

sity of Leiden, Leiden, The Netherlands.

<sup>1</sup>C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and Alan G. MacDiarmid, *Phys. Rev. Lett.* **39**, 1098 (1977).

<sup>2</sup>C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and Alan G. MacDiarmid, *J. Chem. Phys.* **69**, 5098 (1979).

<sup>3</sup>I. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heeger, and A. G. MacDiarmid, *J. Chem. Phys.* **70**, 1132 (1979).

<sup>4</sup>B. R. Weinberger, J. Kaufer, A. J. Heeger, A. Pron, and A. G. MacDiarmid, to be published.

<sup>5</sup>M. J. Rice, *Phys. Lett.* **71A**, 152 (1979).

<sup>6</sup>W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).

<sup>7</sup>L. Mihaly, S. Pekker, and A. Janossy, to be published.

lished.

<sup>8</sup>T. Ito, H. Shirakawa, and S. Ieda, *J. Polym. Sci.* **1**, **12**, 11 (1974).

<sup>9</sup>For a discussion of 1D variable-range hopping, see V. K. S. Shante, *Phys. Rev. B* **16**, 2597 (1977), and references cited therein.

<sup>10</sup>For a review, see B. Abeles, in *Applied Solid State Science*, edited by Raymond Wolfe (Academic, New York, 1976).

<sup>11</sup>Any solitons in the *cis* isomer should be immobile because the isomers that differ by interchange of double and single bonds (*cis-transoid* and *trans-cisoid*) are not equivalent. Thus solitons isolated in different segments, if they existed in these *cis* segments, would be pinned to the ends in order to leave the segments in their lower-energy isomeric form.

## Symmetry of Donor-Related Centers Responsible for Persistent Photoconductivity in $\text{Al}_x\text{Ga}_{1-x}\text{As}$

V. Narayanamurti, R. A. Logan, and M. A. Chin

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 20 August 1979)

We report on the attenuation of ballistic phonons generated in bulk GaAs and propagating through epitaxial layers of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  containing up to  $10^{18}$  Sn or Te donors per cubic centimeter. The latter donors are known to form a complex with an unidentified defect (DX center) whose occupation is changed by photoexcitation. The symmetry of the ionized DX center is shown to be trigonal in the case of Sn and most likely orthorhombic in the case of Te donors.

The phenomenon of low-temperature, persistent impurity photoconductivity in compound semiconductors has attracted considerable recent attention. Most recently this phenomenon has been observed<sup>1-3</sup> in well-controlled, uniformly doped samples of the semiconductor  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , and a large-lattice-relaxation model<sup>1</sup> to explain the results has been invoked. For the case of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  it involves a non-effective-mass-like donor complex labeled a "DX" center. The unoccupied DX center is believed to be resonant with the conduction band, yet sufficiently localized to produce a large lattice relaxation. Even though a large number of recent measurements<sup>1,2,4</sup> have given considerable support to this model, no microscopic information on the nature and symmetry of this important class of defects exists. A novel and direct method of determining such information is through the study of absorption of beams of ballistic phonons of well-defined propagation direction and polarization. The results of such studies on Sn- and Te-related donor centers in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  are reported here. The

highly anisotropic nature of the attenuation provides compelling evidence for a (111) axial distortion in the case of Sn and a (110) distortion in the case of Te DX centers and the existence of donor-related resonant states in the conduction band of GaAs. Both of these features, as we shall see, are crucial to the model of large-lattice-relaxation DX centers in AlGaAs.

In the top of Fig. 1, we show a simple configuration-coordinate diagram proposed by Lang and co-workers<sup>1</sup> for DX centers in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . Curves C and D correspond to vibrations of the unoccupied and occupied defect. The physical significance of the large-lattice-relaxation limit is that the defect level is above the conduction-band minimum in the  $Q=Q_{\text{empty}}$  configuration, but when energy is supplied to distort the local environment of the defect to  $Q=Q_{\text{full}}$  the level drops deep into the gap. The net energy gained in the process,  $E_0$ , is small ( $\sim 0.1$  eV) and is the defect activation energy as measured thermally (e.g., Hall effect). The optical activation energy is, however, large ( $\sim 1.5$  eV) since such transitions

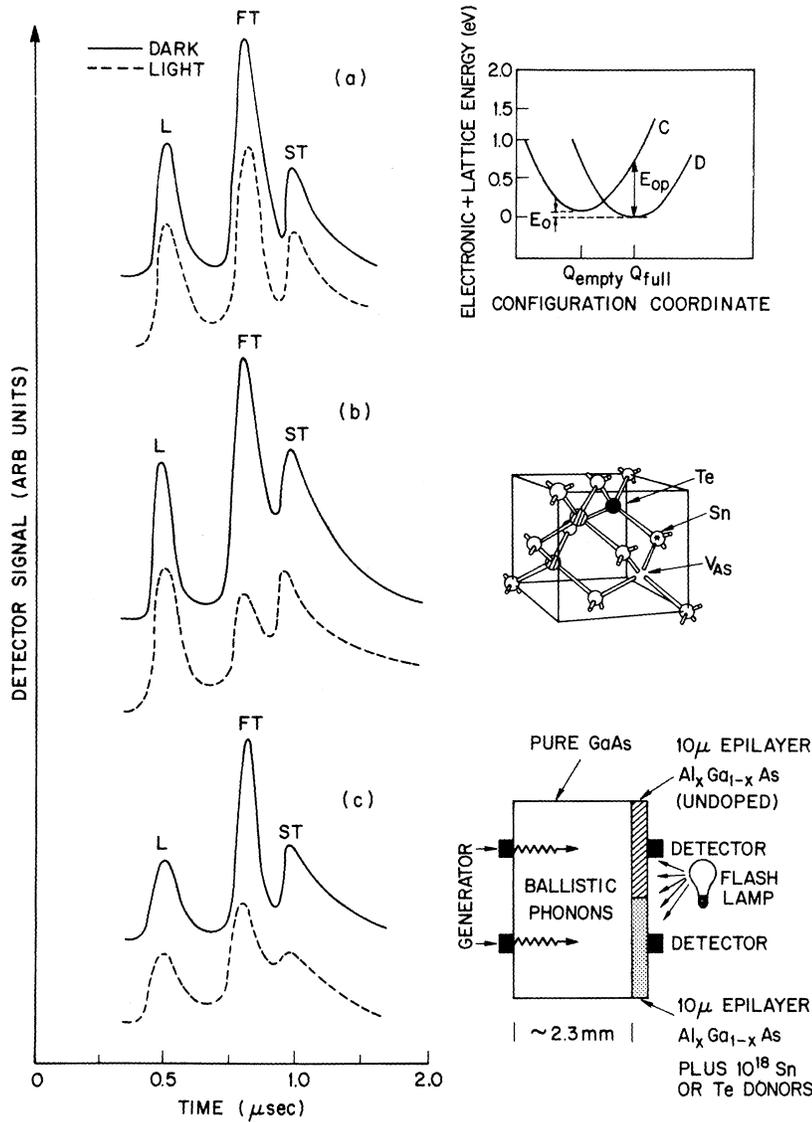


FIG. 1. Ballistic phonon intensities for three different samples of  $Al_{0.5}Ga_{0.5}As$ : (a) nominally undoped material, (b) with  $\sim 10^{18}$  Sn donors per cubic centimeter, and (c) with  $\sim 10^{18}$  Te donors per cubic centimeter. Solid lines are data taken in the dark while the dashed lines are taken after photoexcitation. Propagation direction  $\parallel 110$ . The intensities of the ballistic phonons reveals selective attenuation of certain groups of transverse modes depending upon the symmetry of the donor-related photoconductivity center. The right-hand side of the figure shows a typical configuration-coordinate diagram for such centers. See text. A crystal model of GaAs and a schematic of the experimental arrangement are also shown.

can take place only at constant  $Q$ . Such behavior has been seen with both As-site donors (such as Te or Se) and Ga-site donors such as Sn or Si with somewhat different activation energies. Also shown in Fig. 1 is a crystal model showing possible distortions if the donors are complexed with, say, an As vacancy.

The DX center, depending upon the local atomic distortion, can occupy any of several equilibrium orientations in the lattice. At low tem-

peratures, the center may be expected to reorient by means of a phonon-assisted quantum-mechanical tunneling process.<sup>5</sup> The interaction of the phonon stress field with anisotropic defects can be calculated from the theories of anelastic relaxation of point defects in solids.<sup>6</sup> The absorption coefficient,  $\alpha$ , for a phonon of frequency  $\omega$  will in general be given by

$$\alpha(\omega) = (\Delta S / Sv^2) f(\omega, \omega_0, \Gamma),$$

where  $\Delta S/S$  is the relative change of the elastic compliance,  $f$  is a line-shape function which will depend on  $S$ ,  $\omega_0$  is the tunneling resonance,  $\Gamma$  is a level width, and  $v$  is the sound velocity. According to elastic dipole theory  $\Delta S/S$  depends strongly on the phonon-propagation direction, the phonon polarization, and the defect symmetry. In Table I we list the selection rules for transverse phonon modes for tetragonal, trigonal, and orthorhombic defects. These selection rules are experimentally known to be accurately obeyed for trigonal defects with some exceptions for other symmetries.<sup>6</sup> Selection rules also apply for longitudinal phonon modes. These are not shown in the table since, because of their larger sound velocity, their coupling is weaker, and they will not be discussed in detail in this paper.

The geometry of the experiment is shown schematically in the inset of Fig. 1 (bottom right-hand corner). The phonons were generated at one end of the sample of a semi-insulating GaAs crystal (typical thickness 2.3 mm) by means of a thin-film Constantan heater of area  $\sim 0.25$  to  $0.75$  mm<sup>2</sup>. At the other end of the sample a thick epilayer ( $\sim 10$   $\mu$ m thick) of Al<sub>x</sub>Ga<sub>1-x</sub>As was grown by liquid-phase epitaxy (LPE). One half of this epilayer was typically undoped while the other half was doped with approximately  $10^{18}$  Sn or Te donors. A thin-film granular Al bolometer or tunnel junction (again of typical size  $\sim 0.5$  mm<sup>2</sup>) was used as the phonon detector. Electrical pulses of duration 10 to 100 ns were applied to the generator. The detector output was amplified and signal averaged by means of a Tektronix WP221 transient digitizer. All measurements were done with an ambient sample temperature  $\sim 1.5$  K. The experiments were done either in the dark or in the presence of light generated by a tungsten lamp. Suitable absorbing filters could be inserted between the lamp and crystal for effective illumination of the Al<sub>x</sub>Ga<sub>1-x</sub>As epilayers. The detectors were sufficiently thin to allow transmis-

sion of the light. For clarity we present data for  $x=0.5$  only, and compare these results to those obtained with several different Al compositions in the  $x=0$  to  $x=0.5$  range.

In Figs. 1(a) to 1(c) we show typical ballistic phonon signals taken with the sample in the dark (solid curves) and in the light (dashed lines). The propagation direction in both cases is [110]. The heater power density was extremely low for these measurements (typically 0.03 W/mm<sup>2</sup>). At these low densities the heater temperature is only slightly above ambient and bulk scattering in GaAs is insignificant.<sup>7</sup> In the [110] direction the two transverse modes are nondegenerate and well separated in time. The intensities of the ballistic phonons, in the absence of attenuation, is governed solely by the combined effects of the density of states and phonon focusing<sup>8</sup> effects because of anisotropy. Detailed calculations<sup>9</sup> of the focusing effects for GaAs indicate that the detector shape (when transformed from real space to wave-vector space) is accurately preserved for the longitudinal (L) and the slow transverse (ST) modes. Some distortion of the fast transverse (FT) mode shape occurs but this is minimal in this direction. Thus selection rules for scattering are expected to be meaningful. All of these data in the dark are very similar and the intensities of the three modes can semiquantitatively be described by the known elastic anisotropy of GaAs.

The ballistic phonon intensities, however, change markedly with photoexcitation. In the case of the nominally undoped sample [case (a)] we observe a small decrease of the FT mode signal relative to the other modes. In the case of the Sn-doped sample the FT mode intensity drops dramatically between a factor of 2 and 3 while the ST mode remains virtually unaffected. In the case of the Te-doped sample, we see strong attenuation of both FT and ST modes, with the latter attenuation being somewhat stronger.<sup>10</sup>

TABLE I. Interaction (indicated by X) of various transverse phonon modes with defects of different symmetries in a cubic host lattice.

Mode	Propagation direction	Polarization direction	Stress symmetry	Defect Symmetry		
				Tetragonal $\langle 100 \rangle$	Trigonal $\langle 111 \rangle$	Orthorhombic $\langle 110 \rangle$
T	[100]	[010]	$T_{2g}$		X	X
FT	[110]	[001]	$T_{2g}$		X	X
ST	[110]	[ $\bar{1}\bar{1}0$ ]	$E_g$	X		X
T	[111]	[11 $\bar{2}$ ] or [ $\bar{1}\bar{1}0$ ]	$E_g, T_{2g}$	X		X

The attenuation persists even after the light is switched off as long as the low temperature is maintained. The effects described here have been observed with several different samples and do not depend on Al composition in the range  $x = 0.3$  to  $0.5$ . In this composition range the minimum band gap of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  changes from direct to indirect.<sup>11</sup> Thus the effects we describe cannot be explained by free carrier or band-structure effects due to ordinary piezoelectric or deformation potential scattering. For  $x < 0.3$  we observe strong attenuation in the dark with little sensitivity to light. In this range, the activation energy  $E_0$  for DX centers is negative and the DX centers are always ionized.

Since the unusual data that we have observed parallel the behavior of the DX center in  $\text{Al}_x\text{-Ga}_{1-x}\text{As}$  studied by photocapacitance,<sup>1</sup> we interpret our data as follows: The strong sensitivity to photoexcitation and persistence of the phonon attenuation after the light is switched off (in the  $x = 0.3$  to  $0.5$  range) and the variations we have observed with Sn and Te doping is unequivocal evidence that the attenuation is to be associated with ionized DX centers. Furthermore, from Table I we identify the distortion of the Sn DX center to be trigonal and suggest the existence of donor-related energy states in the conduction band of GaAs. The near equality of  $E_g$  and  $T_{2g}$  scattering for Te donors makes a symmetry identification in this case more difficult. Assuming anelastic relaxation in analogy with the Sn case, the symmetry of Te DX centers is most likely orthorhombic from Table I. Extensive ballistic phonon attenuation measurements in other crystallographic ([111] and [100]) are also consistent with these results. By keeping the detector bias fixed, absolute changes of intensity as a function of photoexcitation could be monitored. Careful inspection of the data reveals attenuation of  $L$  modes. In the case of Sn donors, for example, the weak  $L$ -mode scattering occurs only in the [111] and [110] direction but not in [100] as is to be expected for trigonal centers. The small FT attenuation we observe in the [110] direction in the undoped sample is also to be identified with trigonal centers. Our nominally undoped LPE material is usually  $n$  type and has a background donor concentration in the mid- $10^{16}$  to  $10^{17}/\text{cm}^3$

range. Since the material is grown in quartz tubes and in carbon boats, the most likely donors are Si or C which may be expected to take a GaAl site similar to the case of Sn as observed. For  $x < 0.3$ , as already mentioned, the DX centers are always ionized and our attenuation results are suggestive that this resonance persists down to  $x = 0$ .

In summary, we have described unusual, selective attenuation of ballistic phonons by donor-related persistent photoconductivity centers in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . These results give the first proof of the microscopic nature of these centers, both in terms of their symmetry and the existence of scattering states in the conduction band of GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The latter feature is the essence of the large-lattice-relaxation model while the former gives strong support to the crystal model of the DX center shown in Fig. 1.

We would like to thank D. V. Lang and R. Dingle for many useful discussions and H. G. White for the epilayer growth.

<sup>1</sup>D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977); D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979).

<sup>2</sup>R. J. Nelson, Appl. Phys. Lett. **31**, 351 (1977).

<sup>3</sup>H. J. Queisser and D. E. Theodorou, Phys. Rev. Lett. **43**, 401 (1979).

<sup>4</sup>J. L. Merz, J. P. van der Ziel, and R. A. Logan, Phys. Rev. B **20**, 654 (1979).

<sup>5</sup>J. A. Sussman, Phys. Kondens. Mater. **2**, 146 (1964).

<sup>6</sup>For example, see A. S. Nowick and W. R. Heller, Adv. Phys. **14**, 101 (1965); see also C. A. Bates, Phys. Rep. **35C**, 187 (1978).

<sup>7</sup>Substrates free of Cr impurities ( $< 3 \times 10^{16}/\text{cm}^3$ ) were used to avoid bulk scattering. See, for example, V. Narayanamurti, M. A. Chin, and R. A. Logan, Appl. Phys. Lett. **33**, 481 (1978).

<sup>8</sup>B. Taylor, H. J. Maris, and C. Elbaum, Phys. Rev. Lett. **23**, 416 (1969), and Phys. Rev. B **3**, 1462 (1971).

<sup>9</sup>M. Lax and V. Narayanamurti, to be published.

<sup>10</sup>In some Te-doped samples, the ST mode is almost totally absent after photoexcitation, unlike the Sn-doped and "undoped" cases of Figs. 1 (a) and 1 (b).

<sup>11</sup>R. Dingle, R. A. Logan, and J. R. Arthur, Jr., in *Gallium Arsenide and Related Compounds*, edited by C. Hilsum, The Institute of Physics Conference Series No. 33a (The Institute of Physics, Bistol and London, 1977), p. 210.