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THE NATURE OF THE $E_v + 0.23$ eV AND $E_v + 0.38$ eV
GAMMA-INDUCED CENTRES IN Ge

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S.J. PEARTON
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ABSTRACT

All p-type Ge grown by the Czochralski technique from silica crucibles under an H_2 atmosphere shows two dominant acceptor defects on γ irradiation. Measurements by DLTS are reported which support the hypothesis that these centres ($E_v + 0.23$ eV, $E_v + 0.38$ eV) are most likely due to complexes between oxygen and lattice vacancies.

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CRYSTAL DEFECTS; GAMMA RADIATION; GERMANIUM; IRRADIATION; OXYGEN; PHYSICAL RADIATION EFFECTS; VACANCIES

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1. INTRODUCTION

During our work on the radiation damage centres in Ge, we have observed that two deep acceptor levels in γ -irradiated p-type Ge are predominant. Using deep level transient spectroscopy, their energy levels were measured as $E_V + 0.23$ eV and $E_V + 0.38$ eV. They occur in all typical high purity crystals for nuclear radiation detection (grown from silica crucibles under an H_2 atmosphere), irrespective of the supplier of the material - AAEC, General Electric or Lawrence Berkeley Laboratory. Their concentrations are always similar (within a factor of 3) and their capture cross sections for holes are also similar: $\sigma_p(E_V + 0.23 \text{ eV}) = 8 \times 10^{-15} \text{ cm}^2$, $\sigma_p(E_V + 0.38 \text{ eV}) = 3 \times 10^{-14} \text{ cm}^2$. Clearly they are fundamental to an understanding of the defect chemistry of γ -irradiated Ge; the components of these defect states must be common to virtually all Ge of this class.

Three elements are common electrically inactive impurities in Ge; oxygen, hydrogen and silicon. Oxygen has long been known to have considerable influence on the defects induced in Ge by γ -radiation [Whan 1965]; the actual defect states involving oxygen, however, have not been identified. The amount of oxygen incorporated in the Ge crystal during its growth depends on both the gas ambient and the crucible material - a typical crystal grown from a silica crucible under an H_2 atmosphere may contain $\sim 6 \times 10^{13}$ oxygen atoms cm^{-3} .* Use of an N_2 atmosphere may increase this to $\sim 10^{14} \text{ cm}^{-3}$, whereas growth from a graphite crucible under H_2 may reduce the oxygen content to $\sim 5 \times 10^{12} \text{ cm}^{-3}$ [Hubbard and Haller 1980]. Apart from oxygen, silicon is the other important electrically inactive impurity found in most Ge; this is more easily controlled and may be detected by spark source mass spectrometry. Typical crystals intended for use as high purity nuclear radiation detectors may contain $10^{14} - 10^{17}$ silicon atoms cm^{-3} .** Crystals grown under H_2 atmosphere also typically contain $\sim 10^{13}$ hydrogen molecules cm^{-3} [Hubbard and Haller 1980].

The other impurities always present in p-type Ge are the electrically active shallow level acceptor impurities, generally B, Al or Ga (and P as a minority impurity). These control the electrical purity of the material, and crystals with net impurity densities of $< 10^{10} \text{ cm}^{-3}$ are available.

The problem, therefore, is this: all p-type Ge grown from silica crucibles

*Determined by Li precipitation method

**Analysis by spark source mass spectrometry, (SSMS) at the AAEC research laboratories

show two deep acceptor levels on γ -irradiation, the levels having similar concentrations and hole capture cross sections. One component of the centres is almost certainly a vacancy induced by the γ -irradiation, as the levels are not observed in unirradiated material. All p-type Ge contains electrically active impurities such as B, Al or Ga. All p-type Ge contains at least some electrically inactive oxygen and silicon. All other impurities may be disregarded because if a wide range of crystals is investigated, results cannot be influenced by stray contaminants. What then are the components of the $E_v + 0.23$ eV and $E_v + 0.38$ eV centres?

2. EXPERIMENTAL

A large number of crystals from various suppliers were used in this investigation (Table 1). The material was obtained from General Electric Company (USA), Lawrence Berkeley Laboratory (USA), Sylvania Electric Incorporated (USA) and Hoboken (Belgium), and other crystals were grown at the AAEC Research Establishment. Samples were prepared in the usual manner with Li diffused n^+ contacts (10 minutes, 350°C) and evaporated Pd ohmic contacts. Several were also prepared with Sb diffused n^+ contacts. The irradiations were performed in a 1.6×10^4 Gy h^{-1} ^{60}Co γ -irradiation facility.

Defect spectra were measured by the deep level transient spectroscopy (DLTS) technique [Lang 1974] in the usual manner. Net doping densities were measured at 77 K and 180 K by C-V measurements (1 MHz).

3. RESULTS

Table 1(a) shows the crystals which displayed the two deep acceptor centres after γ -irradiation. DLTS spectra from a range of the material showing the two levels are shown in Figure 1 (AAEC HP Ge), Figure 2 (General Electric HP p-type Ge) and Figure 3 (LBL HP Ge). In LBL and GE material prepared with Sb diffused contacts, copper contamination occurred during the heating; the Cu did not appear to interact with the radiation damage centres (Figure 4).

Samples selected from these crystals were annealed for various times (1-1000 hours) at either 500°C or 675°C prior to irradiation. These samples were considerably hardened to radiation damage compared with their unannealed companions, even though net doping densities had not significantly changed [Pearton 1981]. Annealing under N_2 or H_2 appeared to make no significant difference, thus hydrogen does not appear to be a component of either of the

acceptor centres, as long-term annealing under N_2 ambients leads to the out-diffusion of hydrogen [Hall and Soltys 1978]. The thermal and electrical stability of these centres has also been investigated [Pearton 1982].

The presence of Li suppresses formation of these levels. Figures 5(a) and (b) show the relative damage caused in a Li drifted sample compared with an undrifted companion. The regions investigated are identical ($\approx 80 \mu\text{m}$ from the Li diffused contact). This suppression of the defects by Li has been observed many times on the 'tail' of Li diffused contacts on p-type γ -irradiated samples.

Silicon concentrations of Ge and LBL crystals were determined by spark source mass spectrometry to be in the range $0.008\text{--}3 \mu\text{g g}^{-1}$. Crystals with the highest silicon concentrations were deliberately doped to obtain high levels of this element. The results from these samples show that silicon cannot be a part of the deep acceptor centres. It should be noted at this stage that four different crucible materials had been used for various crystals investigated - silica, graphite, pyrocarbon coated silica, and alumina. Stray contaminants (except oxygen) leached from the crucible during crystal growth can therefore be fairly safely dismissed as possibilities, particularly as the samples came from crystals grown in three different laboratories; no systematic contamination would be expected in any of these crucibles.

At this point, it was clear that all normal high purity p-type Ge crystals grown for nuclear radiation detection display the two acceptor centres on irradiation. However, samples from three 'special' crystals did not show the levels (Table 1(b)). A sample from a deliberately Al-doped AAEC crystal grown from a graphite crucible showed no evidence of the levels after a dose of 10^7 Gy (Figure 6). This sample had an extremely low oxygen content as determined by the rate of Li precipitation; a normal Li diffused contact (10 minutes 350°C) precipitated completely in less than an hour, as determined by a thermal probe used for measuring the conduction type of Ge crystals. (By comparison, lithium contacts prepared on samples from crystals grown in silica crucibles are stable for periods of several years at room temperature). Consequently, in order to make diodes with stable contacts, these samples were prepared for irradiation by diffusing Sb for one hour at 500°C to form an n^+ contact. Even allowing for possible radiation hardening, the centres should be evident at concentrations of $\sim 1\%$ of the net background doping density, judging from results obtained from other material; instead there is no evidence for them down to the sensitivity of the DLTS technique ($<10^{-4}$). The ultimate sensitivity of our system is believed to be $\sim 10^{-5}$ of the background doping density.

The second class of material not to show these levels was deliberately Zn-doped Ge obtained from Sylvania Electric. These crystals were grown specifically for Li drifting, and therefore had a low oxygen content.

The third class of material not to show the levels was normal grade Li-drifting Ge from Hoboken (Belgium). Sections from one of these crystals, denoted 'R' in Table 1(b), had previously shown normal Li drift rates (and therefore low oxygen content). One of four sections from this crystal not previously drifted did show a very low concentration of the acceptor defects after irradiation ($N_T \sim 3 \times 10^{-4}$) of the background doping density. Figures 7(a) and (b) show DLTS spectra from this and one of its companion sections, which showed no evidence of the levels. For the dose received (1.15×10^6 Gy) the defects should have been present at concentrations of several per cent of the background doping density. Lithium contacts to these samples proved stable for the three days required for irradiation.

4. DISCUSSION

The most significant features of the above results may be examined as follows. First, hydrogen and silicon do not appear to be components of either of the deep level acceptor centres. Secondly, high purity ($N_A - N_D \sim 5 \times 10^{10} \text{ cm}^{-3}$) samples, which were over-irradiated so that the net carrier density at 77 K rose by at least several orders of magnitude ($N_A - N_D \sim 2 \times 10^{12} \text{ cm}^{-3}$) due to the introduction of deep radiation induced acceptors, showed high concentrations of the $E_V + 0.23 \text{ eV}$ and $E_V + 0.38 \text{ eV}$ centres ($\sim 10^{12} \text{ cm}^{-3}$), far in excess of the net impurity concentration at 77 K before irradiation. This means that the shallow level impurities are unlikely to be components of the two acceptor centres, though it must be stressed that the doping densities measured for the samples are net impurity densities ($N_A - N_D$).

This leaves oxygen as the likely component of the γ -induced centres in a complex with vacancies. The three crystals with known low oxygen content showed either no evidence of the deep acceptor levels, or else an abnormally low concentration of them. All silica grown crystals will have significant oxygen content (reaction between Ge, H_2 and SiO_2), as discussed above. The graphite grown AAEC crystal (78-8) should have had low O content, but Li contacts on samples from this crystal remained stable for >18 months at room temperature, indicating that this crystal did in fact have quite a high O concentration. The pyrocarbon coated silica crucibles used for some of the LBL crystals could also enable enough O to be incorporated into the melt during

crystal growth to produce significant concentrations of the acceptor centres on irradiation (the reaction of carbon and silica is a source of oxygen).

Additional evidence that oxygen is involved in the formation of the acceptor centres comes from the hardening of annealed material to the production of these centres; it is known that the form of oxygen in Ge can change during heating and, for example, be incorporated into electrically active shallow donor or acceptor centres [Joos et al. 1980]. Note that the oxygen-vacancy centre at $E_C - 0.18$ eV is the dominant level introduced in electron or γ -irradiated Si crystals pulled in similar fashion to the Ge used here [Kimerling 1977].

Attention is drawn to the observation that the $E_V + 0.23$ eV centre displays sensitivity in some samples to infra-red illumination (Figure 8) which may determine how the two acceptor states are populated. The $E_V + 0.38$ eV level does not show this sensitivity. Shallow level defects containing oxygen are also sensitive to infra-red illumination [Hall 1975].

The reduced concentration of the two acceptors in the presence of Li is most likely due to the capture of oxygen into stable Li-O pairs, as well as a much lesser component caused by direct passivation of the induced levels by the Li, as with some laser induced defects.

It is postulated, therefore, that the $E_V + 0.23$ eV and $E_V + 0.38$ eV acceptor centres in γ -irradiated Ge are vacancy associations with oxygen. The levels may be caused by two charge states of the same defect, but this remains to be verified.

5. CONCLUSION

Two deep acceptor centres are induced by γ -irradiation in all p-type high-purity Ge crystals grown for use as nuclear radiation detectors. An extensive study of these centres in crystals grown under widely varying conditions of dopant, crucible material, gas ambient and post growth annealing leads to the conclusion that they are most likely composed of vacancy associations with oxygen.

6. ACKNOWLEDGMENTS

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TABLE 1(a)
p-TYPE CRYSTALS DISPLAYING TWO ACCEPTOR LEVELS ON
IRRADIATION

Supplier	Crystal No.	$(N_a - N_d) / 77 \text{ K}$	Gas Atmosphere	Crucible Material	Dose $(\text{Gy} \times 10^3)$	$(N_a - N_d) / 180 \text{ K}$	Comment
AAEC	78-33	4×10^{10}	H ₂	silica	100	0.11	
AAEC	80-25	3×10^{10}	H ₂	silica	100	0.11	
AAEC	80-23	3×10^{11}	cylinder H ₂	Al ₂ O ₃	150	0.06	
AAEC	78-8	3×10^{10}	H ₂	graphite	150	0.06	n ⁺ contacts stable for >18 months at R.T.
AAEC	78-8	10^{11}	annealed 75 h 675°C, N ₂		150	4×10^{-7}	Radiation hardened
AAEC	78-8	7×10^{12}	annealed 75 h 675°C, H ₂ then 75 h 675°C, H ₂		300	6×10^{-7}	Radiation hardened
AAEC	78-8	10^{13}	annealed 75 h 675°C, H ₂		300	1.5×10^{-7}	Radiation hardened
AAEC	80-11	10^{13}	H ₂	silica	150	0.17	
AAEC	80-11	10^{14}	annealed 75-1000 h 675°C, N ₂		150	0.06	Radiation hardened
AAEC	78-31	1×10^{10}	H ₂	silica	100	0.18	
AAEC	78-31	1×10^{10}	annealed 20-200 h 500°C, N ₂		100	0.10	Radiation hardened
AAEC	77-71	5×10^{10}	H ₂	silica	100	0.16	
AAEC	77-71	5×10^{10}	annealed 20-200 h 500°C, N ₂		100	0.06	Radiation hardened
AAEC	78-86	10^{14}	H ₂	silica	200	0.02	Ga doped
AAEC	crystallites Z.R. bars	3×10^9 5×10^{11}	H ₂	silica	100	0.10	
GEC	4	3×10^{10}	H ₂	silica	50	0.14	[Si] = 0.08 ppm
GEC	6*	1.3×10^{10}	H ₂	silica	50	0.12	[Si] = 0.006 ppm
GEC	7	1.4×10^{10}	H ₂	silica	50	0.13	
LBL	436-11.7*	1×10^{11}	H ₂	pyrocarbon coated silica	50	0.12	[Si] = 3 ppm
LBL	450-11.8	7×10^{11}	H ₂	pyrocarbon coated silica	50	0.11	[Si] = 0.008 ppm
LBL	469-1.9	4×10^{11}	H ₂	silica	50	0.14	[Si] = 0.008 ppm
LBL	441-2.0*	5×10^{10}	H ₂	silica	50	0.14	[Si] = 2.5 ppm
LBL	438-2.3	5×10^{10}	H ₂	pyrocarbon coated silica	50	0.17	[Si] = 0.025 ppm

TABLE 1(b)
p-TYPE CRYSTALS NOT DISPLAYING TWO ACCEPTOR LEVELS
ON IRRADIATION

Supplier	Crystal No.	$(N_a - N_d) / 77 \text{ K}$	Gas Atmosphere	Crucible Material	Dose $(\text{Gy} \times 10^3)$	$\frac{N_T}{(N_a - N_d)} (0.38 \text{ eV}) / 180 \text{ K}$	Comment
AAEC	79-9	9×10^{14}	H ₂	graphite	1000	$< 10^{-4}$	Li-doped. Li contacts precipitated in less than one hour
Sylvania	409H-1	8×10^{15}		zone levelled	700	$< 10^{-4}$	Zn-doped
Sylvania	413C-1	1×10^{16}		zone levelled	700	$< 10^{-4}$	Zn-doped
Hoboken	R	2×10^{13}		zone levelled	115	$< 10^{-4}$	1 of 4 sections showed levels at $\sim 3 \times 10^{-4}$ background doping
Hoboken	B29	2×10^{13}		zone levelled	115	$< 10^{-4}$	Normal Li-driftable Ge

NR: *AAEC 79-9 had Sb diffused (1 h 500°C) n⁺ contact, all others Li diffused n⁺ contact (10 min 350°C). Samples of GEC and LBL material shown with an asterisk indicate these were radiation hardened when prepared with Sb, rather than Li contacts.

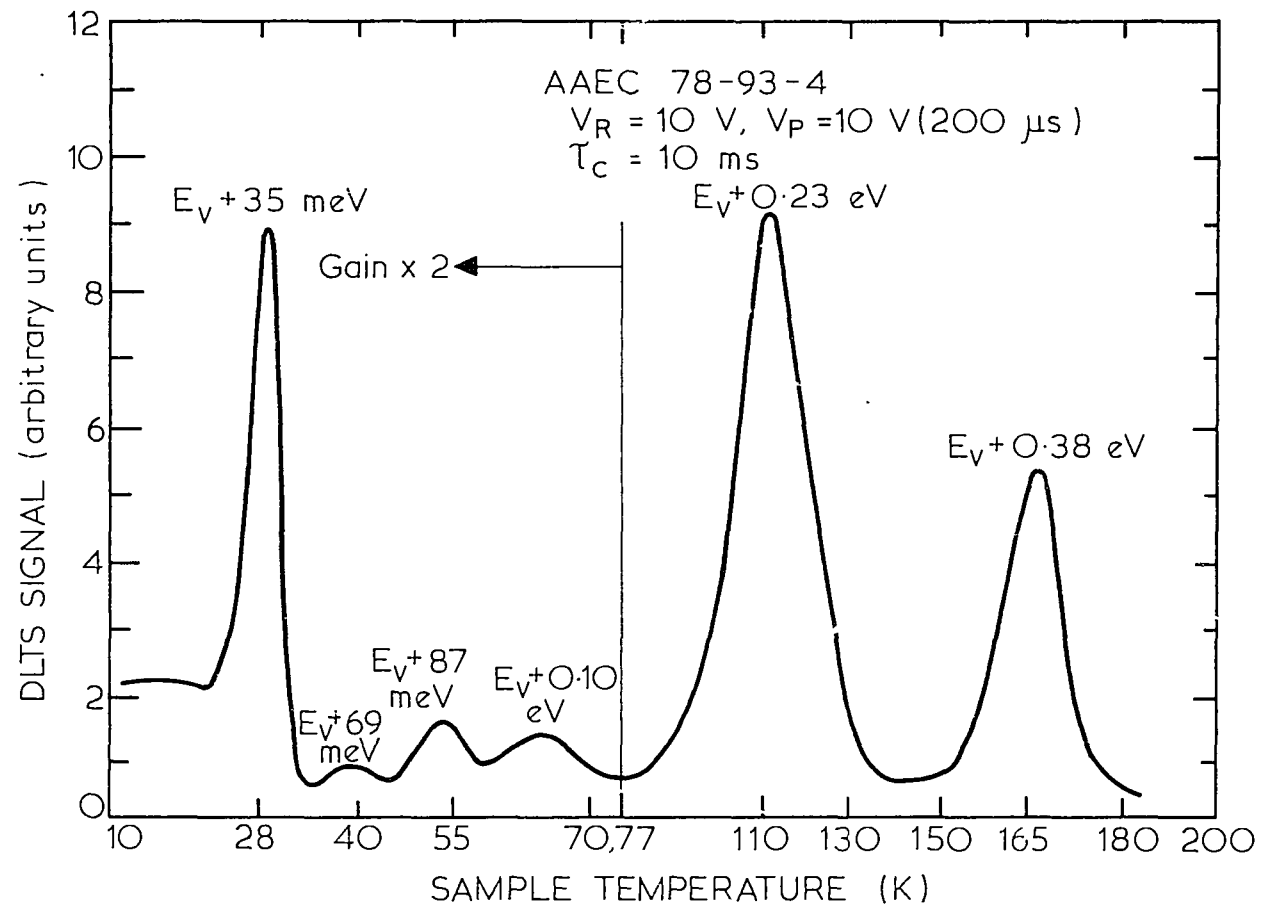


Figure 1 DLTS spectrum from γ -irradiated ($5 \times 10^5 \text{ Gy}$) AAEC HP p-type sample ($N_A - N_D = 4 \times 10^{10} \text{ cm}^{-3}$ prior to irradiation). Sample reverse bias V_R , bias pulse amplitude V_p , correlator time constant τ_C .

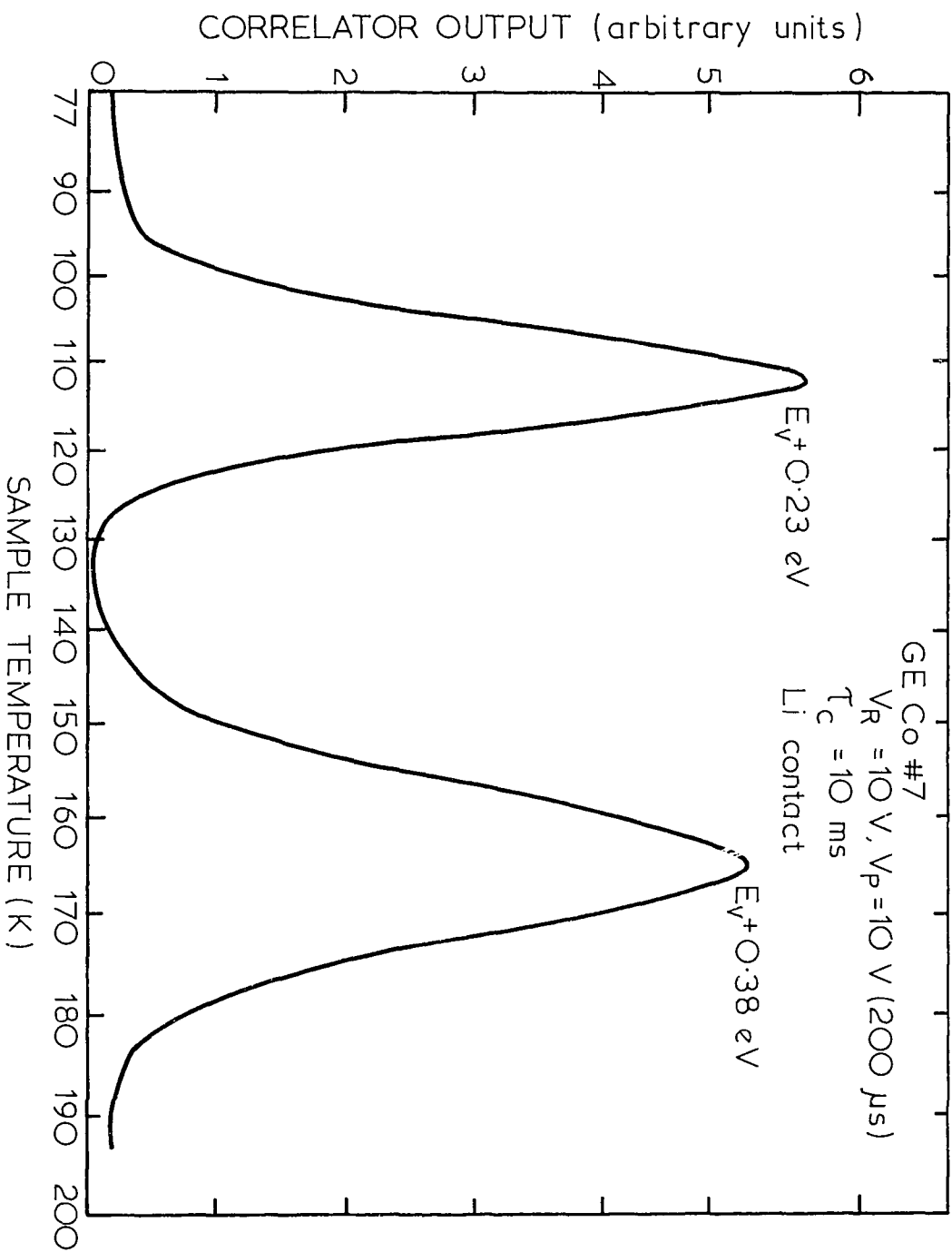


Figure 2 DLTS spectrum from γ -irradiated Ge HP p-type sample ($N_A - N_D = 3 \times 10^{10} \text{ cm}^{-3}$ prior to irradiation).

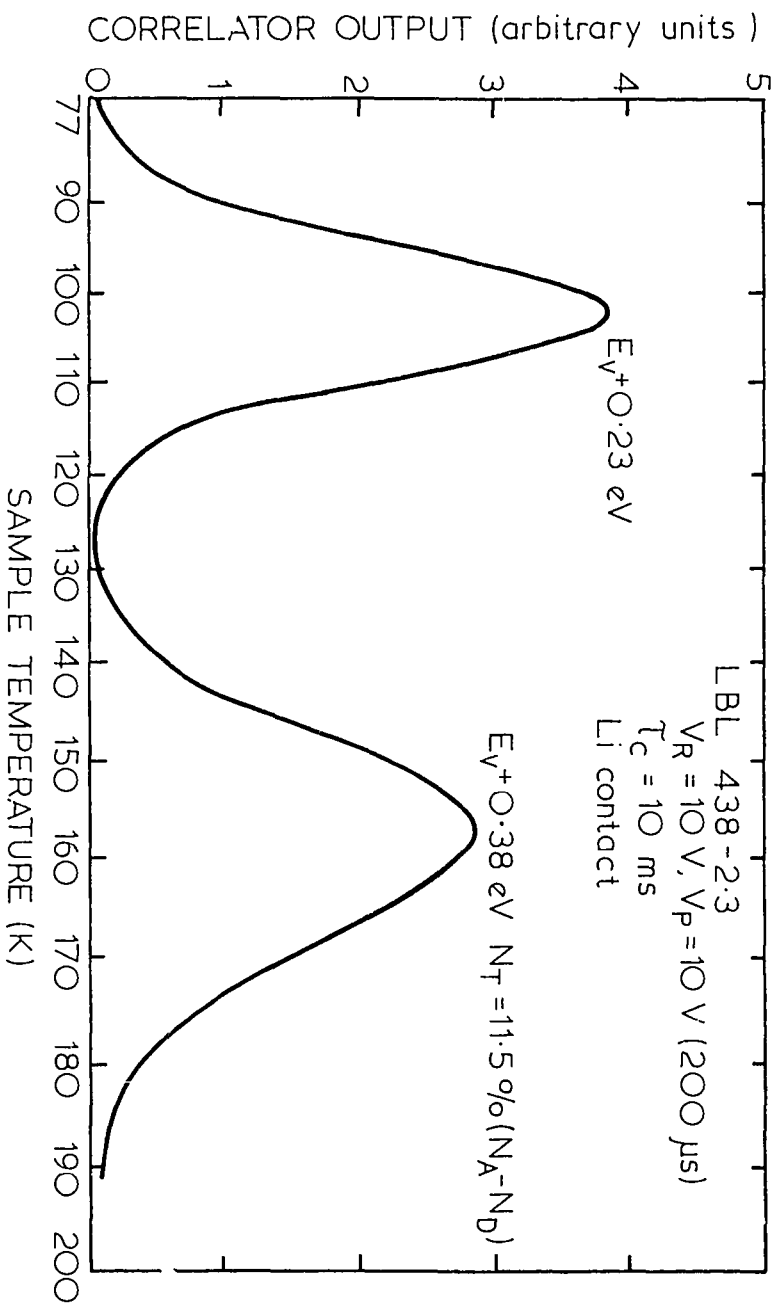


Figure 3 DLTS spectrum from γ -irradiated LBL HP p-type sample ($N_A - N_D = 5 \times 10^{10} \text{ cm}^{-3}$ prior to irradiation). This sample had a Li n^+ contact.

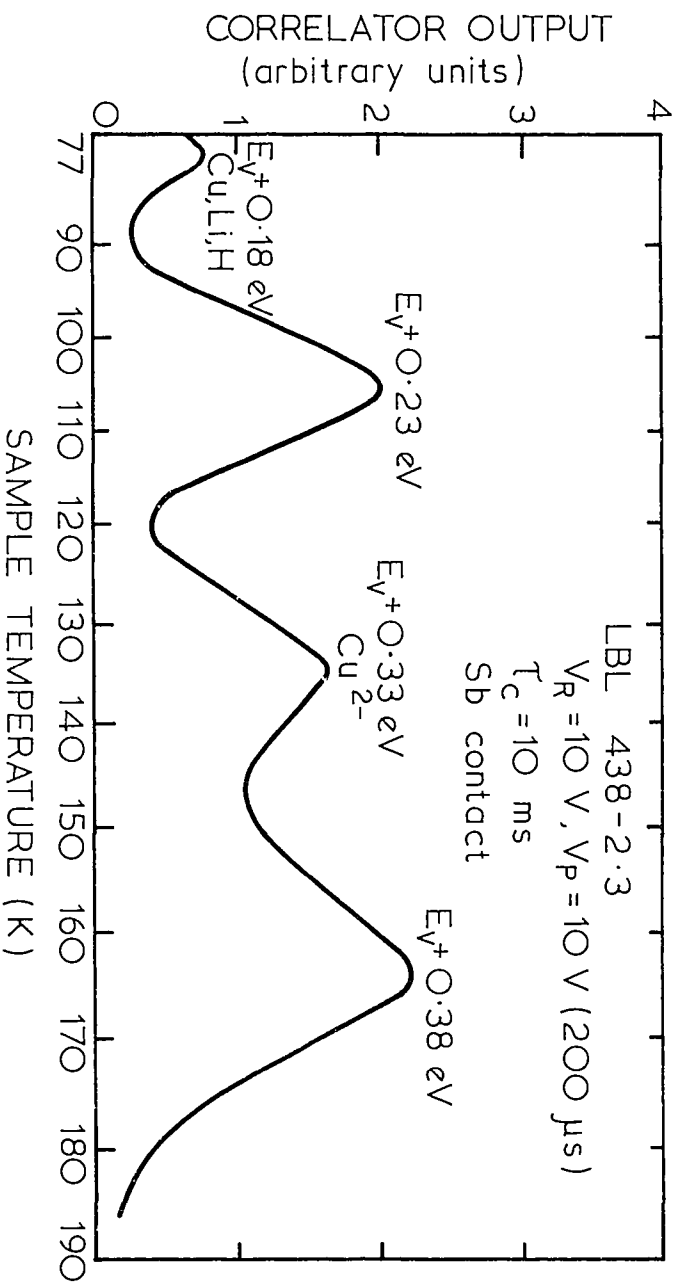


Figure 4 DLTS spectrum from Sb n^+ contacted companion sample to that in Figure 3. Note that Cu contamination occurred during the contact diffusion.

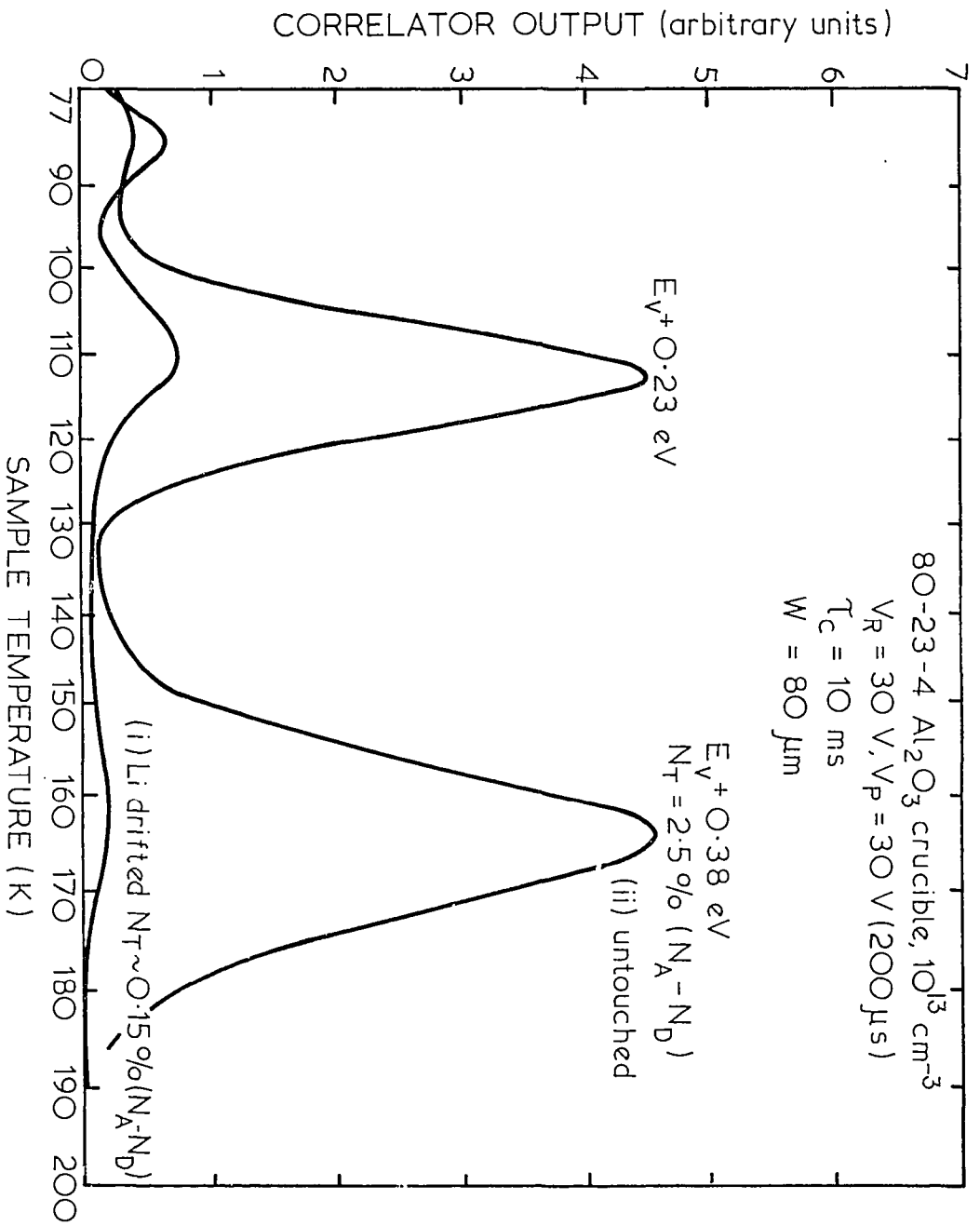


Figure 5 DLTS spectra from γ -irradiated p-type (10^{13} cm^{-3}) sample grown in an alumina crucible (i) Li drifted ($\sim 1 \text{ mm}$) prior to irradiation (ii) untouched. Note the reduced density of the γ -induced defects in the presence of the Li. Spectral conditions have been adjusted to investigate the same depletion depth ($\sim 80 \mu\text{m}$) and give the same relative response.

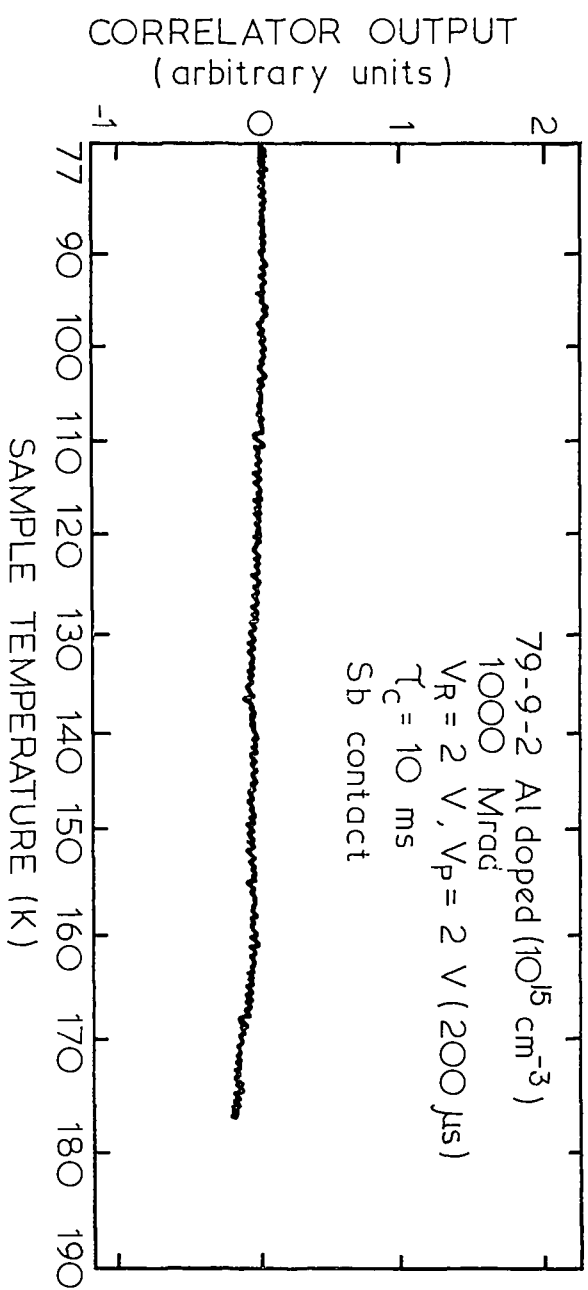


Figure 6 DLTS spectrum from γ -irradiated (10^7 Gy) Al-doped Ge sample ($\sim 10^{15} \text{ cm}^{-3}$). The crystal was grown from a graphite crucible.

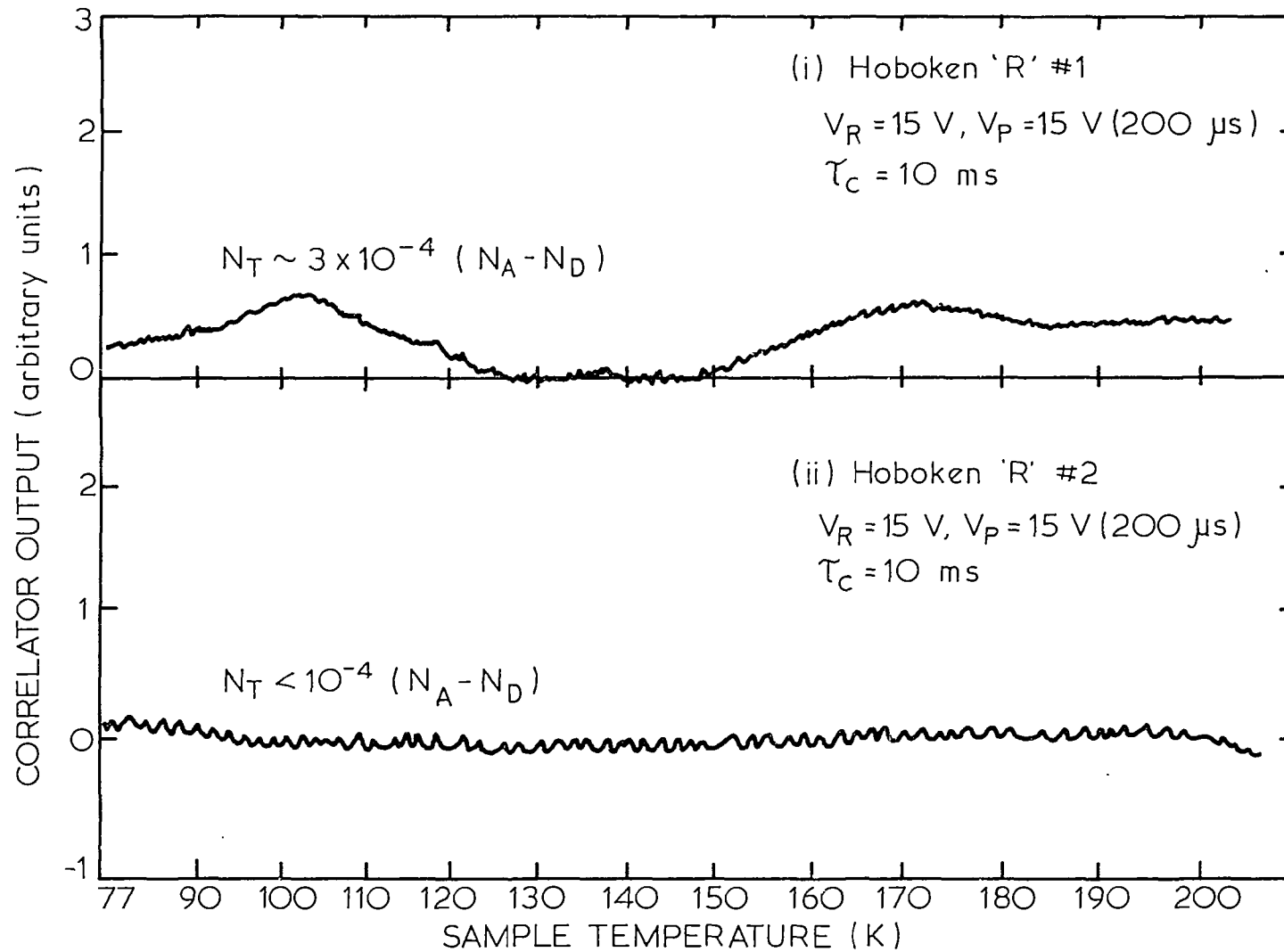


Figure 7 DLTS spectra from γ -irradiated ($1.15 \times 10^6 \text{ Gy}$) Hoboken crystal 'R':
 (i) One section showed a low concentration of the acceptor defects.
 (ii) Typical spectrum from the other three sections - the acceptor centres were not observed.

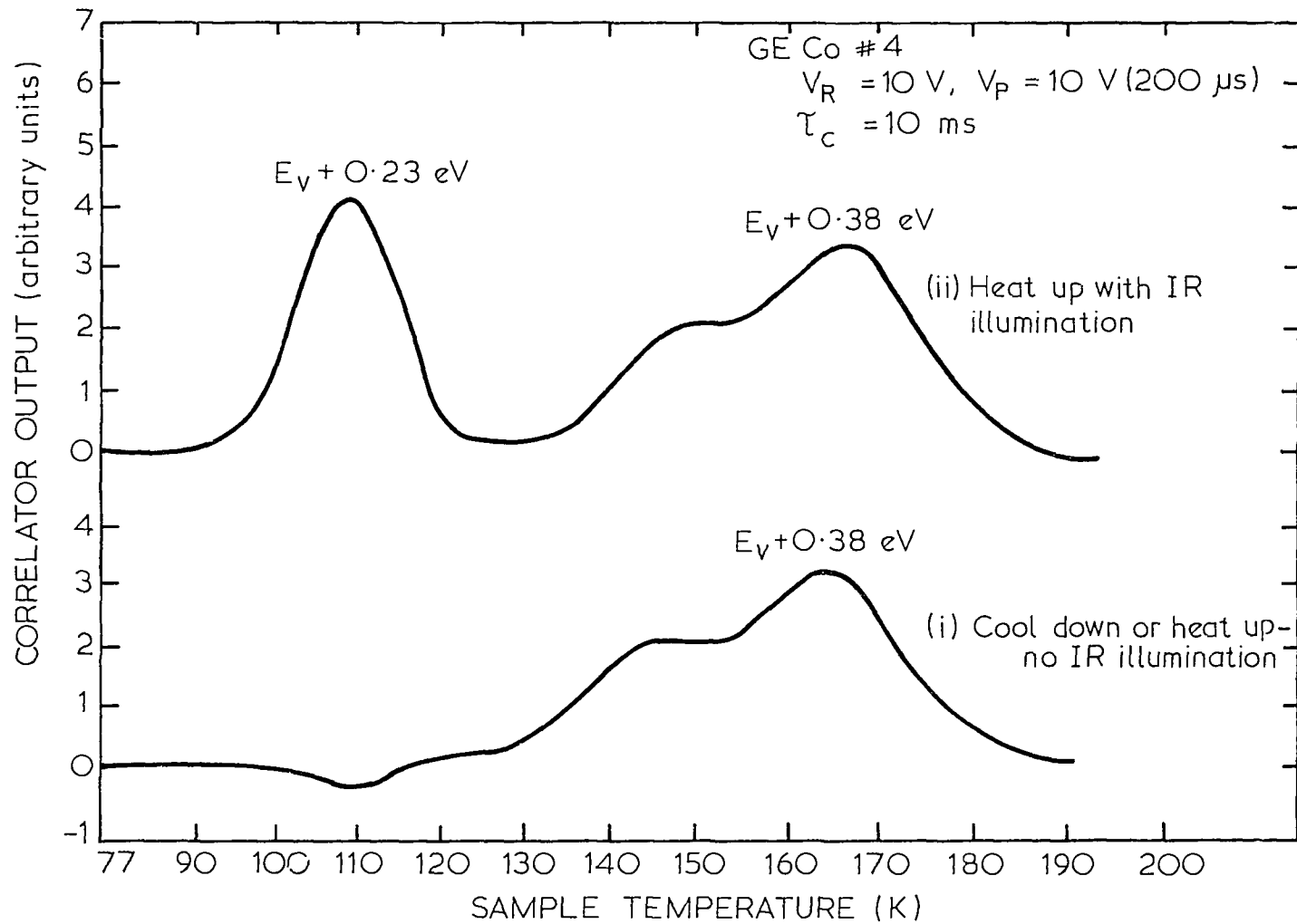


Figure 8 DLTS spectra from γ -irradiated ($5 \times 10^5 \text{ Gy}$) Ge p-type sample showing sensitivity of the $E_V + 0.23 \text{ eV}$ centre to infra-red illumination:
 (i) Sample cooled to 77 K, no infra-red illumination.
 (ii) Sample heated to ambient with infra-red illumination; spectra are recorded with all conditions identical.