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Temperature dependence of the photothermal conductivity of high-purity germanium containing very low concentrations of Al, B, and P

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The temperature dependence of the photothermal conductivity in the far-infrared region (10 to 200 cm^{-1}) is studied in pure germanium containing $\sim 10^{10}$ atoms/cm^3 of Al, B, and P. A theoretical expression for the temperature dependence of the intensities is given which is in excellent agreement with the experimental results. From these very detailed spectra, reliable values for the ground-state energies of the impurities are obtained and a quantitative chemical analysis of the impurity concentration as a function of the position in a Czochralski-grown single crystal is achieved.

I. INTRODUCTION

The photothermal conductivity in the far-infrared region of very pure germanium containing residual impurities of very low concentrations ($\simeq 10^{10}$ atoms/cm^3) has been the subject of several studies in the past.[1-6] A recent review of this subject was given by Kogan and Lifshits.[7] However, surprisingly enough, the temperature dependence of this effect has drawn little attention so far.

It is generally believed that, in order to get a photothermal response, the donors or acceptors are ionized through a two-step process. First, the electrons (or holes) are excited from their ground state to a higher bound state by irradiation with light in the far-infrared region (10–200 cm^{-1}). Then, a subsequent excitation to the free conduction (or valence) band occurs by interaction with thermal phonons. The photoconductivity is measured as a function of the radiation frequency, whereas the sample temperature is held constant, typically between 2 and 10 K. At higher temperatures the photoconductivity signal decreases due to the increase of the carrier density in the free band, while lower temperatures provide too few thermal phonons necessary for the second step of the process. Although the influence of the temperature on the effect is thus qualitativley well understood, the precise temperature dependence has never been studied in a quantitative way. Most authors assume a temperature dependence typically of the form $\exp(-\Delta E/kT)$, where ΔE is the energy difference between the excited level and the conduction (or valence) band edge.[2,3,6,8] However, the agreement with experimental results is rather poor, and estimates for the binding energy of the impurities yield values which are about 3 cm^{-1} too low.[3]

In this paper, we will concentrate upon this aspect. In Sec. II the experimental details will be described, while in Sec. III the results will be presented and analyzed. It will be shown that the measurements are in very good agreement with our calculations of the temperature dependence of the photothermal response. Finally, a qualitative and a quantitative chemical analysis of the samples will be given, based on the photoconductivity data. This analysis will be compared with results based on Hall-effect measurements on the same ingot from which the samples were obtained. Preliminary results of these investigations have been published before.[9]

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

All our germanium samples were cut from the same boule. These ultrapure samples were kindly supplied by Dr. H. J. A. van Dijk of the Philips Research Laboratories, who also performed Hall-effect measurements to determine the residual impurity concentration. The polycrystalline samples, R78*A* and R78*B*, were obtained from both of the ends of the high-purity zone-refined ingot. Then, from the remaining ingot, a single crystal was grown with the Czochralski method. Again from both ends of this crystal two monocrystalline samples J78*A* and J78*B* were cut. Figure 1 shows the variation of the impurity concentration along this single crystal as calculated from Hall-effect measurements, assuming aluminum, boron, and phosphorus as the main impurities and using the known segregation properties of these elements.

The samples used for the photoconductivity measurements were cubes with dimensions of $\sim 1 \times 1 \times 1\ \mathrm{cm}^3$. The cubes were polished and etched, and then electrical contacts were produced by wetting with a mixture of In-Hg (50:50). Although these contacts were not entirely ohmic, we found no evidence that the contacts had any effect on the data.

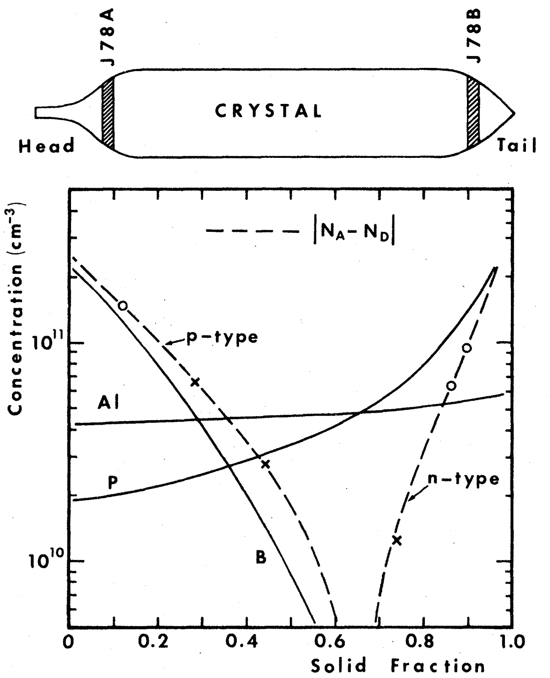

FIG. 1. Distribution of phosphorus, boron, and aluminum impurities along a germanium single crystal, calculated from Hall-effect measurements. (Segregation coefficients used: P: $k_P = 0.1$; B: $k_B = 5.7$; Al: $k_{Al} = 0.9$.) N_A and N_D are the concentrations of the acceptors and donors, respectively.

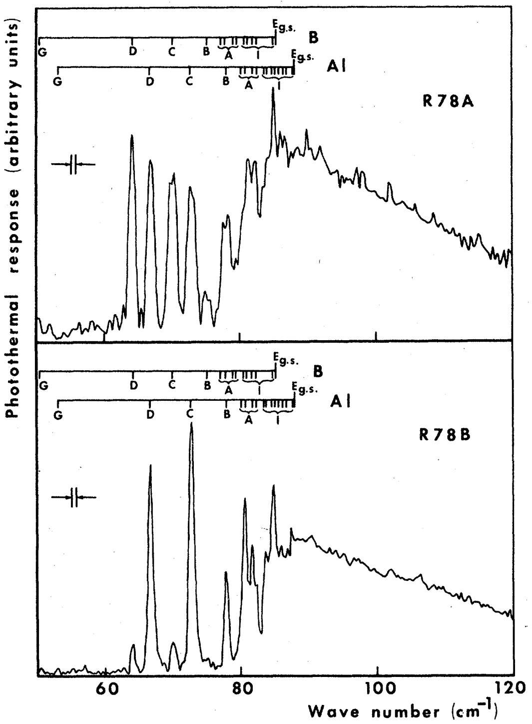

FIG. 2. Photoconductivity spectra of the polycrystalline germanium samples R78*A* and R78*B* containing boron and aluminum impurities. The spectra at the top are from Refs. 4 and 5.

The samples were positioned in a semispherical cavity wherein the chopped far-infrared radiation entered through a conical light pipe. Thermal contact was made by clamping the sample onto the base of the cavity. The clamp and the sample could be heated above the temperature of the surrounding helium bath with an electronically controlled heater system. The temperature of the sample was stabilized within 0.1 K. An Allen-Bradley carbon resistor was used as a thermometer.

Using standard lock-in techniques, the photoconductivity was measured as a function of the wave number of the incident radiation produced by a Grubb-Parson Michelson interferometer operating with phase modulation at 90 Hz. The data were punched on tape, and subsequently handled and analyzed on a PDP-12 laboratory computer linked to a plotter. All spectra were corrected for the varying spectral background of the interferometer by dividing through a spectrum obtained by replacing the Ge sample with a Si bolometer.

III. RESULTS AND DISCUSSION

Figure 2 shows the photothermal response as a function of the wave number of the incident radiation for the polycrystalline samples R78*A* and R78*B* at a temperature of 7.5 K. Indicated are also the expected transitions for boron and aluminum known from the literature.[4,5] From these spectra one can conclude that R78*A* contains B and Al in about equal amounts, while in sample R78*B* the Al concentration exceeds the B concentration as is expected in a zone-refined ingot. Figure 3 shows similar data for the monocrystalline samples; J78*A* contains both B and Al, with B having the highest concentration, while in sample J78*B*, apart from phosphorus, some lithium is present as well.[3,5] In addition, indicated by an asterisk in the figure, in J78*B* some other transitions, with an origin not entirely known, are found; these transitions may be due to a LiO complex.[10] The wave numbers where the transitions are observed agree within 0.2 cm^{-1} with the expected ones from the literature[3-5]; however, due to the limited resolution, the *A* and *I* transitions of aluminum and boron are not fully resolved in these spectra. The continuum in the spectra is caused by direct optical transitions from the ground state into the valence (or conduction) band. In this context, it is interesting to note that with the method of photothermal ionization both donor and acceptor impurities can be seen simultaneously in one sample.

The strength of a spectral line is proportional to the thermal ionization probability of the excited states

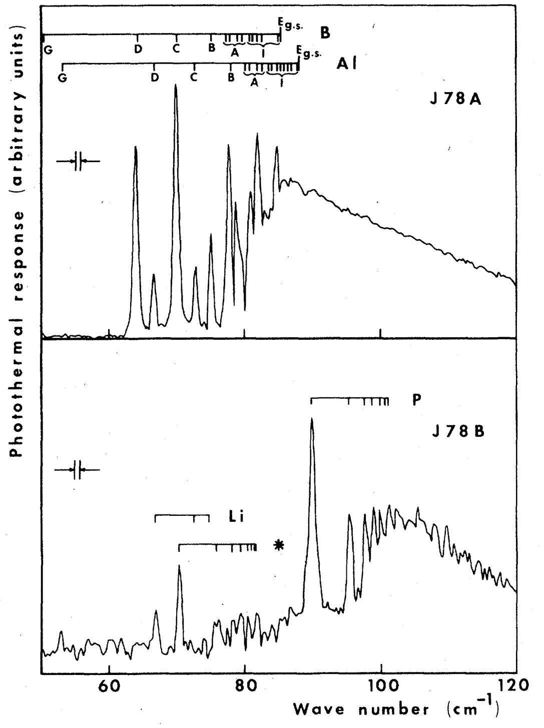

FIG. 3. Photoconductivity spectra at $T = 7.5$ K of the monocrystalline germanium samples J78*A*, containing boron and aluminum, and J78*B*, containing phosporus, lithium, and probably a LiO complex. The spectra at the top are from Refs. 3, 4, 5, and 12.

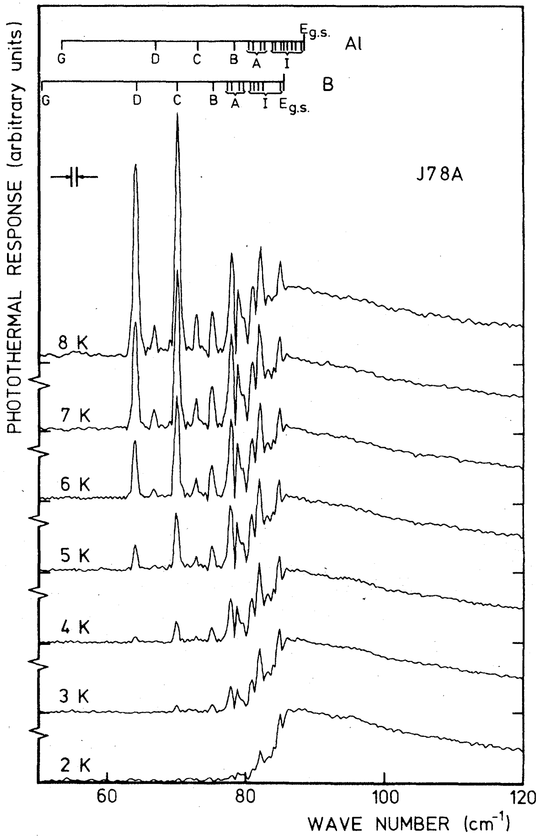

FIG. 4. Photoconductivity spectra at several temperatures of the monocrystalline germanium sample J78*A*. Impurity concentration B: 2.1×10^{11} atoms/cm^3, Al: 4.3×10^{10} atoms/cm^3.

and this can be studied by comparing the line intensities at various temperatures with the height of the continuum.[2] Figure 4 shows the spectrum of sample J78*A*, containing aluminum and boron, at different temperatures. All these spectra are corrected for the spectral background of the interferometer and are normalized to the same continuum height. Similar measurements were also performed on a sample containing phosphorus.

From the voltage drop across the sample, the current through the sample and the measured change in voltage in a typical experiment, it is possible to get a rough estimate of the number of carriers involved. Typical data yield for the number n of the free carriers in the band $n \sim 10^8$ (cm^{-3}) and the change Δn in carriers due to photothermal ionization $\Delta n \sim 10^5$ (cm^{-3}). This means that n and Δn are small compared with the total number of impurity states. Therefore the average number of optical excitations to one of the excited levels may be considered as independent of temperature at very low temperature. Since the excited levels are very localized in $\vec{k}$ space,[11] thermal ionization from this level will at low temperatures only take place to the nearest band extremum. The average number of ionizations in equilibrium is found in the usual way by optimizing the number of possibilities for ionization at constant total energy. Hereby the strong Coulomb interaction of electrons in an excited state has to be taken into account which can be done in a similar way as in considerations regarding donor and acceptor ionization probabilities.[12] In this manner the line intensity I, which is proportional to the average number of ionizations is found to be given by

$$I = A\left[1 + \frac{1}{gg'}\exp\left(\frac{\Delta E}{kT}\right)\right]^{-1} , \tag{1}$$

for both donors and acceptors. Here, ΔE is the energy difference between the intermediate level and the band edge, g is the degeneracy of the excited level, and g' is the degeneracy of the band. The factor A is proportional to the concentration of the impurity and to the optical transition probability for the spectral line under consideration. For donor states, where spin-orbit interaction is small, thermal processes with spin flip may be neglected so that g' is the band degeneracy apart from spin, thus $g' = 1$ for germanium. Although for acceptor states the situation is less obvious, the degeneracy of the valence band in germanium will be taken only as the effective-mass degeneracy at $\vec{k} = 0$, yielding $g' = 2$.

Figure 5 shows the relative line intensities for the phosphorus spectrum, plotted on a logarithmic scale, as a function of the inverse temperature. The solid curves in this figure represent computer fits of Eq. (1) to the experimental data, using ΔE and A as adjustable parameters. The degeneracy factors g were deduced from measured level splittings due to magnetic fields. Here our own observations[9,13] confirmed the splittings found in the literature for the lower levels of the donors[11] and acceptors,[14,15] and extended the results to higher levels. As is shown in Fig. 5, the measured temperature dependence of the line intensities is within experimental accuracy in agreement with Eq. (1). Similar results were obtained for the Al and B spectra of sample J78*A*. Table I collects the numerical results of the computer fits for the parameters A and ΔE. In the fitting procedure also the product gg' was varied by integer values. It was not possible however to obtain a reasonable fit for other values of gg' than those quoted which supports the assumption of the neglect of spin in the band degeneracy made above.

The energy of the ground state E_{gs} of the impurity involved is now simply the sum of ΔE and the energy of the optical transition E_{trans} (as obtained from the measured spectra). In this way it is possible to obtain the ground-state energies of boron, aluminum and phosphorus as presented in Table II. As can be seen from this table, these experimentally found values are in excellent agreement with the theoretically deduced values of Jones and Fisher[16] for B and Al and of Reuszer and Fisher[17] for P.

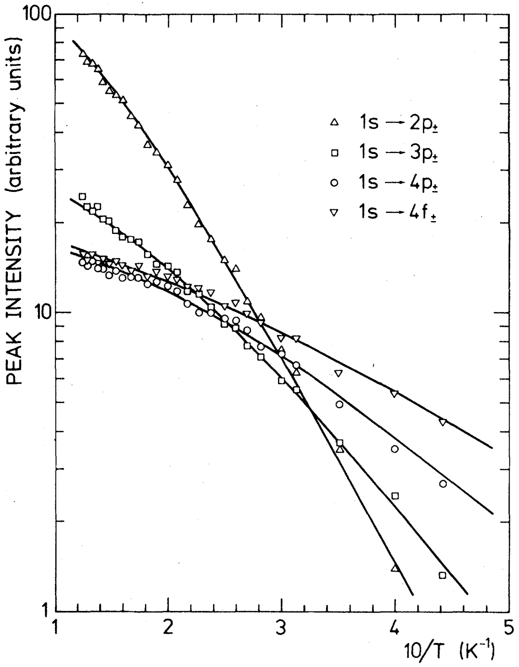

FIG. 5. Logarithmic plot of the relative line intensities vs $10/T$ for several phosporus lines. The solid curves represent computer fits to Eq. (1). (See also Table I.)

As a factor A is proportional to the impurity con-

TABLE I. Values of A and ΔE as obtained from a computer fit from the temperature dependence of various lines in the B, Al, and P spectra [see Eq. (1)].

Transition		$E_{\text{trans}}(\text{cm}^{-1})$	g	A (arb. units)	$\Delta E(\text{cm}^{-1})$
Boron	D	64.0 ±0.2	4	450 ± 15	20.5 ±0.2
	C	70.1	3	265 ± 8	14.4 ±0.2
(J78*A*)	B	75.2	2	44 ± 1	9.3 ±0.2
	A_3	77.9	1	123 ± 3	6.6 ±0.2
	A_2	78.9	1	78 ± 2	5.6 ±0.2
Aluminum	D	66.7 ±0.2	4	70 ± 7	20.5 ±0.6
	C	72.8	3	41 ±3	14.1 ±0.5
(J78*A*)	I_5	85.0	1	36 ± 2	2.3 ±0.5
Phosphorus	$1s \rightarrow 2p\pm$	90.0 ±0.2	4	285 ± 10	12.9 ±0.2
	$1s \rightarrow 3p\pm$	95.5	4	44 ± 3	7.5 ±0.2
	$1s \rightarrow 4p\pm$	97.9	4	26 ± 2	5.3 ±0.3
	$1s \rightarrow 4f\pm$	99.0	2	33 ± 3	4.0 ±0.3

TABLE II. Energies of the ground state of B, Al, and P in germanium, measured in cm^{-1}.

	B	Al	P
E_{gs} (experimental, this work)	84.5 ± 0.2	87.1 ± 0.3	103.0 ± 0.2
E_{gs} (theoretical, Refs. 12 and 13)	84.5 ± 0.2	87.1 ± 0.2	102.9 ± 0.3

centration, it is in principle possible to get some information on the relative impurity content from a determination of A. Assuming the same transition probability for transitions between similar states of different donors or acceptors, the ratio of the A factors for corresponding lines will therefore indicate the ratio of the concentrations of the impurities. For sample J78A one finds for the ratio of the A factors for the C and D transitions of boron and of aluminum a value of 6.4 ± 0.5. This value can be compared with the concentrations obtained from Hall-effect measurements as presented in Fig. 1. From this figure one concludes that for sample J78A the ratio of the concentrations of B and Al is

$$(2.1\times10^{11}\ \mathrm{cm}^{-3})/(4.3\times10^{10}\ \mathrm{cm}^{-3})=5\pm1\ ,$$

which is in good agreement with the value obtained from the photoconductivity measurements.

In conclusion we can remark that we have given a theoretical expression for the temperature dependence of the photoconductive response which is in excellent agreement with our experimental results. The values found from these data for the ground-state energies of various impurities confirm theoretical calculations very well. In addition, we have shown that the concentration ratios of the impurities as obtained from photoconductive measurements are in reasonable agreement with values obtained from Hall-effect measurements.

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