Optical and Electrical Studies of Electron-Bombarded GaSb*

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Studies were made on n- and p-type gallium antimonide irradiated with 4.5-MeV electrons. Hall-effect measurements showed that acceptors were produced in the n-type samples and that donors as well as acceptors were produced in the p-type samples. Infrared absorption and photoconductivity studies gave evidence for four defect levels: $E_v+0.075$ eV, $E_v+0.48$ eV, E_c- (0.12 to 0.20) eV, E_c- (0.47 to 0.50) eV. The absorption associated with the level $E_v+0.075$ eV is similar to that observed in donor-compensated GaSb. Previous studies have indicated that such a level is present also in undoped p-type material. The present work provides direct evidence that some of the residual "impurities" normally found in GaSb are lattice defects. Carrier capture cross sections have been estimated for the various levels. The values indicate that the level E_c- (0.47 to 0.50) eV is an acceptor level, while the level E_c- (0.12 to 0.20) eV is probably a donor level.

INTRODUCTION

RADIATION damage has been studied extensively for germanium and silicon. Investigations have also been made on the III-V compound semiconductors, gallium arsenide, and indium antimonide. Little has been done on gallium antimonide since the early study[1] of the effects of neutron irradiation on the electrical properties. Electron irradiation which may be expected to produce simpler types of defect centers has not been studied. Effects of impurities or defect centers in gallium antimonide have been observed in the measurements of infrared absorption,[2,3] photoluminescence,[2] and photoconductivity.[4] These measurements may be effective means for the study of irradiation effects in this material as in the case of silicon. A special interest in the study of irradiation effects in GaSb comes from the fact that some kind of lattice defect has been suspected to be the cause of rather high hole concentrations, $\sim 10^{17}$ cm^{-3}, in purest crystals grown. It has been suggested that the residual acceptors are gallium vacancies.[5] Recently, Effer and Etter[6] reported that crystals with much lower hole concentrations can be grown from antimony rich melts. The authors concluded also that lattice defects are responsible for the high hole concentrations usually obtained. It is, therefore, interesting to determine whether electron bombardment produces defect centers which can be identified with the residual acceptors.

In the work reported here, absorption and photoconductivity studies as well as electrical measurements were made on n- and p-type GaSb samples irradiated with 4.5-MeV electrons from a linear accelerator. The samples were kept at ~ 0°C during the irradiations, and the measurements were made after the samples had been warmed up to room temperature. The optical measurements were made with a Perkin-Elmer double pass prism spectrometer. For the photoconductivity measurements, a system built by Habegger[4] with a 960 cps chopper and a phase-sensitive detection system was used.

The samples used were cut from single-crystal ingots grown by Louise Roth in this laboratory. The p-type samples were undoped and had carrier concentrations of $\approx 1.4\times10^{17}$ cm^{-3}. The n-type samples were Te doped, having carrier concentrations of $\approx 1.7\times10^{17}$ cm^{-3}. In order to study the annealing of irradiation effects, samples were kept at 500°C for an hour in an atmosphere of helium before the irradiations. This was done in order to exclude possible effects of annealing by itself. The annealing of the irradiated samples was carried out under the same conditions.

RESULTS OF EXPERIMENT

Resistivity and Hall Coefficient

N-type samples. The electron concentration and mobility are reduced by the electron irradiation. Table I gives the data measured before and after an irradiation of 3×10^{16} electrons/cm^2. At the low temperature, 77°K, the carriers in the sample were nearly degenerate, and the subsidiary minima in the conduction band at

TABLE I. Resistivity ρ, Hall coefficient R, and Hall mobility μ_H, of an n-type sample before and after an irradiation of 3×10^{16} electrons/cm^2.

	$T=300$°K		$T=77$°K	
	Before	After	Before	After
ρ Ω cm	9.5×10^{-3}	3.7×10^{-2}	3.5×10^{-3}	4.86×10^{-2}
R cm^3/C	−36	−86	−21	−66
μ_H	3800	2300	6000	1350

* Work supported in part by the U. S. Office of Naval Research and the Advanced Research Projects Agency.

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[5] E. B. Owens and A. J. Strauss, in *Ultrapurification of Semiconductor Materials*, edited by M. S. Brooks and J. K. Kennedy (The Macmillan Company, New York, 1962); W. P. Alfred, in *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold Publishing Corporation, New York, 1962), Vol. 1.

[6] D. Effer and P. J. Etter, Phys. Chem. Solids **25**, 451 (1964).

≈ 0.08 eV above the band edge should not have an appreciable effect. We assume that the carrier concentration is given by $1/Rec$ at this temperature, R being the Hall coefficient. Thus we get from the given data a carrier removal rate of ≈ 7 carriers per cm path of a bombarding electron. This rate is comparable with the rate ≈ 10 cm^{-1} for n-type InSb in irradiations by 4.5-MeV electrons at liquid-nitrogen temperature.[7] In InSb however, the effect of electron irradiation on carrier concentration is largely annealed out upon warming to room temperature. In n-type GaAs, the removal rate has been determined only for room temperature irradiations with 0.95-MeV electrons.[8] The rate, 0.45 cm^{-1}, is very small; however, it has also been found that a large part of the increase of thermal resistivity of GaAs produced by electron bombardment anneals below room temperature.[9] Probably much less annealing takes place below room temperature in GaSb than in InSb and GaAs. Appreciable annealing was noticed after an irradiated sample was kept at room temperature for many days.

P-type samples. The resistivity and Hall coefficient of a p-type sample after successive irradiations are given in Figs. 1 and 2 as functions of $1/T$. The Hall curves cross at one point which corresponds to $T=200°$K and a Fermi level at 0.05 eV above the valence band. The irradiations increased the carrier concentration at temperatures above 200°K and decreased the carrier concentration at lower temperatures. Clearly both donor and acceptor levels were introduced by the irradiation. The point of crossing corresponds to an electron distribution at which the effects of donor and acceptor levels cancel each other. The Fermi level varied with temperature, e.g., the Hall curve for 22×10^{16} cm^{-2} irradiation corresponds to a variation of the Fermi level from 0.065 eV at 300°K to 0.028 eV at 77°K. The results indicate that some levels were introduced in or close to this range of energy. The variation in the electron population of these levels produced the change from a net donor effect at low temperature to a net acceptor effect at high temperature.

It is difficult to determine reliably the spectrum of introduced defect levels from the Hall data. When the net electron or hole contribution from the levels can be readily obtained for various temperatures and Fermi level positions, it is still difficult to deduce the spectrum of many levels with possibly different concentrations. The problem for GaSb is further complicated by the fact that there is no exhaustion range where the electron population of the impurities remains substantially constant while the Fermi level varies with temperature. A change in carrier concentration due to irradiation is accompanied by a change in the electron population of the impurities due to the shift of the Fermi level. Thus,

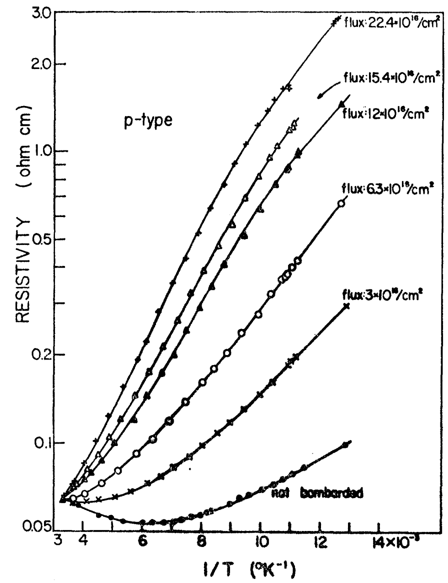

FIG. 1. Resistivity as a function of reciprocal temperature for p-type samples after various irradiations.

the change of Hall coefficient resulting from an irradiation does not give the total electron or hole contribution from the introduced levels. In order to extract the information, it is necessary to know the spectrum of impurity levels in the unbombarded material, the reliable determination of which presents a problem in itself. Some of the defect levels have been determined from the following results on infrared absorption and photoconductivity.

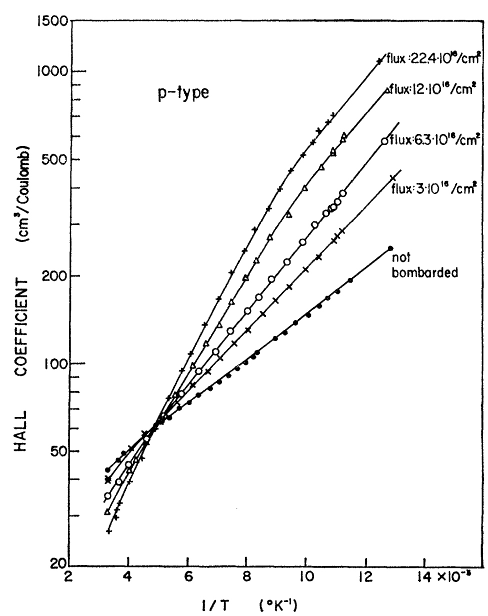

FIG. 2. Hall coefficient as a function of reciprocal temperature for p-type samples after various irradiations.

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[8] L. W. Aukerman and R. D. Graft, Phys. Rev. **127**, 1576 (1962).
[9] F. L. Vook, Phys. Rev. **135**, A1750 (1964).

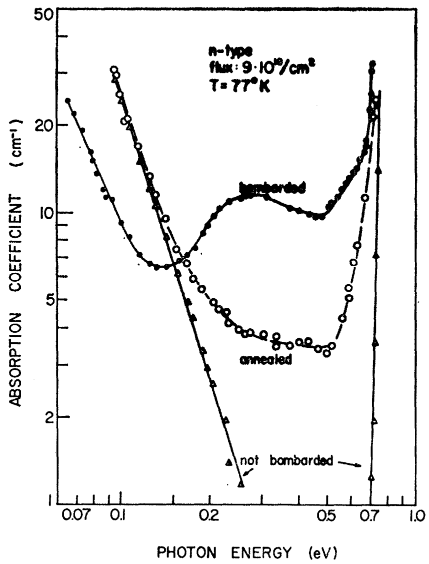

FIG. 3. Absorption coefficient as a function of photon energy for an n-type sample before and after an irradiation of 9×10^{16} electrons/cm^2.

Absorption and Photoconductivity

N-type samples. The effects of electron bombardment can be seen in Fig. 3 which shows the results of measurements made at 77°K. The effects seen more clearly at the low temperature are noticeable also in room temperature measurements. The curve for the unbombarded sample shows free carrier absorption at $h\nu<0.3$ eV which increases smoothly with decreasing photon energy. The curve for the bombarded sample shows that the irradiation reduced the absorption in the range $h\nu<0.15$ eV. We attribute the reduction to the decrease of carrier concentration produced by the irradiation. The curve for the bombarded sample was measured many days after the irradiation during which time some annealing occurred, and electrical data were not taken at the time of the optical measurements. A comparison between the changes in absorption and carrier concentration can be made using the data obtained on a sample irradiated with a flux of 3×10^{16} electrons/cm^2. The room temperature Hall coefficient was increased by a factor of 2.4 according to Table I, and optical measurements made at that stage showed that the long-wavelength absorption was reduced by nearly the same factor, 2.1.

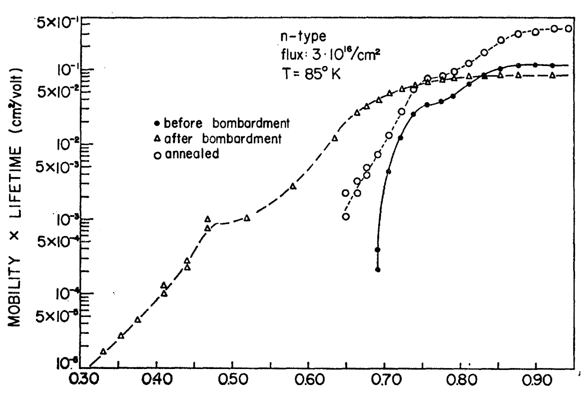

FIG. 4. Photoconductivity as a function of photon energy for an n-type sample before irradiation, after an irradiation of 3×10^{16} electrons/cm^2, and after annealing at 500°C. The photoconductivity is expressed in terms of the product of mobility and lifetime of photogenerated carriers [see Eq. (1)].

The curve for the bombarded sample shows that a broad absorption band with a peak at $h\nu\approx0.3$ eV was introduced by the irradiation. The absorption is apparently associated with electron excitations from some defect level to the conduction band. The curve indicates that the level lies somewhere in the range 0.12–0.2 eV below the conduction band. The level will be designated N_1.

The absorption of the bombarded sample shows a break at about 0.5 eV where it rises with increasing photon energy. The sample was subjected to some annealing by the application of a current of about one ampere for half a minute. The absorption measured after this annealing is given by the dashed curve in Fig. 3. The absorption band peaking near 0.3 eV was largely removed by the annealing, and the rise of absorption at 0.5 eV is clearly seen. Comparison of the "bombarded" and "annealed" curves shows that the component which rises at 0.5 eV was not affected appreciably by the annealing. The results indicate that defect centers were introduced which were different from those giving level N_1. The level of these centers lies 0.5 eV below the conduction band and will be designated N_2.

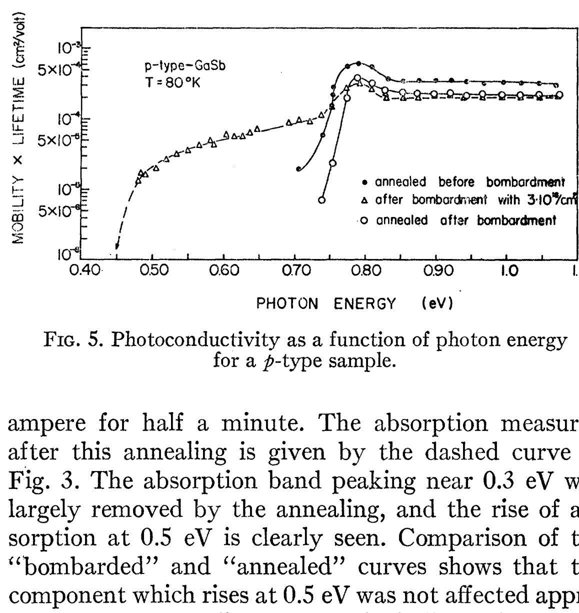

FIG. 5. Photoconductivity as a function of photon energy for a p-type sample.

The results of photoconductivity measurements are shown in Fig. 4. The quantity $\mu\tau$ plotted is calculated from the change of sample conductance ΔG:

$$\mu\tau=(\Delta G/G)(l^2/A)(1/I_0), \tag{1}$$

where l and A are, respectively, the length and the cross section of the sample and I_0 is the number of photons absorbed by the sample per unit time. The quantity calculated in this way gives the product of mobility and lifetime of the photogenerated carriers. The curve measured after the bombardment extends to much lower photon energies showing the effect of introduced defect levels. The break seen at ~0.47 eV seems to be associated with the onset of excitations from level N_2. With further decrease of photon energy, the signal dropped gradually. The range of measurement was limited by the sensitivity of detection. It is possible that the response had a threshold near 0.3 eV which is expected of level P_2 discussed below.

Detailed annealing studies have not yet been made. It was found that in the samples irradiated with 3×10^{16} electrons/cm^2, the optical absorption and the photoconductivity as well as the resistivity and the Hall coefficient recovered their prebombardment values after one hour of annealing at 500°C.

P-type samples. The photoconductivity in *p*-type samples was also extended to smaller photon energies by electron bombardment, as shown in Fig. 5. The photoconductive signal in the bombarded sample extended to 0.48 eV where it dropped sharply. No signal was detectable at 0.44 eV. The result indicates that a defect level was introduced at ≈0.48 eV above the valance band. The level will be designated P_2. In an *n*-type sample, the level would give a photoconductive signal beginning at 0.32 eV and could be responsible for the tail end of the *n*-type spectrum, as mentioned above.

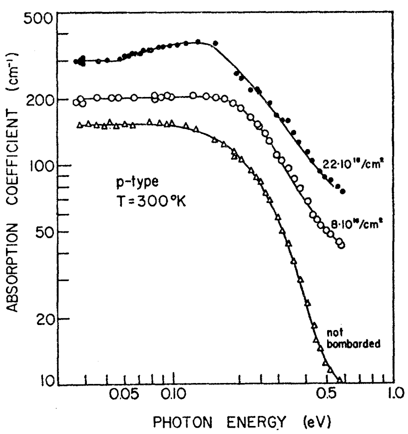

Fig. 6. Absorption coefficient at 300°K as a function of photon energy for a *p*-type sample before and after various irradiations.

The effect of irradiation on the infrared absorption at room temperature is shown in Fig. 6. The absorption in the unbombarded sample is associated with intervalence band transitions of holes.[10] The increase of absorption produced by the bombardments is consistent with the increase of carrier concentration at room temperature discussed earlier. In addition to a general increase of absorption, the curve measured after the heavier irradiation indicates a new hump in the region 0.05–0.2 eV. This effect is seen more clearly in the 77°K data shown in Fig. 7. The free-carrier concentration having been strongly reduced at the low temperature, the absorption before the irradiations was produced largely by electron excitations from the valence band to the residual acceptor levels. The absorptions measured after the bombardments have apparently a different origin. They dropped off at low-photon energies within the range of measurement, in contrast to the continuing rise observed before bombardment. Apparently the residual acceptor levels were filled with electrons from bombardment produced donors, and the observed absorption originated from electron excitations to a higher lying defect level. This level will be designated P_1. The dashed curve in Fig. 7 was measured at 10°K. It shows a sharper low-energy cutoff beginning at 0.075 eV.

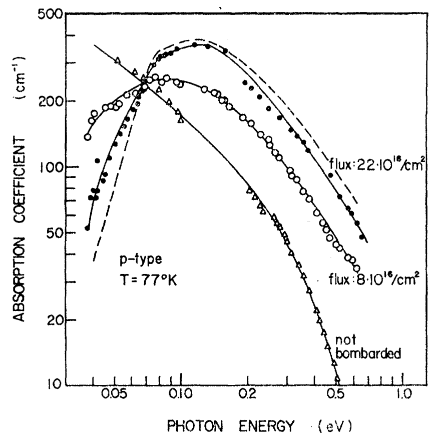

Fig. 7. Absorption coefficient at 77°K as a function of photon energy for a *p*-type sample before and after various irradiations.

Similar absorption has been observed at low temperatures in *p*-type GaSb compensated with Te or Se donor impurity. Figure 8 shows the absorption curves for the bombarded sample and a Te-compensated sample. The similarity of the curves indicates that the

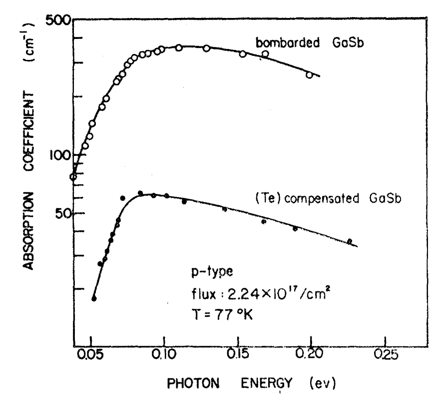

Fig. 8. Absorption spectra for a *p*-type sample irradiated with 2.24×10^{17} electrons/cm^2 and an unirradiated *p*-type sample compensated with tellurium.

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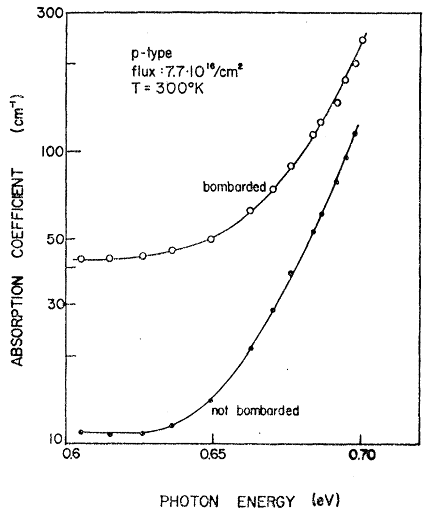

FIG. 9. Absorption coefficient as a function of photon energy for an unirradiated p-type sample and a sample irradiated with 7.7×10^{16} electrons/cm^2.

absorptions are associated with the same kind of centers. Absorption[3] and photoconductivity[4] studies indicate that the level is the higher level of a two-level acceptor[11] which is present in undoped as well as in compensated material, and that compensation merely brings out the effect of this level by raising the Fermi energy above the first level of the acceptor. The Fermi energy in the bombarded sample at 77°K was not higher than that of some compensated samples. On the other hand, the absorption in the bombarded sample was higher by an order of magnitude than the absorption observed in any of the compensated samples. Furthermore, it increased with irradiation. We conclude therefore that electron irradiation increases the concentration of such centers.

The effect of the level discussed above shows up also in the absorption near the intrinsic edge. The level lies about 0.075 eV above the valence band. The Fermi level in undoped p-type material is sufficiently high, $\approx$0.07 eV above the valence band, for such levels to have a considerable electron population. Figure 9 shows that the absorption in the unbombarded sample began to rise at a photon energy about 0.075 eV below the intrinsic absorption threshold of 0.72 eV. The effect is apparently associated with electron excitations from the levels to the conduction band, and it is in fact one of the indications for the presence of such levels in undoped p-type material. The curves in Fig. 9 show that the absorption in question has been increased by the bombardment despite the fact that the bombardment lowered the Fermi level (increased the carrier concentration) at room temperature, thereby decreasing the electron population of the levels. These results support the conclusion that electron bombardment produces more of the centers giving the 0.075-eV level.

[11] The presence of double-level acceptors in undoped GaSb was deduced by R. T. Bates, R. D. Baxter, and F. J. Reid, Bull. Am. Phys. Soc. 8, 214 (1963), from the analysis of the temperature dependence of Hall coefficient.

DISCUSSION

Four irradiation-introduced levels have been found in absorption and photoconductivity studies: level N_1 at $E_c-(0.12$ to $0.20)$ eV, level N_2 at $E_c-(0.47$ to $0.50)$ eV, level P_2 at $E_v+0.48$ eV, and level P_1 at $E_v+0.075$ eV. Hall measurements showed that both donor and acceptor levels are introduced. Some information useful for deducing the natures of the various levels may be obtained by considering the sensitivity of the photoconductive response. The product $\mu\tau$ calculated from the measured signal is related to the carrier capture cross section, σ, of the defect level involved:

$$\sigma=(1/vn\tau)=(\mu/vn)(1/\mu\tau), \tag{2}$$

where μ, v, and n are, respectively, the mobility, the thermal velocity, and the concentration of the majority carriers, the carriers generated in the observed photoconductivity being majority carriers. Using the known values of the effective masses, $m_e=0.052m$ and $m_h=0.23m$, and the measured mobilities and carrier concentrations, we get

$$\sigma_e\approx7\times10^{-17}(10^{-5}/\mu\tau)\ \text{cm}^2$$
to be used with the data in Fig. 4,

$$\sigma_h\approx7\times10^{-16}(10^{-5}/\mu\tau)\ \text{cm}^2$$
to be used with the data in Fig. 5.

The values of $\mu\tau$ and the estimated carrier capture cross sections are listed in Table II for the four levels. In the p-type sample, the signal associated with levels N_2 should extend the spectrum in Fig. 5 to $\approx$0.32 eV and the signal from level P_1 should begin at 0.075 eV. No signal within the sensitivity of measurement was detected below 0.48 eV, giving an upper limit of 10^{-6} cm^2/V for $\mu\tau$ for these two levels. Similarly, an upper limit of $\mu\tau$ can be set for level N_1 in the n-type sample. The signal due to level P_1 in the n-type sample should begin at 0.725 eV and the signal due to level N_1 in the p-type sample should begin at 0.68–0.6 eV. No clear indication of a step at the appropriate energy can be seen in the respective spectrum, however in each case the presence of signal due to another level makes it

TABLE II. Electron and hole capture cross sections σ_e and σ_h of the various defect levels. The capture cross sections are estimated from the values of $\mu\tau$ obtained from the photoconductivity data given in Figs. 4 and 5.

Level	Level energy electron-volt	$\mu\tau$ cm^2/V n-type	p-type	σ_e cm^2	σ_h cm^2
P_1	$E_v+0.075$		$<10^{-6}$		$>0.7\times10^{-14}$
P_2	$E_v+0.48$	$(>10^{-5})$	$>2\times10^{-5}$	$(<0.7\times10^{-16})$	$<3.5\times10^{-16}$
N_2	$E_c-(0.47$ to $0.50)$	$>10^{-3}$	$<10^{-6}$	$<0.7\times10^{-18}$	$>0.7\times10^{-14}$
N_1	$E_c-(0.12$ to $0.20)$	$<10^{-5}$		$>0.7\times10^{-16}$	

difficult to assess an upper limit of $\mu\tau$ for the level in question. In the case of level P_2 in the n-type sample, the value given is based on the assumption that the low-energy tail of the spectrum is associated with this level.

For level N_2, σ_h is larger than σ_e by orders of magnitude, indicating that N_2 is an acceptor level. Level P_1 has a fairly large σ_h; this is consistent with the interpretation that it is an acceptor level. Level N_1 is close to the conduction band and its capture cross section for electrons is not too low. It is reasonable to assume that it is a donor level. It is difficult to postulate about the nature of level P_2 from the available data.

The identification of level P_1 with a level found in unbombarded samples shows directly the importance of lattice defects in determining the normal carrier concentration in GaSb. The level is probably associated with lattice vacancies, either commonly postulated Ga vacancies of Sb vacancies, as a simple interpretation of the work of Effer and Etter[6] would indicate. Neither type of defects can be convincingly ruled out as capable of giving acceptor levels.

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Polarization of Silver Nuclei in Metallic Iron and Nickel*

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Nuclei of Ag^{104} and Ag^{110m} were polarized at temperatures between 0.0105 and 0.97°K, employing the large hyperfine magnetic fields induced at the nuclei of silver atoms dissolved in iron and in nickel. The temperature and angular dependences of γ-ray angular distributions were used to determine the magnitudes of the hyperfine structure constants. Nonconservation of parity in beta decay was used to determine the signs of the internal fields, using germanium detectors to count positrons from Ag^{104} and electrons from Ag^{110m}. The hyperfine fields were found to be negative in both iron and nickel. Analysis of the γ-ray data on one-hour Ag^{104} yielded approximate values for the internal fields: H_i(Ag in Fe) $= -350\pm100$ kG, H_i(Ag in Ni) $= -108\pm30$ kG. Cobalt-60 γ-ray thermometry was used, and the problems of thermometry at 0.01°K are discussed. Nuclear spins of four levels in Cd^{110} were determined unambiguously, confirming earlier work, which was re-interpreted where necessary. The energy levels (spins) are 2162 keV (3+), 2219 keV(4+), 2479 keV(6+), 2926 keV(5+). The 1384-keV γ ray in Cd^{110} was found to be $(91.7\pm2.8)\%$ magnetic dipole and $(8.3\pm2.8)\%$ electric quadrupole. The 1505-keV γ ray was $(78.9\pm4.8)\%$ magnetic dipole and $(21.1\pm4.8)\%$ electric quadrupole. An approximate value of $+2.9\pm1.3$ nm was determined for the nuclear moment of Ag^{110m}.

I. INTRODUCTION

SINCE the discovery by Samoilov, Sklyarevskii, and Stepanov[1] that large hyperfine magnetic fields are induced at nuclei of atoms dissolved in iron, several such fields have been measured. No quantitative theory for these induced fields exists; in fact even an unambiguous qualitative understanding is not presently available. It seems important, therefore, to make systematic measurements of induced fields at nuclei of various elements throughout the periodic table, with emphasis on those systems that are most accessible to theoretical study. With this aim we have performed nuclear orientation experiments on silver atoms in iron and nickel lattices. This study complements measurements on the other group IB metals, copper[2,3] and gold.[4,5]

The theory and applicability of the technique are discussed in Sec. II. The apparatus is described in Sec. III. Section IV deals with the important subject of thermometry. In Sec. V nuclear results are derived, and in Sec. VI the induced magnetic fields at Ag nuclei in Fe and Ni are deduced.

II. THEORY OF THE MEASUREMENTS

The general theory of nuclear orientation has been formulated by several authors.[6–8] Only those parts of the theory that are applicable to the polarization of nuclei in ferromagnets are summarized here.

* Work supported by the U. S. Atomic Energy Commission.
† Present address: Department of Chemistry, Ohio University, Athens, Ohio.
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