the differing influence of In-In and In-Pb nearest neighbors.<sup>1</sup> As the indium concentration is increased, this splitting becomes washed out as might be expected, but it is remarkable that the structure in the  $d\sigma/dV$  curves which is identifiable with the impurity band continues to be clearly distinguishable. One might have expected that in concentrated alloys impurity effects would be absorbed into the main body of the lattice vibrational spectrum; such apparently is not the case.

The phonon spectrum below 9.5 meV [Fig. 2(b)]. –It is evident that the amplitudes of the structure associated with the T (3.5 to 5 meV) and L (8 to 9 meV) modes<sup>5,9</sup> are decreased with increasing alloying. This is to be expected since the growth of the impurity band would reduce the phonon density of states in these alloys near the transverse and longitudinal peaks. In spite of the difference in mass and valence between the Pb and In atoms it is surprising that there is no large shift in energy of the L and T peaks. Within the present theoretical knowledge of the phonon spectra of substitutional alloys, a detailed quantitative

analysis of these data is difficult. We are extending these measurements to cover the full range of solid solubility of indium in lead; these as well as other tunneling experiments on this alloy system will be presented in detail elsewhere.

\*Work supported by the U. S. Air Force Office of Scientific Research through Grant No. 565-64.

<sup>1</sup>J. M. Rowell, W. L. McMillan, and P. W. Anderson, Phys. Rev. Letters 14, 633 (1965).

<sup>2</sup>J. G. Adler and J. E. Jackson, to be published.

<sup>3</sup>J. S. Rogers, thesis, University of Alberta, Edmonton, Canada, 1964 (unpublished).

<sup>4</sup>J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters <u>10</u>, 336 (1963).

<sup>5</sup>D. J. Scalapino and P. W. Anderson, Phys. Rev. <u>133</u>, A921 (1964).

<sup>6</sup>W. L. McMillan and J. M. Rowell, Phys. Rev. Letters 14, 108 (1965).

<sup>7</sup>A. F. G. Wyatt, Phys. Rev. Letters <u>13</u>, 160 (1964). <sup>8</sup>J. G. Adler, J. S. Rogers, and S. B. Woods, Can. J. Phys. 43, 557 (1965).

<sup>9</sup>J. M. Rowell and L. Kopf, Phys. Rev. <u>137</u>, A907 (1965).

# EVIDENCE FOR IMPURITY STATES ASSOCIATED WITH HIGH-ENERGY CONDUCTION-BAND EXTREMA IN n-CdTe

## A. G Foyt

Lincoln Laboratory,\* Massachusetts Institute of Technology, Lexington, Massachusetts

#### and

## R. E. Halsted

General Electric Research and Development Center, † Schenectady, New York

#### and

## William Paul

Division of Engineering and Applied Physics,<sup>‡</sup> Harvard University, Cambridge, Massachusetts (Received 28 October 1965)

The resistivities of several samples of n-CdTe have been found to increase by factors greater than 10<sup>4</sup> between 1 and 28 000 kg/cm<sup>2</sup> at room temperature. The interpretation of these results in terms of deionization into an impurity level<sup>1</sup> yields a pressure coefficient for the separation of this level from the lowest (000) conduction band large enough to suggest that the level is associated with the higher lying (100) conduction band, a model originally suggested by Paul<sup>2</sup> to explain Sladek's<sup>3</sup>

### results on n-GaAs.

12 samples of *n*-CdTe, similar to those described by Segall, Lorenz, and Halsted,<sup>4</sup> were measured. All of the samples show the same qualitative characteristic of a relative insensitivity to pressure at low pressures, followed by a sharp rise at high pressures. We show in Fig. 1 the  $\rho$  vs *P* relation for five undoped samples in which a decrease in resistivity at zero pressure is believed to be correlated with an increasing excess of Cd. The samples

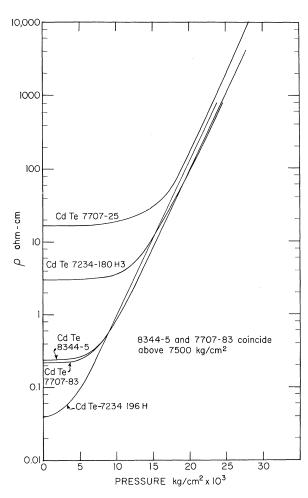


FIG. 1. Pressure dependence of the resistivity of n-CdTe.

converged to a common resistivity at high pressures. No hysteresis was observed between the curves for increasing and decreasing pressure. The other samples, which had been deliberately doped with known impurities in most cases, showed a quantitatively different resistivity dependence on temperature and pressure.

It is evident from the fact that the resistivity increases exceed  $10^4$  that the decrease of electron mobility caused by an increase in average electron mass, either in the (000) minimum or because of electron transfer to higher mass minima, may be ignored initially. We have therefore analyzed these results using a model with a single conduction band of state density  $N_c$ , a donor level of density  $N_d$ , and a starting electron concentration, resulting from compensation, of  $n_0$ . The donor is separated by an energy  $\Delta = E_c - E_d$  from the bottom of the conduction band.

The conduction electron density n is then given by the expression

$$n = N_c \exp[(E_F - E_c)/kT]$$
$$= n_0 - \frac{N_d}{1 + \alpha \exp[(E_c - E_F - \Delta)/kT]}$$

where  $E_{\rm F}$  is the Fermi energy,  $E_c$  the energy of the bottom of the conduction band,  $\alpha$  a degeneracy factor for the impurity, and where the approximation of Boltzmann statistics is used for the conduction band. This leads to the following expression connecting  $\Delta$  and  $\rho$ :

$$\frac{\Delta(P)}{kT} = \ln \frac{c}{n_0} \frac{\alpha x(x-1)}{1+(m-1)x},$$

where  $x = \rho/\rho_0$ ,  $\rho_0 = (n_0 e \mu)^{-1}$ ,  $m = N_d/n_0$ , and  $\mu$  is the electron mobility in the band. At high pressures, x > 1, so that

$$\frac{\Delta(P)}{kT} = \ln \frac{N_c}{n_0} \frac{\alpha x}{m-1}.$$

A graph of  $\ln x$  vs P then has a slope of  $\left[\partial \Delta(P) / \partial P\right] / kT$ , and a zero pressure intercept of

$$\frac{\Delta(0)}{kT} - \ln \frac{\alpha}{m-1} - \ln \frac{N_c}{n_c}$$

From Fig. 1, the five samples have identical slopes, in the region of high pressure, of  $12.6 \times 10^{-6} \text{ eV/kg cm}^{-2}$ . The intercepts at zero pressure lead to values of  $\Delta(0)/kT - \ln[\alpha/(m-1)]$  between 0 and -0.5.

The first and most important thing to note is that the pressure coefficient found for the ionization energy of the impurity is far greater than is expected for either hydrogenic or deep-lying impurities. For hydrogenic donor impurities, the effect of pressure on the ionization energy may be calculated from the expression

$$\epsilon_I = \epsilon_H m^*/m_e \kappa^2,$$

where  $\epsilon_{\rm H}$  is the ionization energy of hydrogen,  $m^*$  is the effective mass,  $m_{\ell}$  the free electron mass, and  $\kappa$  is the dielectric constant. Holland and Paul<sup>5</sup> verified the predicted coefficient for silicon, about 10<sup>-8</sup> eV/kg cm<sup>-2</sup>. We can make a similar estimate for this pressure coefficient in *n*-CdTe, using Thomas's value<sup>6</sup> for the increase in energy gap with pressure to give  $\partial m^*/\partial P$  and, for lack of data on CdTe, DeMeis's' determination of the change in dielectric constant in GaAs. We find  $\partial \epsilon_I / \partial P \approx 10^{-7}$ eV/kg cm<sup>-2</sup>, which is much smaller than our measured pressure coefficient.

The value of  $\partial \Delta / \partial P$  is also considerably larger than is expected on the basis of previous measurements on deep-lying impurities. The pressure coefficients of the ionization energies of the several levels provided by gold in Ge<sup>8</sup> and Si,<sup>9</sup> and of unknown impurities in GaAs<sup>10</sup> were found to be a fraction of the coefficient for the energy gap.

It is evident that the impurity level we are dealing with is very close to the conduction band at atmospheric pressure since it takes a finite pressure to begin deionization. Nevertheless, the measured pressure coefficient is greater than the largest band-gap coefficient reported for CdTe.<sup>6</sup> Significantly also, it is very close to the coefficient found for the separation with pressure of the (000) and (100) band minima in group 4 and group 3-5 semiconductors of the same crystal structure.<sup>11</sup> It seems possible, therefore, that the state of the impurity into which the conduction band is deionizing at high pressures is one described predominantly by (100) band function.

We should like to know the dependence  $\Delta(P)$ . Unfortunately,  $\alpha$  and m are not known, so that the zero-pressure intercept  $\Delta(0)$  is uncertain. Setting  $\alpha = 1$  and m = 2 gives  $\Delta(0)$  between 0 and -0.0125 eV. This does not mean, however, that the impurity level is located at this position at atmospheric pressure, since the impurity levels associated with (000) and (100) band edges may be perturbed nonlinearly as the two band edges become close in energy.

A more thorough examination of the dependence  $\Delta(P)$  will require further detailed analysis of these and additional samples. We intend to examine samples with different active impurities, where we expect to find about the same value of  $\partial \Delta/\partial P$ , but different values of  $\Delta(0)/kT - \ln[\alpha/(m-1)]$  and of  $\Delta(P)$  near P = 1 kg/cm<sup>2</sup>.

There have been a few references to this sort of impurity state in the literature. Their existence has been considered from a theoretical point of view, by Peterson<sup>12</sup> and by Kaplan.<sup>13</sup> Bate<sup>14</sup> interpreted Hall-effect and resistivity data on *n*-GaSb in terms of an impurity level which was above the lowest (000) conduction-band edge, and which was associated with the higher lying (111) minima, Zwerdling et al.<sup>15</sup> interpreted optical measurements on Si on the basis of an impurity level associated with the spin-orbit split-off valence band, and Paul suggested the present model to explain the large pressure coefficient found by Sladek for the ionization energy of donor impurities in n-GaAs.

The energy of the (100) minima is not settled by this experiment, although it would be straightforward to find it for samples where the electrons are transferred into these minima rather than into associated impurity levels. However, recent pseudopotential calculations<sup>16</sup> place the  $X_1$  (100) minima about 2 eV above the central minimum. Also, the uv reflectivity measurements of Cardona and Greenaway<sup>17</sup> suggest an energy separation of 5.4 eV between the valence-band  $(X_5)$  state and the  $X_1$  state; if we assume a valence bandwidth at the X point between 1 and 2 eV, which is normal in these materials, we are again led to an energy separation between the  $X_1$  and  $\Gamma_1$  states of at least 2 eV. The  $L_1$  minima are supposed to be 1.5 eV above the  $\Gamma_1$  minimum.<sup>16</sup> If these deductions are correct, our interpretation of the present experiments implies a much greater contribution of the  $X_1$  (100) band than we would intuitively expect, and also requires an explanation of why the  $L_1$  minima do not similarly contribute. Also, the existence of the Gunn-effect oscillations<sup>18</sup> must be explained either on the basis that the electrons can gain the 1.5 to 2 eV of energy (note, the fundamental gap is  $\sim 1.5$ eV) to reach the  $L_1$  or the  $X_1$  minima, or that the mobility reduction is caused by their falling into impurity levels. These impurity levels may capture electrons either because they are at high energies (in the continuum, and associated with the higher minima) or because of some other strongly energy-dependent capture cross section. These considerations suggest several experiments to settle which model is correct, but the resolution of these problems should give us new insight into the physics of the Gunn effect in CdTe, the striking properties of the impurities in the present experiment, the interpretation of the uv spectra, and the accuracy of the pseudopotential calculations.

It is to be noted that many members of the germanium family-for example, Ge, Sn, GaAs, InP, GaSb, GaP, and AlSb-have conduction VOLUME 16, NUMBER 2

bands with nonequivalent extrema within 0.5 eV of each other. In these cases, we suspect that the appropriate description of the donor impurity states should take more account of the contributions of the higher lying extrema than has been done previously. The implications of admixture of band functions from subsidiary minima into impurity wave functions for optical properties near the fundamental gap, especially recombination phenomena, are obvious. Furthermore, the possible existence of resonant scattering states of the impurity at energy levels degenerate with the continuum provides an extra source of mobility reduction which is seldom considered.

We wish to acknowledge helpful discussions with Professor A. L. McWhorter regarding interpretation of the data. We especially wish to thank Mr. David MacLeod for very carefully performing the pressure measurements.

<sup>1</sup>In this Letter, the word "impurity" is taken to mean

any deviation from perfect periodicity in the crystal; i.e., it includes stoichiometric defects as well as chemical impurities.

<sup>2</sup>W. Paul, in <u>Proceedings of the International Confer</u>-<u>ence on Semiconductors, Paris, 1964</u> (Dunod, Paris, 1964), p. 550.

<sup>3</sup>R. J. Sladek, in <u>Proceedings of the International</u> <u>Conference on Semiconductors, Paris, 1964</u> (Dunod, Paris, 1964), p. 545.

<sup>4</sup>B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. <u>129</u>, 2471 (1963).

<sup>5</sup>M. G. Holland and W. Paul, Phys. Rev. <u>128</u>, 30 (1962).

<sup>6</sup>D. G. Thomas, J. Appl. Phys. Suppl. <u>32</u>, 2298S (1961).

<sup>7</sup>W. M. DeMeis and W. Paul, to be published.

<sup>8</sup>M. G. Holland and W. Paul, Phys. Rev. <u>128</u>, 43 (1962).

<sup>9</sup>M. I. Nathan and W. Paul, Phys. Rev. <u>128</u>, 38 (1962). <sup>10</sup>J. Feinleib, S. H. Groves, W. Paul, and R. Zallen, Phys. Rev. 131, 2070 (1963).

<sup>11</sup>W. Paul, J. Appl. Phys., Suppl. <u>32</u>, 2082 (1961). <sup>12</sup>G. A. Peterson, in <u>Proceedings of the International</u> <u>Conference on Semiconductors, Paris, 1964</u> (Dunod,

Paris, 1964), p. 771.

<sup>13</sup>H. Kaplan, J. Phys. Chem. Solids <u>24</u>, 1593 (1963).
<sup>14</sup>R. T. Bate, J. Appl. Phys. <u>33</u>, 26 (1962).

<sup>15</sup>S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters 4, 173 (1960).

<sup>16</sup>M. L. Cohen and T. K. Bergstresser, private communication; and Phys. Rev. (to be published).

<sup>17</sup>M. Cardona and D. L. Greenaway, Phys. Rev. <u>131</u>, 98 (1963).

<sup>18</sup>A. G. Foyt, W. Paul, and A. L. McWhorter, Solid State Device Research Conference, Princeton, New Jersey, June, 1965 (unpublished); A. G. Foyt and A. L. McWhorter, to be published.

## IS A THEORY OF COMBINED POINCARÉ AND INTERNAL INVARIANCE IMPOSSIBLE?

#### Ronald Mirman

Physics Department, Long Island University, The Brooklyn Center, Zeckendorf Campus, Brooklyn, New York (Received 3 December 1965)

There has recently been some discussion of the difficulties of constructing relativistic SU(6) theories.<sup>1-4</sup> From these papers it has been generally concluded that it is necessarily impossible to succeed in such an endeavor. We wish here to challenge the word "necessarily." Of course, until there has been constructed a complete theory of this type, and until the theory has been subjected to exhaustive, and successful, comparison with experiment, one cannot say that such a theory is possible. What we will consider here is whether it can be concluded that it is impossible to find a Lie group of finite order, containing both the Poincaré and SU(3) groups as subgroups, that gives a reasonable mass spectrum. We believe that no reason has, at least yet, been presented to indicate that such a group cannot be found.

The most important difficulty is that posed by O'Raifertaigh,<sup>1</sup> and by Roman and Koh.<sup>2</sup> They show that within the context of Lie algebras of finite order, if the mass operator has a discrete spectrum, then that spectrum must be a single point. Actually the theorem could be extended and continuous spectra can almost certainly be ruled out. The assumption of discrete spectra enters the proof in two ways. The major assumption is the existence of eigen-

<sup>\*</sup>Operated with support from the U.S. Air Force.

<sup>†</sup>Work supported in part by the Aerospace Research Laboratories, Office of Aerospace Research, U. S. Air Force.

<sup>‡</sup>Supported in part by the Office of Naval Research under Contract No. Nonr 1866(10), and by the Advanced Research Projects Agency under Contract No. Sd-88 and by the Division of Engineering and Applied Physics.