb cross sections.

Anomalously large variations in Hall mobility, such as with decreasing excitation intensity at low tempera-

[28] H. Reiss and C. S. Fuller, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 238.

[29] J. I. Pankove has observed evidence for the existence of the 0.09 eV and 0.45-eV levels in measurements on GaAs p-n junctions. See J. I. Pankove and M. J. Massoulie, Bull. Am. Phys. Soc. 7, 88 (1962).

ture or with increasing temperature at fixed intensity through the thermal quenching region for GaAs:Si:Cu crystals, or with decreasing excitation intensity at room temperature for a variety of photosensitive crystals which are in the process of quenching, must be associated with gross inhomogeneous imperfection distributions which result in "spurious" readings of Hall voltage. Such inhomogeneity effects are also removed by elevating the temperature.

ACKNOWLEDGMENTS

The authors are indebted to J. Blanc and L. R. Weisberg for helpful discussions, and to E. Stofko for mounting the crystals.

PHYSICAL REVIEW VOLUME 128, NUMBER 5 DECEMBER 1, 1962

Temperature Dependence of Photo-Hall Effects in High-Resistivity Gallium Arsenide. II. Two-Carrier Effects*

RICHARD H. BUBE† AND HAROLD E. MACDONALD‡
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey
(Received June 18, 1962; revised manuscript received September 10, 1962)

Analysis of photoelectronic properties of high-resistivity photoconductors by means of the temperature dependence of photo-Hall effects has been applied to a number of problems in GaAs crystals involving two-carrier conductivity. Such problems include: (1) the identity of the carriers involved in trapping processes in GaAs:Si:Cu crystals; (2) the influence of optical quenching of photoconductivity on the photo-Hall effect in photosensitive GaAs:Si:Cu crystals; and (3) an understanding of the imperfection centers present in densities up to 10^{19} cm^{-3} in annealed crystals of GaAs.

INTRODUCTION

A PREVIOUS paper[1] discussing the application of the temperature dependence of photo-Hall effects to high-resistivity GaAs crystals in which one-carrier conductivity dominates, has described the potentialities and the incentive for this investigation. The effects to be described in this paper as two-carrier effects are those involving a change in the sign of the Hall constant with variations in light intensity or temperature. It is not meant to imply that none of the scattering effects described in the previous paper on one-carrier effects plays a role in the phenomena discussed here, but rather that the major effects are those dependent upon the simultaneous conductivity by both electrons and holes.

In some respects the ability of the Hall effect to detect changes in conductivity type with changes in photoexcitation intensity and/or temperature provides an even more dramatic illustration of the utility of supplementing photoconductivity analysis with photo-Hall measurements than that provided by its use in one-carrier scattering effects. The Hall mobility is quite sensitive to changes in conductivity type, or to the onset of two-carrier conductivity where one-carrier conductivity had previously been dominant. The Hall mobility for two-carrier conductivity in the low magnetic field range can be expressed as:

$$\mu_H=(p\,\mu_p^2-n\,\mu_n^2)/(p\,\mu_p+n\,\mu_n), \tag{1}$$

where p and n are the concentrations of holes and electrons, respectively, and μ_p and μ_n are the hole and electron mobilities, respectively. In this simple formulation we have assumed that the correlation factor between Hall mobility and microscopic mobility, dependent upon the band structure and the type of scattering, is unity.

The following problems are the ones to which the present research is addressed:

(1) In GaAs:Si:Cu crystals, what type of carrier is involved in trapping effects?

(2) In GaAs:Si:Cu crystals which show high photosensitivity at low temperature, what is the nature of optical quenching of that photosensitivity?

(3) In GaAs crystals which have been annealed to produce high trap densities, what is the nature of these traps? Specifically, (a) what carriers are involved in the photoconductivity at room temperature and above, in the range in which the deeper of these traps is filled by photoexcitation? (b) What carriers are involved in the photoconductivity at lower temperatures? (c) What carriers are involved in trapping effects in these crystals? (d) Can a unified level scheme be proposed which takes into account the high densities and the results of these photo-Hall effect measurements?

* The research reported in this paper was sponsored by the Electronics Research Directorate, Air Force Cambridge Research Laboratories, Office of Aerospace Research, U. S. Air Force, under Contract AF19(604)8353.

† Present address: Stanford University, Stanford, California.
‡ Present address: California Institute of Technology, Pasadena, California.

[1] R. H. Bube and H. E. MacDonald, preceding paper [Phys. Rev. 128, 2062 (1962)].