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.

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

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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:

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

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?

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

EXPERIMENTAL

The GaAs:Si:Cu crystals used in this investigation are those for which photoelectronic analysis has been previously reported.[2] They were prepared by compensating initially high-conductivity *n*-type GaAs:Si by diffused copper.

The annealed crystals showing high trap densities are described also in other publications more fully.[3–5] The effects may be briefly summarized as follows. A variety of annealing effects have been found involving the introduction or removal of high densities of trapping imperfections with ionization energies of approximately 0.2 and 0.5 eV. In Bridgman-grown crystals, these high densities were introduced by annealing with Cu present at 500°C; they were removed again by annealing in molten KCN at 700°C. In floating-zone[6] grown crystals, high densities were also introduced by annealing with Cu present at 450°C but could equally well be introduced by annealing only in KCN at 700°C. Traps introduced into floating-zone crystals by annealing with Cu present at 450°C are not removed by annealing subsequently in KCN at 700°C. All annealing times were 16 h. Speculations and discussion relevant to the mechanisms of imperfection formation and the identity of these imperfections are to be treated elsewhere.[4,5] It is sufficient for the purposes of this paper to summarize this material by pointing out that these imperfections must be crystal defects, since detailed analysis of the crystals shows that all impurity densities including hydrogen, carbon, and oxygen are orders of magnitude smaller than the measured imperfection densities. It has also been shown that the annealed crystals with high trap densities have a smaller heat conductivity and a higher density (g/cm^3) than unannealed crystals.

Ohmic contacts were made to the crystals with melted indium and measurements of the temperature dependence of photo-Hall effects were made in an inert atmosphere of dry helium in the special Hall effect apparatus designed for high-resistivity materials. The method is a dc technique using two Cary 31V vibrating-reed electrometers for detection of the voltage drop in the crystal and of the Hall voltage. Details will be found in another publication.[7] For measurements at fixed excitation intensity, an incandescent intensity of about 10^3 ft-c was used, as discussed in the previous paper.[1] Lower intensities were obtained by the interposition of neutral density stainless steel mesh filters.

[2] J. Blanc, R. H. Bube, and H. E. MacDonald, J. Appl. Phys. **32**, 1666 (1961).
[3] J. Blanc, R. H. Bube, and L. R. Weisberg, Bull. Am. Phys. Soc. **7**, 89 (1962).
[4] J. Blanc, R. H. Bube, and L. R. Weisberg, Phys. Rev. Letters, **9**, 252 (1962).
[5] J. Blanc, R. H. Bube, and L. R. Weisberg (to be published).
[6] Floating-zone-grown GaAs crystals were obtained from Bell Telephone Laboratories and from Services Electronics Research Laboratory. No significant difference was found between the crystals grown in the two laboratories. Crystal 102A described in this paper is a Bell Telephone Laboratories sample.
[7] H. E. MacDonald and R. H. Bube, Rev. Sci. Instr. **33**, 721 (1962).

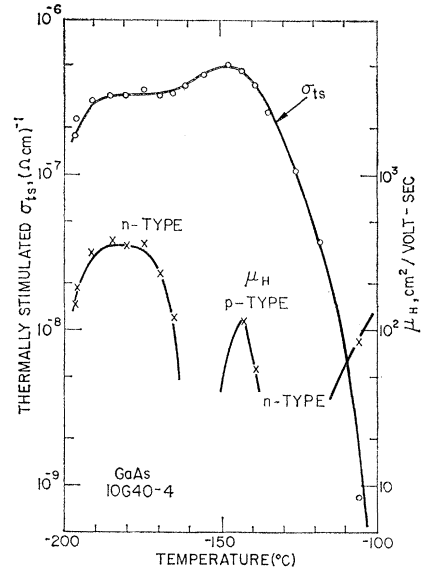

FIG. 1. Thermally stimulated conductivity and Hall effect for shallow trap in GaAs:Si:Cu crystal 10G40-4.

RESULTS

Trapping in GaAs:Si:Cu Crystals

By the measurement of thermally stimulated Hall effect in "pure" high-resistivity GaAs, the previous paper[1] shows that electron trapping dominates in these crystals. The same is not true for high-resistivity crystals of GaAs which have been impurity-diffused or otherwise annealed. GaAs:Si:Cu crystals display two prominent thermally stimulated conductivity maxima, one corresponding to shallow traps with depth of about 0.2 eV, and the other corresponding to deep traps with depths of about 0.5 and 0.7 eV.[2]

The shallow traps are generally present in low densities and can be measured only in those crystals with a long free-electron lifetime, hence a high photosensitivity, at low temperatures. The measurement for crystal 10G40–4 is shown in Fig. 1. The low-temperature peak associated with the shallow traps has a definite structure indicating at least two components. The thermally stimulated Hall effect shows that the shallower corresponds to the emptying of an electron trap, and that the deeper corresponds to the emptying of a hole trap. After the hole trap has passed its maximum, the Hall effect returns once again to *n* type. The picture is of both an electron trap and a hole trap with closely similar depths.

The deep traps were investigated by the thermally stimulated Hall effect in another crystal with sufficiently low dark conductivity that the trap emptying contribution to the current could be clearly distinguished. The results are given in Fig. 2. Below −50°C, measurements

of Hall mobility corresponding to carriers released from traps could not be obtained, probably because of the effect resulting in anomalously low mobility values in the range of thermal quenching as discussed in the previous paper.[1] Only the high-temperature part of the thermally stimulated Hall effect is shown, therefore, starting with a maximum at about −25°C, corresponding to the 0.5-eV trap, and with the deeper trap being represented by thermally stimulated conductivity of the same order of magnitude as the dark conductivity at about +30°C. A large contribution to the conductivity associated with trap emptying is made by holes over the whole range, the steep dependence of Hall mobility between 0 and 100°C arising from two-carrier conductivity, the holes being contributed by trap emptying and the electrons being contributed by donors. The data also allow the possibility of some electron trap emptying from traps slightly deeper than the shallower hole trap, a possibility which is confirmed in measurements on annealed crystals as described in a later section.

Optical Quenching in GaAs:Si:Cu Crystals

The nature of optical quenching at low temperatures has been investigated for a photosensitive GaAs:Si:Cu crystal. The dependence of Hall mobility on crystal conductivity obtained in this way is compared with the variation of Hall mobility with photoexcitation intensity in the absence of quenching in Fig. 3. The strong dependence of Hall mobility on photoexcitation intensity at low temperatures for this crystal, presumably because of gross inhomogeneities, has been discussed in the previous paper.[1] Two methods of

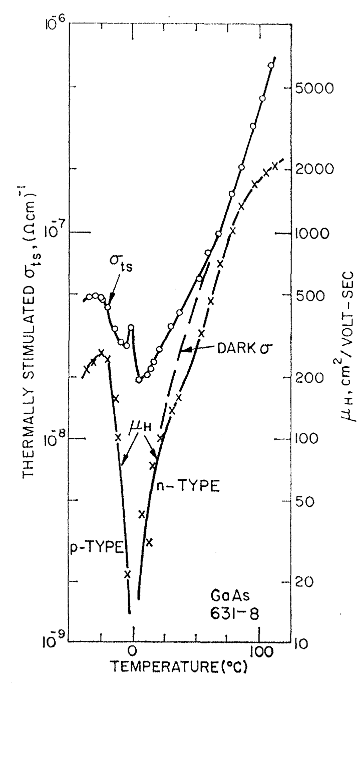

FIG. 2. Thermally stimulated conductivity and Hall effect for deep traps in GaAs:Si:Cu crystal 631–8.

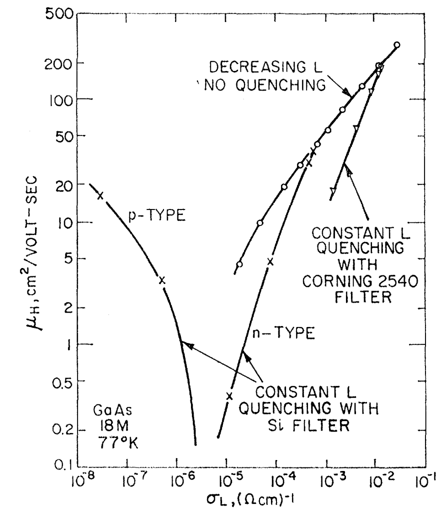

FIG. 3. Hall mobility as a function of photoconductivity during optical quenching. Bias excitation L through water filter.

quenching were used. In the first, quenching was by white light through a Corning 2540 filter. Figure 3 shows that for the same photoconductivity, the Hall mobility is always lower if the conductivity is reduced by quenching than if the conductivity is reduced by decreasing the excitation intensity. Similar results have been found for optical quenching in CdS crystals.[8,9] The implication is that the Hall mobility is being decreased by an increase of two-carrier participation in the conductivity because of the holes being optically freed from sensitizing centers by the quenching radiation, as well as being decreased by the inhomogeneity effect which is directly connected with the magnitude of the photoconductivity. This implication was demonstrated more completely by using a silicon filter for the quenching radiation, thus eliminating any possibility of excitation by the same light. A change in conductivity type from *n* type to *p* type is observed when the quenching is very strong (photoconductivity decreased by a factor of 10^4), thus substantiating the hypothesis that optical quenching involves the initiation of two-carrier conductivity.

Annealed GaAs Crystals with High Trap Densities

Photoelectronic analysis of "pure" high-resistivity GaAs crystals subjected to annealing reveals the introduction of high trap densities (up to 10^{19} cm^{-3}) with depths of about 0.2 and 0.5 eV. The results of temperature-dependent photo-Hall effect on these crystals is particularly illustrative of how much more information can be gained by adding this new dimension to the analysis. The behavior of two crystals is described here in parallel, one a floating-zone grown crystal (102A) annealed for 16 h at 700°C in molten KCN, and

[8] R. H. Bube and H. E. MacDonald, Phys. Rev. **121**, 473 (1961).
[9] R. H. Bube, H. E. MacDonald, and J. Blanc, J. Phys. Chem. Solids **22**, 173 (1961).

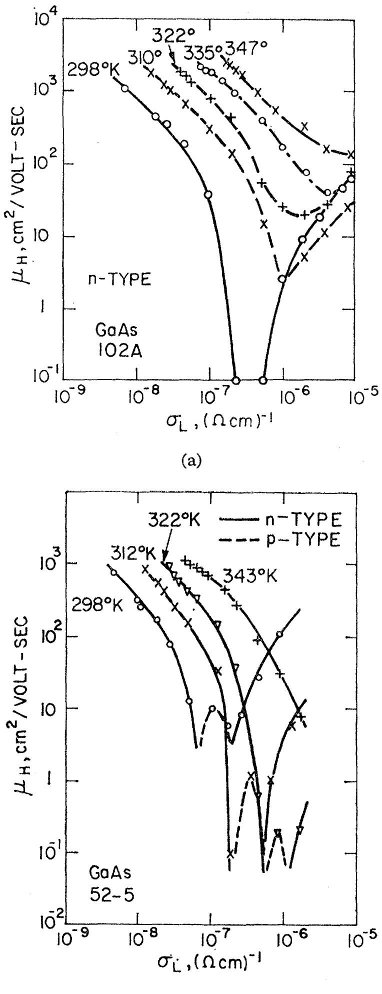

FIG. 4. Hall mobility as a function of photoconductivity, as varied by changing the light intensity, at different temperatures for (a) floating-zone-grown crystal 102A after annealing, and (b) Bridgman-grown crystal 52–5 after annealing.

the other a Bridgman-grown crystal (52-5) annealed for 16 h at 450°C in the presence of Cu corresponding to about 10^{16} cm^{-3} if completely incorporated.

These crystals are n type in the dark at room temperature, become p type at low photoexcitation intensities as the photoexcited electrons are trapped in the 0.5-eV traps, and then become n type at higher photoexcitation intensities after the traps are filled.[9] The examination of this behavior as a function of temperature is shown for the two crystals in Figs. 4(a) and 4(b). The curves of Fig. 4(a) do not actually contain a p-type region, but merely drop to a minimum n-type mobility. The minimum in n-type mobility or the maximum in p-type mobility [Fig. 4(b)] shifts to higher photoconductivities at higher temperatures. If the reasonable assumption is made that the rate-determining step in this process is the release of trapped electrons from the 0.5-eV traps, we may plot the values of conductivity for the minimum n-type mobilities or the maximum p-type mobilities as a function of $1/T$, to obtain the depth of these electron traps. A straight line is obtained on such a plot, giving a trap depth of 0.56 eV.

The measurement of photoconductivity and photo-Hall mobility as a function of temperature for these same two crystals is given in Figs. 5(a) and 5(b), using the maximum light intensity used for the data of Figs. 4(a) and 4(b). Once again the behavior of the two different types of crystal are closely similar. Upon cool-

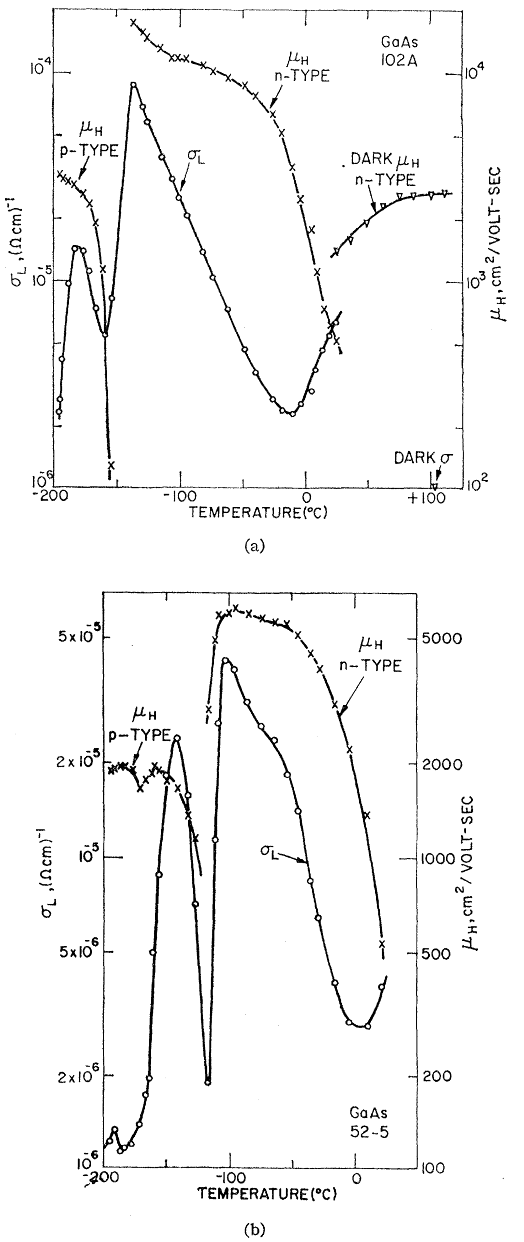

FIG. 5. Temperature dependence of photoconductivity, photo-Hall mobility, and dark Hall mobility for (a) floating-zone-grown crystal 102A after annealing, and (b) Bridgman-grown crystal 52–5 after annealing.

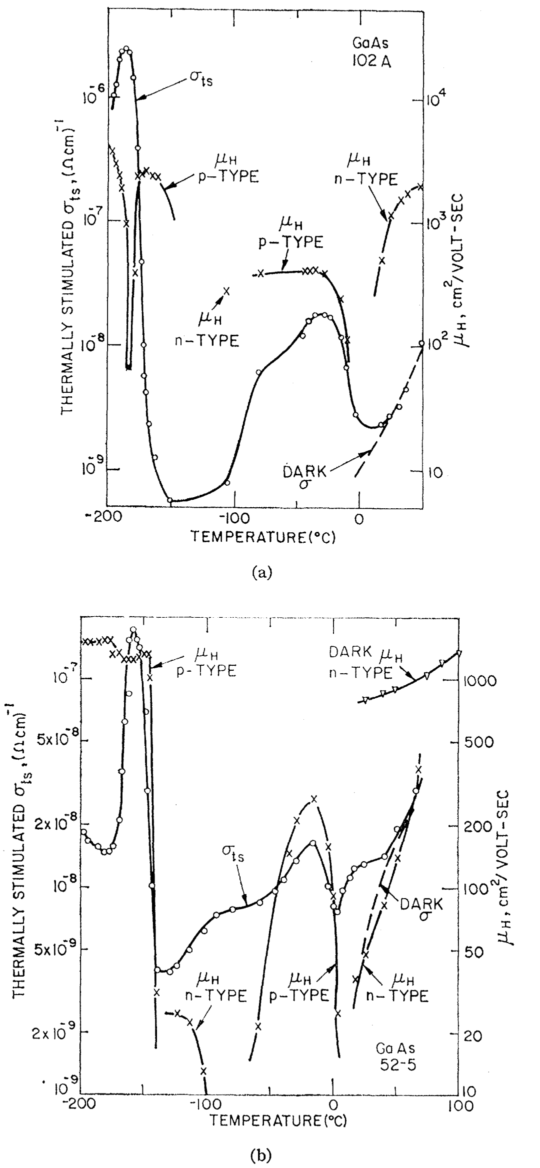

FIG. 6. Temperature dependence of thermally-stimulated conductivity and thermally-stimulated Hall effect for (a) floating-zone-grown crystal 102A after annealing, and (b) Bridgman-grown crystal 52–5 after annealing.

ing, the n-type Hall mobility rises steeply, reaches a maximum value, and then drops off again as at low temperatures the photoconductivity abruptly changes to p type. The rapid increase in n-type Hall mobility upon cooling, in view of the existence of a two-carrier régime, suggests the existence of a hole trap with depth between 0.4 and 0.5 eV which reduces the free-hole density, as the 0.56-eV electron trap had reduced the free electron density at room temperature. The sudden change from n- to p-type conductivity suggests the presence of a shallow electron trap which removes free electrons from the conduction band at low temperatures.

The direct measurement of the trapping properties of these crystals through thermally stimulated conductivity and Hall effect is shown in Figs. 6(a) and 6(b). The first traps to empty at the lowest temperature are hole traps. Then the Hall mobility drops at about the center of the thermally stimulated conductivity peak to a minimum, more pronounced in Fig. 6(a) than in Fig. 6(b). This drop may be associated with the emptying of an electron trap with slightly larger ionization energy than the hole trap.[10] Except for this transient decrease, however, the measured hole mobility retains the same high value throughout the temperature range between -200 and -150°C, both before and after trap emptying, a value between 2000 and 3000 cm^2/V-sec. The absence of a clearly n-type thermally stimulated current does not contradict the evidence from Figs. 5(a) and 5(b) that a high density of shallow electron traps are present: even if the drop in Hall mobility in the middle of the thermally stimulated current peak is not to be associated with the simultaneous emptying of electron and hole traps, the fact that the hole traps empty first means that most of the electron traps would be emptied by recombination with the freed holes before being emptied thermally.

After the principal low-temperature peak has been passed, there is an indication of electron trap emptying at the foot of the current peak of the deeper traps. Then strong evidence is obtained for the emptying of holes from the deep traps, the Hall effect finally becoming n type at high temperatures as the dark conductivity dominates. Once again the absence of a clearly n-type thermally stimulated current does not contradict the evidence for a high density of 0.56-eV electron traps according to the results of Figs. 4(a) and 4(b). The trap depth of the deeper hole traps is found to be about 0.45 eV, and the discussion presented above concerning recombination emptying is applicable to the 0.56-eV electron traps.

DISCUSSION

A comparison of the trapping processes in GaAs:Si:Cu crystals and annealed GaAs crystals indicates a close similarity. In contrast to "pure" GaAs for which electron trapping dominates, both of these treated types of GaAs give evidence of both electron and hole trapping. This similarity is perhaps to be expected from the fact that the GaAs:Si:Cu crystals and the Bridgman-grown annealed crystals pass through an almost identical Cu-impurity diffusion process. That the traps cannot be associated directly with the Cu is shown by the fact that (1) the incorporated Cu concentration is several orders of magnitude smaller than the trap density, and (2) the introduction

[10] Another possibility is that when the holes are released from shallow traps, the trap pair is now negatively charged and hence the effect of 10^{19} Coulombic scattering centers might be expected until the electron traps also emptied. The failure of the conductivity to show any strong dip as would be caused by a decrease in mobility argues against this effect being the dominant one.

of the same traps in floating-zone-grown crystals can be done by annealing in a Cu-free surround. This portion of the investigation will be discussed in another publication.[5]

The information on the high-density traps may be summarized as follows: (1) a high density of 0.56-eV electron traps, as indicated by Figs. 4(a) and 4(b); (2) a high density of 0.4–0.5 eV hole traps indicated by Figs. 5(a) and 5(b), to be identified with the 0.45-eV hole traps indicated in Figs. 6(a) and 6(b); (3) a high density of 0.2-eV electron traps, as indicated by Figs. 5(a) and 5(b), or by a two-carrier analysis of the dip in Hall mobility shown in Fig. 6(a); and (4) a high density of 0.15-eV hole traps, as indicated by the data of Figs. 6(a) and 6(b). Note that the only information available before the temperature-dependent photo-Hall measurements was that there were two traps with depths of about 0.2 and 0.5 eV and of unknown type.

The additional observation from Fig. 6(a) that the low-temperature hole mobility is essentially the same high value both before and after the 10^{19} cm^{-3} shallow hole and electron traps have emptied, implies that there is Coulomb scattering from these traps neither when they are filled nor empty. It would seem that this condition can be fulfilled only by the hypothesis that these hole and electron traps exist in pairs. Then when occupied by a hole and an electron, respectively, they are each neutral. When unoccupied, the hole trap has a negative charge and the electron trap a positive charge, but because of their proximity their effect in scattering is still only the relatively weak effect of a dipole.

The dependence of photo-Hall effect on photoexcitation intensity at room temperature can be correlated with the relative density of 0.56-eV electron traps and 0.7-eV hole traps of the type indicated in Fig. 2. These 0.7-eV hole traps[11,12] are present in almost all crystals, do not have a density change in annealing processes which increase the density of the other levels by several orders of magnitude, and are probably caused by an impurity such as oxygen. If the density of 0.7-eV levels exceeds that of the 0.56-eV levels, as it does in "pure" as-grown high-resistivity GaAs, then photoexcitation at room temperature produces no change in conductivity type but instead an increase in electron mobility as described previously.[1] A portion of the photo-excited electrons reduce the scattering by charged 0.56-eV levels by being trapped there, and most of the photo-excited holes are trapped by the 0.7-eV levels or shallower hole traps. If however, the density of 0.56-eV levels exceeds that of the 0.7-eV levels, as it does by several orders of magnitude in the annealed crystals, the ability of the crystal to trap electrons exceeds its ability to trap holes. Photoexcitation at room temperature therefore causes a change in conductivity type which completely obscures the increase in electron mobility associated with reducing the scattering of the 0.56-eV centers through electron trapping.

The fact that the four levels described above occur in about equal densities and respond to the same type of treatment suggests a relationship between them. A possible hypothesis consistent with other data is that the 0.56-eV electron trap and the 0.45-eV hole trap represent two crystal defects of complementary nature, and that the shallower traps arise from pairs of these defects.

Another simplification in the level scheme for GaAs is possible if the 0.56-eV electron traps increased in density by annealing are identified with the 0.56-eV electron traps observed in measurements of "pure" high-resistivity GaAs crystals,[11] and in measurements of high-resistivity GaAs:Si:Cu crystals.[2] Similarly, the 0.45-eV hole traps increased in density by annealing can probably be identified with the 0.45-eV sensitizing centers detected in both "pure" high-resistivity[1] GaAs and in GaAs:Si:Cu crystals.[2]

In view of the close similarity between photoconductivity phenomena in GaAs:Si:Cu crystals and in CdS:I:Cu crystals, it is natural to inquire as to whether further similarities can be detected in the energy level schemes. A possible empirical correlation is indicated by the summary of Table I. As summarized through recent investigations of CdS:I:Cu crystals,[13] the Cu acceptor level lies about 1.2 eV above the valence band and is important in determining electrical and luminescence properties of the material. It is not the sensitizing center for photoconductivity, however; the sensitizing centers are believed to be crystal defects, such as cation vacancies, with a level lying about 1.1 eV above the valence band. The role of the Cu is simply to compensate those donors which are left uncompensated by crystal defects. The Cu acceptor level in GaAs is located at 0.14 eV above the valence band,[14,15] and investigations by Hall and Racette[16] indicate a second level which should probably be identified with the 0.47-eV level measured by temperature dependence of

TABLE I. Comparison of hole ionization energies in GaAs:Si:Cu and CdS:I:Cu.

	Cu impurity (eV)	Sensitizing centers (eV)
CdS:I:Cu	1.2	1.1 (defect)
GaAs:Si:Cu	0.14 0.47	0.09 (?) 0.45 (defect)

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[12] C. H. Gooch, C. Hilsum, and B. R. Holeman, J. Appl. Phys. Suppl. **32**, 2069 (1961).

[13] R. H. Bube, E. L. Lind, and A. B. Dreeben, Phys. Rev. **128**, 532 (1962).

[14] D. Meyerhofer, *Proceedings of the International Conference on Semiconductor Physics, Prague*, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961). F. D. Rosi, D. Meyerhofer, and R. V. Jensen, J. Appl. Phys. **31**, 1105 (1960).

[15] J. M. Whelan and C. S. Fuller, J. Appl. Phys. **31**, 1507 (1960).

[16] R. N. Hall and J. H. Racette, Bull. Am. Phys. Soc. **7**, 234 (1962).

conductivity in high-resistivity GaAs:Cu crystals.[2] Sensitizing centers in GaAs lie 0.09 and 0.45 eV above the valence band.[1] Here also the 0.45-eV level is to be associated with crystal defects rather than with the Cu impurity, and the importance of purity for the observation of the 0.09-eV level[1] argues that this level is also associated with a crystal defect. Thus, in both GaAs and in CdS there is evidence for the existence of crystal defects which act as sensitizing centers for photoconductivity, and which have approximately the same ionization energies as Cu impurity. Pankove and Massoulie[17] have observed injection induced luminescence in GaAs *p-n* junctions corresponding to a band with maximum at 0.95 eV (the difference between the band gap and 0.45 eV) and to a level located 0.09 eV from a band edge. It is tempting to associate the 0.09-eV level with the shallow hole traps in the annealed crystals, but it is not clear that this can reasonably be done on the basis of existing data.

CONCLUSIONS

The application of the techniques of temperature-dependent photo-Hall effects to photoelectronic properties of GaAs crystals involving two-carrier conductivity is able to provide considerable information not otherwise obtained.

Hole trapping is an important phenomenon in GaAs crystals annealed under various conditions, and is detectable through the measurement of thermally stimulated Hall effect.

Measurement of the Hall effect during the optical quenching of photoconductivity in a photosensitive GaAs:Si:Cu crystal confirms the hypothesis that optical quenching involves the freeing of holes. The measured photoconductivity is observed to change from *n* type to *p* type with quenching.

Photo-Hall analysis of annealed crystals showing high trap densities of 10^{19} cm^{-3} indicates the existence of a system consisting of two shallow donor and acceptor levels corresponding to a pair of defects, and two deep donor and acceptor levels, corresponding to isolated defects.

ACKNOWLEDGMENTS

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

[17] J. I. Pankove and M. J. Massoulie, Bull. Am. Phys. Soc. **7**, 88 (1962).