by Pearson is lacking.[25] The specific heat, in contrast with the specific heat of rubidium, is also normal in this region.

The author is indebted to numerous people for assistance and discussion during these experiments which extended over a period of years, and wishes to express his appreciation especially to Dr. R. Berman, Dr. Z. S. Basinski, Dr. I. Simon, Dr. W. B. Pearson, and Dr. J. J. M. Beenakker.

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[25] F. M. Kelley and W. B. Pearson, Can. J. Phys. **33**, 17 (1955).

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Fast-Neutron Bombardment of GaSb

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Fast-neutron irradiation decreases the carrier concentration of polycrystalline samples of *n*- and *p*-type GaSb, indicating the production of low-lying traps. Vacuum heat treatment evidently removes such traps but also introduces additional acceptors, indicating a different rate of annealing for bombardment produced interstitial and vacancy atoms. Irradiation and heat treatment of *n*-type GaSb therefore results in the production of material of lower carrier concentration and reirradiation results in the conversion to *p*-type material. Repeated irradiations followed by heat treatments, however, do not reduce the net effective concentration of electrons in *n*-type material below $\sim 5\times 10^{17}$ cm^{-3}. The mobility of all samples is decreased by bombardment. Heat treatment subsequent to irradiation increases the mobility of *n*-type material but decreases the mobility of *p*-type samples still further below the decrease produced by bombardment. Low-temperature (-125°C) irradiation and subsequent warm-up and cool-down curves indicate the presence of defects of low thermal stability. No evidence was obtained for regions of low resistivity resulting from superlattice disordering as a result of quenching as might be expected from the thermal spike picture. The type and position of fast-neutron-introduced lattice defects is discussed with relation to previous models for Ge and InSb.

INTRODUCTION

The effect of fast-neutron bombardment on the electrical properties of InSb has recently been reported.[1] This paper reports the results of similar studies carried out on polycrystalline GaSb.[2] This material, like InSb, is one of a series of semiconducting intermetallic compounds composed of elements of the third and fifth columns of the periodic table. Its electrical and optical properties have been studied by a number of workers.[3–7] It is characterized by a zincblende structure, a forbidden energy gap of ~ 0.7 ev at room temperature, and electron and hole mobilities of ~ 2000 and ~ 800 cm^2 volt^{-1} sec^{-1}, respectively.

Prior to this work Moyer[8] exposed several *p*-type GaSb specimens in the Brookhaven reactor and observed a decrease in hole concentration. Behavior other than expected was observed on annealing, consistent with the observations to be reported here.

EXPERIMENTAL PROCEDURES

All room-temperature fast-neutron exposures were carried out in the Oak Ridge graphite reactor in a fission chamber with a fast-neutron flux comparable to or greater than the thermal-neutron flux, and two specimens were irradiated at -125°C in a low-temperature facility of comparable flux distribution. Specimens were cut in the form of rectangular plates and were characterized by measurements of Hall coefficient R and resistivity ρ as a function of temperature (77 to 300°K) before and after bombardment. The conductivity was recorded during exposure. In order to reduce effects of nuclear doping (both Ga and Sb transmute to donor impurities giving Ge and Te, respectively), several of the specimens were shielded against thermal and resonance neutrons by wrapping with layers of Cd and In foil. After exposure and measurement, the specimens were subjected to various annealing treatments and recharacterized. Some of the specimens were reirradiated after extensive annealing periods.

RESULTS

The effect of reactor irradiation on the conductivity of representative samples of shielded and unshielded *n*- and *p*-type GaSb is indicated in Fig. 1 and the initial carrier concentration, temperature of exposure, and the initial rate of removal of current carriers calculated under the assumption that the mobility is initially

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[1] J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. **93**, 894 (1954); **95**, 1177 (1954).

[2] We are indebted to Dr. Raymond L. Smith of the Franklin Institute for the *p*-type samples and to Dr. H. P. R. Frederikse of the National Bureau of Standards for the *n*-type samples used in these experiments.

[3] H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953).

[4] D. P. Detwiler, Phys. Rev. **94**, 1431 (1954).

[5] H. N. Liefer and W. C. Dunlap, Jr., Phys. Rev. **95**, 51 (1954).

[6] Blunt, Hosler, and Frederikse, Phys. Rev. **96**, 576 (1954).

[7] Briggs, Cummings, Hrostowski, and Tanenbaum, Phys. Rev. **93**, 912 (1954).

[8] J. W. Moyer (private communication).

unaffected are listed in Table I. These data indicate that the conductivity of both *n*- and *p*-type samples, shielded or unshielded, decreases monotonically during irradiation. The removal rate of current carriers appears to be temperature dependent, but is approximately equal for all samples of high carrier concentration. The initial removal rate of holes for *p*-type material is less for a sample of low initial carrier concentration, whereas the initial rate of removal of electrons for *n*-type material is not markedly dependent upon initial carrier concentration and does not appear to approach a saturation condition. Slow-neutron-produced donor atoms would not be expected to affect appreciably the initial removal rate of carriers, since the principal transmutations appear with a finite half-life.

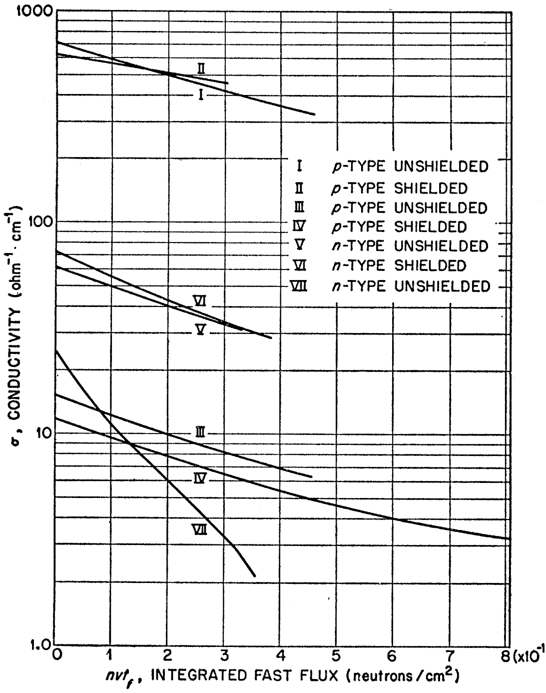

FIG. 1. The effect of reactor irradiation on the conductivity of polycrystalline samples of *n*- and *p*-type GaSb. Some samples were shielded with In and Cd foil against thermal and resonance neutrons.

TABLE I. Initial behavior of carrier concentration in irradiated GaSb.

Sample	Type	Shielded	Original carrier concentration n^0 cm^{-3}	Temperature of exposure T_e °C	Removal rate $-[dn/d(nvt)_f]_{t=0}$
I	*p*	No	14.25×10^{17}	37	2.57
II	*p*	Yes	12.95×10^{17}	46	1.40
III	*p*	No	2.59×10^{17}	42	0.68
IV	*p*	Yes	1.36×10^{17}	47	0.41
V	*n*	No	18.50×10^{17}	24	4.90
VI	*n*	Yes	12.30×10^{17}	41	2.97
VII	*n*	No	5.80×10^{17}	29	4.40
VIII	*n*	Yes	6.36×10^{17}	34	3.06
IX	*n*	No	6.71×10^{17}	−125	10.35
X	*p*	No	8.20×10^{16}	−128	1.26

The Hall coefficient and resistivity data for a typical *p*-type sample are shown in Figs. 2 and 3. Prolonged irradiation apparently introduces a sizeable number of hole traps with an apparent depth of ~0.14 ev. That some of these hole traps are thermally annealable is indicated by the fact that a relatively short (~1 hour) low-temperature (~140°C) heat treatment increased the hole concentration and conductivity considerably and decreased the slope of the Hall coefficient curve to a value corresponding to ~0.12 ev.

It has been previously shown that vacuum heat treatment at ~500°C for Ge[9] and ~350°C for InSb[1] removes essentially all fast-neutron-introduced donors and acceptors, leaving only those donor or acceptor atoms resulting from nuclear transmutations. The behavior of GaSb under similar treatment is more complicated. Curves IV of Fig. 2 might be interpreted as an indication that extended high-temperature vacuum anneal removes most of the irradiation-produced acceptors but all of the curves of Fig. 3, obtained after successive periods of vacuum anneal at increasing temperatures, indicate that a large number of additional holes are being introduced by some mechanism.

The purest GaSb currently available is *p*-type, with an initial carrier concentration of 10^{17} cm^{-3}, doping with Te being necessary to produce *n*-type material. A

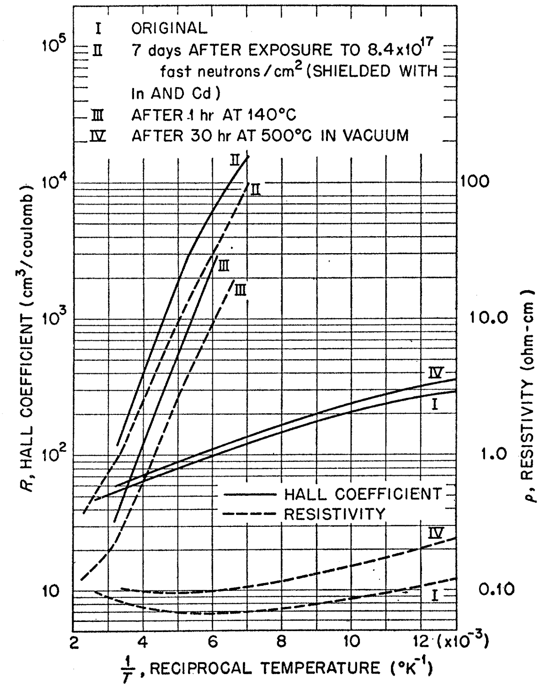

FIG. 2. Hall coefficient and resistivity of *p*-type GaSb as a function of temperature. (I) Prior to irradiation, (II) after irradiation, (III) after 1 hour at 140°C, (IV) after 30 hr at 500°C in vacuum.

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[9] Cleland, Lark-Horovitz, and Pigg, Phys. Rev. 78, 814 (1950).

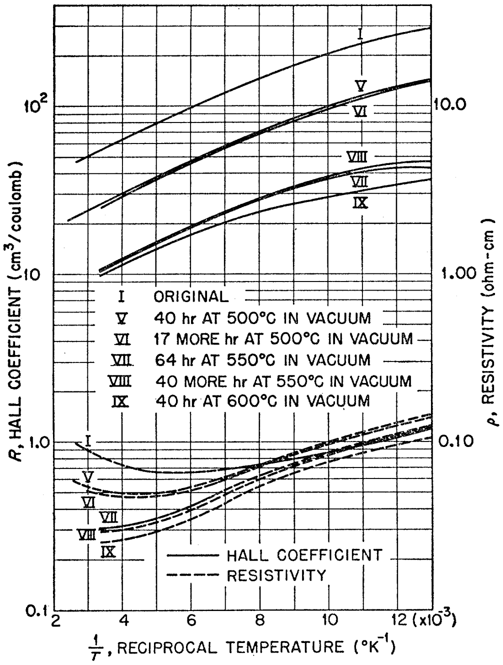

FIG. 3. Hall coefficient and resistivity of *p*-type GaSb as a function of temperature. (I) Prior to irradiation, (V–IX) after various heat treatments.

slight departure from true stoichiometry in the original melt, amounting to 1 part in 10^5 of Sb vacancies, has been suggested as the cause of this initial *p*-type character.[10] Moreover, Detwiler[11] has reported that vacuum annealing in the temperature range from 700 to 900°C resulted in the deposit of free Sb on the cool portions of the furnace tube. Consequently, it would appear reasonable to assume that evaporation of Sb from the surface during the successive anneals discussed above produces Schottky-type defects in the Sb superlattice. These defects would be expected to act as acceptor states and increase the *p*-type character of the specimens. In addition, the introduction of any acceptor-type impurity by diffusion during the annealing process or different rates of annealing of the interstitials and vacancies produced by irradiation might also explain the increase in *p*-type character resulting from extensive high-temperature annealing.

In order to differentiate between the various possibilities outlined above, a companion specimen to the one shown in Figs. 2 and 3 was subjected to the same series of extended high-temperature vacuum anneals wihout being previously irradiated. The results indicate that there is no large increase in acceptor concentration for an unirradiated sample. This seems to exclude the possibility of either Schottky defect production or the introduction of an acceptor-type impurity by diffusion as the explanation for the increased acceptor concentration, since these two processes should also be operative in unirradiated material as well. We therefore postulate that different annealing rates of the various irradiation produced interstitials and vacancies are responsible for the experimental results obtained here. This point will be examined in greater detail below.

The Hall coefficient and resistivity data for a typical *n*-type sample are shown in Fig. 4. The decrease in carrier concentration and conductivity as a result of irradiation indicates that electron traps are produced. That some of these electron traps are also thermally annealable is indicated by the fact that a 1.5-hour anneal at 110°C increased the carrier concentration and conductivity slightly. Curves IV and V, however, indicate that extended high-temperature vacuum anneal decreases greatly the net effective donor concentration of such material. This is presumably the same type of behavior as that observed on *p*-type samples, and is therefore also assumed to be caused by differential annealing of irradiation produced interstitials and vacancies. The net result of irradiation and heat treatment of *n*-type GaSb, therefore, is the production of material with a lower carrier concentration. Reirradiation further decreases the net effective donor concentration as is shown in Curves VI of Fig. 4 and Curves VII indicate again that some of the irradiation produced electron traps are thermally annealable.

The samples numbered V and VI of Fig. 1 and Table I were reirradiated after extended annealing. The results

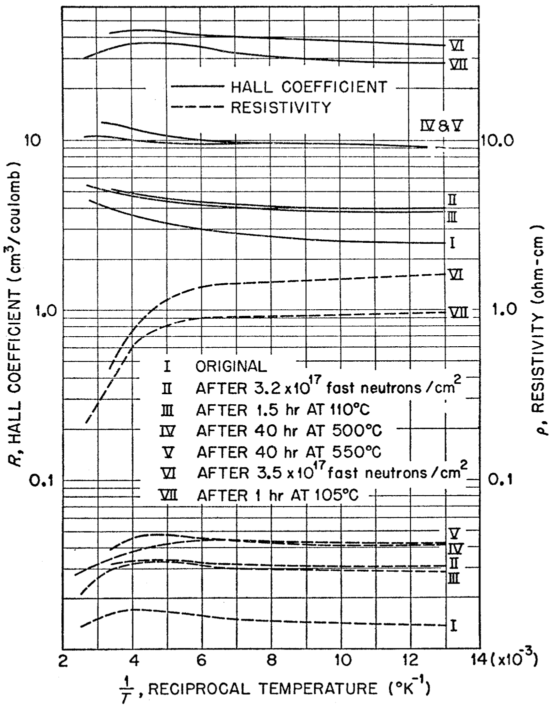

FIG. 4. Hall coefficient and resistivity of *n*-type GaSb as a function of temperature after various reactor irradiations and vacuum heat treatments.

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[10] H. J. Hrostowski (private communication).

[11] D. P. Detwiler, Phys. Rev. 97, 1575 (1955).

are listed as samples VII and VIII of Table I. Figure 5 indicates that the conductivity of sample VIII passes through a minimum at an exposure of $\sim 1\times 10^{18}$ fast neutrons cm^{-2}. Hall coefficient measurements after a total exposure of 1.6×10^{18} fast neutrons cm^{-2} reveal that conversion to p-type material has occurred. Moreover, the slope of the log ρ *vs* $1/T$ curve measured after exposure is quite steep in the room-temperature range, indicating a large ionization energy for the bombardment-produced acceptors (>0.2 ev), but is much decreased toward low temperature, revealing a wide range of acceptor energies.

Continued reirradiation and heat treatment, however, does not reduce the net effective concentration of electrons in n-type GaSb below $\sim 5\times 10^{17}$ cm^{-3}, at least in the polycrystalline material used here. The original irradiation of Sample VIII of Fig. 5 was 4×10^{17} fast neutrons cm^{-2} and the decrease in net effective electron concentration after heat treatment was 6.2×10^{17} cm^{-3}. The second irradiation of 1.6×10^{18} fast neutrons cm^{-2} and subsequent heat treatment, however, reduced the net effective electron concentration by only 1.5×10^{17} cm^{-3}.

Fast-neutron irradiation decreases the mobility of both n- and p-type samples of GaSb, an effect that is similar to that previously observed for other semiconductors.[1,12,13] The effect of heat treatment after irradiation was to improve the mobility of the n-type samples, but each succeeding higher-temperature vacuum anneal decreased the mobility of the p-type samples still further below the decrease produced by bombardment. The apparent mobility of the n-type sample of Fig. 5 after conversion to p-type was only ~ 1 cm^2 volt^{-1} sec^{-1} at 300°K.

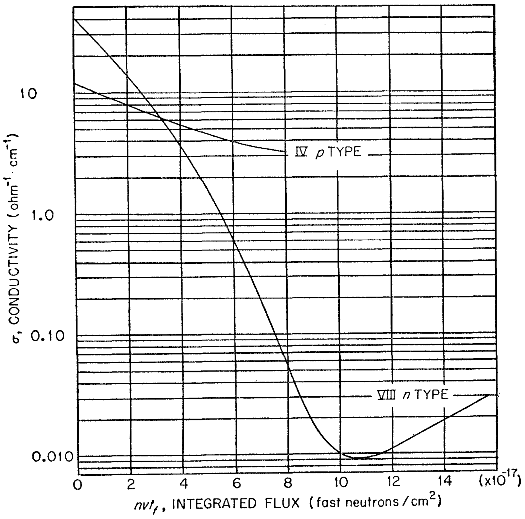

FIG. 5. The effect of reactor irradiation on the conductivity of an irradiated and heat-treated n-type sample of GaSb. The effect of reactor irradiation on the conductivity of a p-type specimen is also indicated.

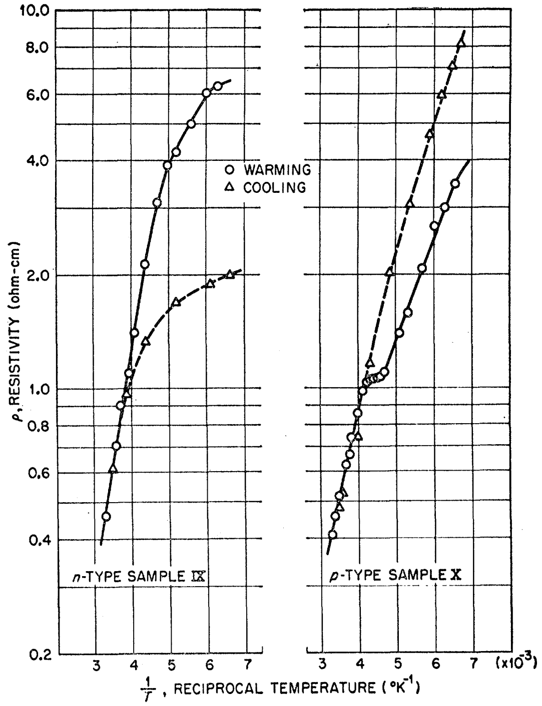

FIG. 6. Warming and cooling resistivity curves as a function of temperature of n- and p-type samples of GaSb after exposure to 3.5×10^{17} fast neutrons cm^{-2} at −125°C.

Two GaSb samples, one n- and one p-type, were irradiated at −125°C. The initial rate of carrier removal was increased at this temperature (samples IX and X of Table I) over the values observed for room-temperature exposure, indicating more efficient carrier-trapping. The behavior of resistivity as a function of temperature, obtained by warming and cooling in the reactor subsequent to the low-temperature exposure, is shown in Fig. 6. The resistivity at −125°C is increased by a factor of three for the p-type specimen and decreased by about the same factor for the n-type specimen as a result of thermal cycling. Furthermore, the resistivity of the p-type sample shows an interesting, almost discontinuous change in the range −60 to −40°C during the initial warm up which is absent in the cooling curve. These results indicate strongly that a group of electron traps which decrease the electron concentration in n-type material and which enhance the hole concentration in p-type material (by minority carrier trapping) are introduced by the low-temperature irradiation and that warming anneals the defects responsible for these traps well below room temperature. Similar indications of defects of low thermal stability have been obtained on n- and p-type Ge after low-temperature exposure.[12,13]

DISCUSSION

If it is assumed that the defects produced in GaSb by bombardment can be described in terms of simple

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[12] Cleland, Crawford, and Pigg, Phys. Rev. **98**, 1742 (1955).
[13] Cleland, Crawford, and Pigg, Phys. Rev. **99**, 1170 (1955).

lattice defects, it is possible in principle to construct a model of the energy-level spectrum associated with these defects. Because of the binary nature of the compound, an interstitial may be either a Ga or Sb atom and a vacancy may be either type of vacant lattice site. Thus four possible simple defects can exist. In addition, a forbidden energy gap of 0.7 ev at room temperature[5] and a dielectric constant of[7] 14 are very analogous to Ge, where application of the hydrogenic model has indicated the possibility of multiple ionization of the defects.[14] It is therefore possible that states corresponding to both the first and second ionization energies of each of the types of interstitial atoms and states corresponding to the energies required to put successively two electrons into each of the two types of vacancies will lie in the forbidden energy gap and participate in altering the carrier concentration.

It is not yet possible on the basis of the experimental results presented here to formulate a detailed model of the defect energy levels produced by fast-neutron bombardment of GaSb; however, several general conclusions can be made. Both *n*- and *p*-type samples of high initial carrier concentration decrease in conductivity during irradiation at about the same rate. However, the rate of decrease in *p*-type material is strongly dependent on initial hole concentration whereas the rate of decrease in *n*-type material is not dependent on initial electron concentration. Moreover, one of the reirradiated *n*-type samples was converted to *p*-type by sufficient exposure. In view of these results, it appears that the electron traps are deep-lying and, if several such traps are present, at least one of them lies below the middle of the forbidden band and hence is capable of acting as an acceptor. In *p*-type material, on the other hand, the hole traps are apparently shallow, since the rate of hole removal is strongly dependent on the initial position of the Fermi level. The apparent depth of one of these hole traps is ~ 0.14 ev. In general, the behavior of GaSb is quite similar to that of Ge.

The complex annealing behavior of irradiated GaSb is not well understood. If it is assumed that the presence of interstitial atoms is indirectly responsible for the hole traps,[14] their removal or partial removal relative to vacancies would have the effect of increasing the net acceptor concentration in *p*-type and of decreasing the net donor concentration in *n*-type material. The mechanism of such a process is not very clear. However, clustering of interstitials, migration to dislocations, or grain boundaries are possible processes which might account for this behavior. Such effects have been observed to accompany low-temperature annealing (0 to 120°C) in bombarded Ge[15] and Mayburg[16] finds similar indications at higher temperatures (500 to 600°C) in quenched material.

There is a second possible mechanism for the increase in acceptor concentration resulting from exposure and subsequent heat treatment which requires the assumption that the Ga interstitial is much the more mobile defect. Hence, the Ga interstitials could recombine with either Ga or Sb vacancies with near equal probability. Although the Ga atom in the Sb site would increase the energy of the crystal and hence be a metastable configuration, the binding energy in such a position would be considerable. Such a process would have the result of increasing the total acceptor concentration by virtue of the two incomplete orbitals localized at that site. This explanation would not be valid if the Sb interstitials also had an appreciable mobility, since they would tend to distribute themselves indiscriminantly over the remaining vacancies and the donors produced by misplaced Sb atoms would be equal in concentration and cancel the effect of acceptors produced by misplaced Ge atoms.

Although it is possible to explain the annealing behavior of irradiated GaSb by either of these mechanisms, the saturation of the acceptor concentration increase, as evidenced by results obtained on annealing the reirradiated *n*-type specimens, remains puzzling. This can be understood only in terms of the first mechanism and then only if the interstitial sinks become nearly saturated by the first exposure and anneal. Such an explanation would probably rule out the possibility of interstitial clustering, since it is difficult to see how this process could be readily saturated. It should be remembered, however, that the specimens in question are polycrystalline and hence it is possible that much of the complexity may be associated with grain boundaries. Investigations on single crystals are necessary before the question of annealing mechanism can be answered with any degree of certainty.

The possibility of a different type of lattice damage, the so-called thermal-spike picture, has been suggested for InSb[1] and could also occur in GaSb. The resultant disorder following any atomic rearrangement or interchange as a result of quenching should provide a metallic-type behavior and greatly decrease the resistivity of the disordered region. No evidence for such behavior was observed in InSb or GaSb at room temperature. It is possible, however, that any superlattice disordering may be unstable at room temperature. Several specimens were accordingly irradiated at ~ -125°C to a total flux of $\sim 5\times 10^{17}$ fast neutrons cm^{-2}, and again no electrical evidence for such an effect was observed for this length of exposure and temperature.

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[14] H. M. James and K. Lark-Horovitz, Z. physik. Chem. **198**, 107 (1951).

[15] Cleland, Crawford, and Pigg (unpublished).

[16] S. Mayburg, Phys. Rev. **95**, 38 (1954).