

# Identification of donor species in high-purity GaAs using optically pumped submillimeter lasers\*

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An optically pumped NH<sub>3</sub> laser has been used in conjunction with careful doping experiments in high-purity GaAs to determine the ionization energy of isolated tin donors. The energy obtained is 5.820 meV, which corresponds to a central-cell correction of 0.081 meV. This technique for impurity analysis is estimated to be sensitive to donor concentrations of less than 10<sup>11</sup> cm<sup>-3</sup>.

The recent development of optically pumped submillimeter lasers<sup>1-3</sup> has greatly increased the number and power of available lines for spectroscopy. In particular, we have found that the 280.5- $\mu$  laser line from TEA CO<sub>2</sub> laser-pumped NH<sub>3</sub><sup>4</sup> is ideal for investigation of isolated shallow-donor impurities in GaAs. By Zeeman tuning the hydrogenic  $1s-2p$   $m = -1$  transition of residual and intentionally added donors through this laser line, we have obtained the first accurate measurement of the isolated binding energy and a positive identification of a specific donor impurity, tin, in GaAs.<sup>5</sup> This accurate determination for tin may make it possible to calculate other donor central-cell corrections, and the experimental technique should permit identification of the residual<sup>6</sup> and other intentionally added donors in high-purity GaAs.

The laser configuration employed was similar to that used by Chang and Bridges,<sup>1</sup> except that a TEA CO<sub>2</sub> laser was used instead of a cw source to generate the desired NH<sub>3</sub> line, whose wavelength was determined with a scanning Fabry-Perot interferometer. The unattenuated NH<sub>3</sub> radiation, with peak power of several watts, saturated the impurity transitions, and the unsaturated line shape was only observed after attenuating by nearly a factor of 100. Further reduction of intensity did not appear to affect the linewidth, and the measurements were made with an attenuation of approximately 125. For comparative purposes, spectra were also obtained with a conventional cw H<sub>2</sub>O laser. The submillimeter radiation was directed via light pipes onto the GaAs sample, which was immersed in liquid helium and located within the bore of a superconducting solenoid. The sample photoconductivity was then monitored as the magnetic field was varied.

The samples were grown on semiinsulating GaAs substrates with an AsCl<sub>3</sub>-Ga-H<sub>2</sub> vapor-phase system. Before introducing tin into the growth system, the donor and acceptor concentrations ( $N_d$  and  $N_a$ ) for samples from a consecutive series of runs were obtained from Hall and resistivity measurements<sup>7</sup> to determine the residual impurity concentration for a given reactor and set of starting materials. When the residual  $N_d$  and  $N_a$  were found to be relatively constant, subsequent samples were doped by adding small measured amounts of tin to the gallium melt. The total  $N_d$  and  $N_a$  (both residual and tin donors and acceptors) were then determined from electrical measurements on the doped samples.<sup>8</sup> The number of tin donors was also estimated from the measured tin added to the gallium melt and the effective segregation coefficient of tin (the ratio of the tin concentration incorporated in the sample to that in the

gallium melt).<sup>9</sup> In Table I we have summarized these results for the samples discussed in this letter. Sample No. 1 is the undoped control sample, grown just previous to the addition of tin, which had two different residual donor species (see Fig. 1) of total concentration  $1.3 \times 10^{14}$  cm<sup>-3</sup>. Since the residual impurity concentration in this sample was approximately the same as that in the samples of the two preceding runs, tin was added to the growth system to produce sample No. 2. Sample No. 3 is a tin-doped sample with only one residual donor (see Fig. 2), grown in a different reactor with different starting materials than those used for samples No. 1 and No. 2.

The data obtained using optically pumped submillimeter lasers, shown in Fig. 1, give the strongest support to the identification of the tin donor. The peaks observed at 280.5  $\mu$  correspond to the  $1s-2p$   $m = -1$  hydrogenic impurity transition. The presence of residual donor species in undoped GaAs, whose ground-state energies are slightly different because of small central-cell corrections, has been reported recently.<sup>6</sup> In the undoped sample studied here, transitions from two unidentified donor species are observed. The spectrum of the tin-doped sample shows an additional well-resolved transition corresponding to the tin donor. In both samples the peaks are narrow with the broadest having an energy half-width of approximately 0.10 cm<sup>-1</sup>. Furthermore, no shift in position of the residual donor peaks is observed in the tin-doped sample. Therefore, we believe that these measurements provide the first observation of an *isolated* donor species in intentionally doped GaAs.<sup>10</sup>

Previous work by Stillman *et al.*<sup>11</sup> has determined that the effective hydrogenic Rydberg for GaAs donors, defined in the parabolic band approximation as

$$R_y^* = \frac{m_0^* e^4}{2 \epsilon_0^2 \hbar^2},$$

has the value  $R_y^* = 46.10 \pm 0.15$  cm<sup>-1</sup> (5.715 meV). Furthermore, the ionization energies of the residual impurities responsible for the photoconductivity peaks at 60.51 and 67.95 kG in Fig. 1 were calculated to be 47.24 cm<sup>-1</sup> (5.856 meV) and 46.82 cm<sup>-1</sup> (5.804 meV), respectively. The ionization energy of the tin donor can be determined by a linear interpolation between these values, using the magnetic field measurements of the three  $1s-2p$   $m = -1$  donor transitions shown in Fig. 1. Using this method, we find that the tin donor in GaAs has an ionization energy of  $46.95 \pm 0.15$  cm<sup>-1</sup> (5.820 meV) and an absolute central-cell correction of  $0.65 \pm 0.15$  cm<sup>-1</sup> (0.081 meV), in good agreement with the values previously obtained from an unidentified donor.<sup>11,12</sup>

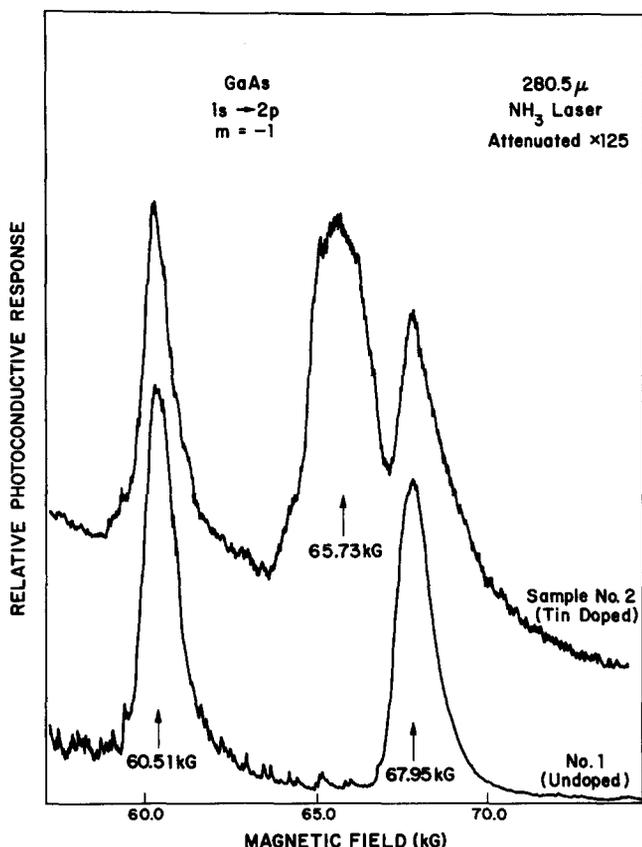


FIG. 1. Photoconductivity spectra for an undoped and tin-doped GaAs sample. The transition at 65.73 kG is attributed to the tin donor. Magnetic fields were determined by observing NMR in  $^{27}\text{Al}$  simultaneously with the photoconductivity peaks.

The magnetospectroscopy data for three samples taken at  $78.45 \mu$  with a cw  $\text{H}_2\text{O}$  laser are shown in Fig. 2 for comparative purposes. (Data were also taken at  $79.09 \mu$ .) The peaks in these spectra correspond to the  $1s-2p$   $m = +1$  hydrogenic impurity transition. For the undoped sample No. 1, four peaks are observed which arise from the two residual donor impurities observed in the  $\text{NH}_3$  spectra. We attribute the presence of two peaks for each of the central-cell-shifted species to a combination of spin-splitting and excited-state nonparabolicity. Although the different transition energies for spin-up and spin-down electrons are not in quantitative agreement with theories for nonparabolicity in the donor states, similar splitting is found in cyclotron resonance measurements.<sup>13</sup> The tin-doped sample No. 2, with three donor species, exhibits five peaks (instead of six) because of overlap of the high-field tin peak with a residual donor transition. This donor is not present in the other tin-doped sample (No. 3) where we observe the spin-up and spin-down transitions corresponding to the tin donor.

Examination of the spectra taken with the  $\text{NH}_3$  laser (Fig. 1) and the  $\text{H}_2\text{O}$  laser (Fig. 2) demonstrates the advantages of the former for the purpose of discrimination among different donor species in GaAs. The donor peaks for the  $1s-2p$   $m = -1$  transition, when magnetically tuned for coincidence with the  $\text{NH}_3$  laser, are found

TABLE I. Donor concentrations ( $\text{cm}^{-3}$ ) for undoped (sample No. 1) and tin-doped (samples No. 2 and No. 3) GaAs.

Sample No.	Electrical measurements			Segregation coefficient
	Total	Residual	Tin	Tin
1	$1.3 \times 10^{14}$	$1.3 \times 10^{14}$	...	...
2	$3.0 \times 10^{14}$	$1.3 \times 10^{14}$	$1.7 \times 10^{14}$	$2 \times 10^{14}$
3	$2.7 \times 10^{14}$	$1.8 \times 10^{14}$	$9.2 \times 10^{13}$	$7 \times 10^{13}$

to be extremely narrow.<sup>14</sup> For this case the major contribution to the breadth of the transitions is predicted to arise from the quadratic Stark effect—that is, from the interaction of the electric field of the charged donors and acceptors with the induced dipole moment of the donor wave function.<sup>15</sup> Since this Stark perturbation always lowers the energy of the  $2p$   $m = -1$  state, the resultant effect (due to the random distribution of charged sites) is an asymmetric line shape with a tail on the low-energy (high-magnetic-field) side. The  $1s-2p$   $m = -1$  transition shown in Fig. 1 clearly exhibits such asymmetry.

For the case of the  $1s-2p$   $m = +1$  transitions which can be reached with the  $\text{H}_2\text{O}$  laser line, other broadening effects dominate. In particular, since the  $2p$   $m = +1$

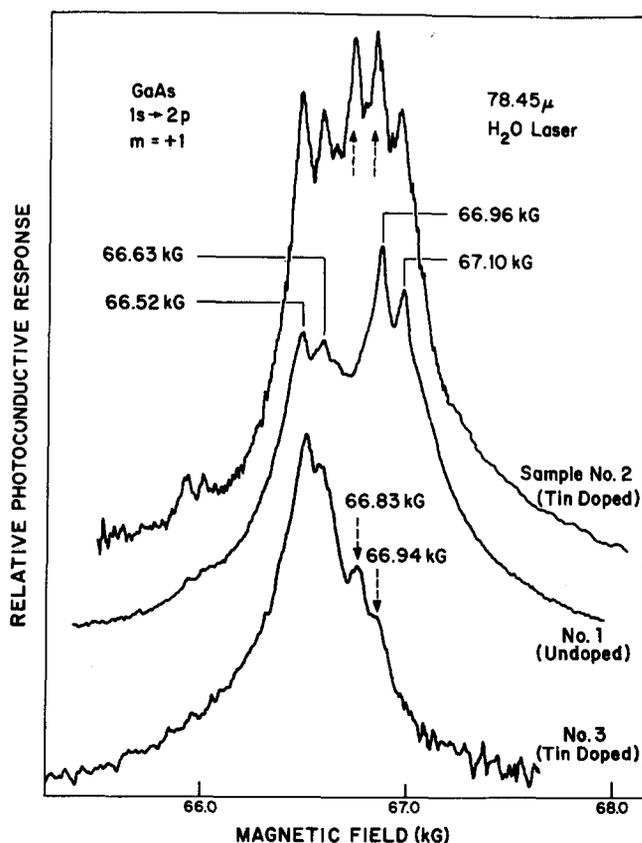


FIG. 2. Photoconductivity spectra for the samples in Table I, measured using a cw  $\text{H}_2\text{O}$  laser. Two spin-split peaks corresponding to the tin donor are indicated by dashed lines at 66.83 and 66.94 kG.

energy lies above the continuum at these magnetic fields, decay to lower energy states is possible, shortening the lifetime and broadening the line. As a consequence of the broadened linewidth and spin splitting, it is difficult to precisely determine the tin binding energy from the H<sub>2</sub>O laser measurements. However, these measurements do reveal several interesting points: (a) The residual and tin donor peaks remain at the same energies in different samples grown in different reactors with different starting materials; (b) the tin donor peaks do not shift in energy in this donor concentration range (sample No. 2 has twice as many tin donors as sample No. 3); (c) the relative integrated spectral response from the residual and tin donors is in reasonable agreement with the relative donor concentration as determined from electrical measurements (see Table I).

Using NH<sub>3</sub> laser sources in conjunction with careful doping experiments, it should be possible to determine the ionization energies of a number of other shallow-donor species in GaAs and identify the residual donors in high-purity GaAs. This should lead to further purification of the material. The technique used here promises to be a powerful analytical tool for nondestructive trace impurity analysis. From the results obtained in the present experiments for tin donors, we conservatively estimate that it will be possible to detect shallow donors at concentrations of less than 10<sup>11</sup> cm<sup>-3</sup> in high-purity *n*-type GaAs.

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- <sup>4</sup>H.R. Fetterman, H.R. Schlossberg, J. Waldman, C.D. Parker, and P.E. Tannenwald in *Proceedings of the VII International Quantum Electronics Conference, Montreal, 1972* (unpublished).
- <sup>5</sup>Tentative identification of the tin donor has also been reported by J.M. Chamberlain, P.E. Simmonds, R.A. Stradling, and C.C. Bradley [in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw* (unpublished)], but the donor binding energy was not determined.
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- <sup>7</sup>C.M. Wolfe, G.E. Stillman, and J.O. Dimmock, *J. Appl. Phys.* **41**, 504 (1970).
- <sup>8</sup>Since the residual  $N_d$  and  $N_a$  in the series of runs were relatively constant (and assuming that the addition of the tin did not increase the residual  $N_d$ ), the tin donor concentration could be determined with reasonable assurance.
- <sup>9</sup>C.M. Wolfe, G.E. Stillman, and W.T. Lindley in *Proceedings of the Second International Symposium on GaAs* (Institute of Physics and the Physical Society, London, 1969), p. 43.
- <sup>10</sup>Previous studies of intentionally doped GaAs were made with samples which had broad (approximately 5-cm<sup>-1</sup> half-width) donor absorption lines. Such linewidths do not appear to be characteristic of the spectra of isolated impurities in GaAs [C.J. Summers, R. Dingle, and D.E. Hill, *Phys. Rev. B* **1**, 1603 (1970)].
- <sup>11</sup>G.E. Stillman, D.M. Larsen, C.M. Wolfe, and R.C. Brandt, *Solid State Commun.* **9**, 2245 (1971).
- <sup>12</sup>The ionization energy of the donors in GaAs is increased by nonparabolicity effects which deepen the 1s state by about 0.17 cm<sup>-1</sup>.
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- <sup>14</sup>While the lines shown in Fig. 1 appear relatively broad in magnetic field, the "magnetic dispersion" for this transition is quite small, approximately 0.08 cm<sup>-1</sup>/kG in this region.
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## Mass motion as observed by light-beating spectroscopy

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In the power spectra of the scattered light from silver chloride colloidal particles in water, a Lorentzian shifted from zero frequency has been observed in addition to the zero-centered one. The shifted peak is attributed to the mass motion due to liquid flow resulting from the heating of the illuminated part by the laser beam.

Light-beating spectroscopy is an accepted method of measuring narrow spectral lines, particularly those obtained by scattering laser light from various samples.<sup>1,2</sup> In this letter we wish to report an observed interaction between the original laser beam and the scattering medium as observed in the power spectra of the scattered light.

The spectrometer used is similar to those already reported in the literature.<sup>2</sup> The laser used was a Spectra Physics Model No. 124A He-Ne laser. The scattered light is accepted by the photomultiplier whose output is connected to a Tektronix 1L5 spectrum analyzer. The

spectrum analyzer output is averaged by an active integrating circuit. The time-averaged spectrum is then recorded and squared to obtain the power spectra of the scattered light.

The entire system has been checked by measuring the light scattered from a dilute suspension of polystyrene latex spheres and from carbon particles suspended in water containing a detergent additive. In both cases the power spectrum of the scattered light is a Lorentzian whose half-width corresponds to that predicted by theory and to the size of the scattering particles. In both cases the absorption of laser light by the solution was less