

# Re-evaluation of energy levels of oxygen–vacancy complex in n-type silicon crystals: I. Weak compensation

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## Abstract

Experimental temperature dependences of the carrier concentration in n-Si crystals irradiated with  $^{60}\text{Co}$  gamma rays cannot be described adequately with the oxygen–vacancy complex in silicon regarded as a monovalent defect with one acceptor level at  $E_c - 0.17$  eV. This can be done solely within the framework of a two-level model assuming the existence of (i) two independent monovalent defects or (ii) one divalent defect with levels having close energies. Analysis of published evidence suggests that the hypothesis assuming that the A-centre is an amphoteric centre with acceptor  $E_c - (0.15-0.16)$  eV and donor  $E_c - (0.19-0.20)$  eV levels is the most reasonable. Adopting this hypothesis entails a conclusion that there exists a pair correlation between complexes generated upon irradiation of O–V and  $C_i\text{--}O_i$  complexes.

## 1. Introduction

The operation characteristics of silicon radiation detectors are largely determined by the kinetics of recombination processes in the semiconductor bulk. As a rule, such processes are analysed in terms of recombination via isolated monovalent centres (Shockley–Read–Hall recombination statistics), considered in detail in [1, 2]. However, this recombination model is frequently insufficient for describing the nonequilibrium kinetics of recombination in heavily irradiated silicon crystals, and electron transitions between neighbouring centres should also be taken into account [3, 4]. The possibility of such transitions between deep levels has been established recently on the basis of magnetospectroscopic data [5], with inter-centre electron transitions observed for pairs of defects in which one of the components is a vacancy–oxygen (V–O) complex (A-centre).

To substantiate the possibility of electron transitions between two deep centres, an assumption has been made [5] that the V–O complex is amphoteric, i.e., the inter-centre recombination mechanism is operative on the condition that the defect has not only neutral ( $A^0$ ) and negatively ( $A^-$ ) charged states, but also a positive state ( $A^+$ ). A hypothesis was put forward that the  $A^+$ -centre has a donor level in the lower half of the energy gap at  $E_c - 0.76$  eV. To verify this hypothesis,

theoretical calculations have been carried out [6]; however, for the hypothesis to be conclusively confirmed, it is desirable to have some additional experimental evidence in favour of the multicharged nature of the complex in question.

Such evidence can be readily furnished by Hall-effect measurements on lightly doped silicon crystals with shallow-donor and A-centre concentrations  $N_D \leq 10^{14} \text{ cm}^{-3}$  and  $N_A \approx (10^{15} - 10^{16}) \text{ cm}^{-3}$  [7]. However, to make a conclusion that the A-centre has a deep donor level, rather precise data on the entropy ( $\Delta S_A$ ) and enthalpy ( $\Delta H_A$ ) of ionization of the acceptor state of this defect are necessary. It is desirable that the error in determining  $\Delta H_A$  is not higher than 3%.

As shown in [8], Hall-effect measurements can ensure the necessary precision in determining the defect parameters of semiconductors. Therefore, the problem of obtaining  $\Delta S_A$  and  $\Delta H_A$  for such a well-known defect as the vacancy–oxygen complex in silicon seems to be rather simple at first glance. However, the available experimental data concerning the acceptor level of the A-centre,  $E_A(-/0)$ , show much wider scatter than it would be expected on analysing the presumed errors of the Hall-effect technique. For example, the most frequently cited ionization energy  $\Delta E_A = E_c - E_A(-/0) = \Delta H_A - T \Delta S_A$  [9]

$$\Delta E_A = 0.160 + 1.1 \times 10^{-4} T \text{ (eV)}. \quad (1)$$

Later studies [10] gave a close value  $\Delta H_A = 0.170\text{--}0.173$  eV for strongly compensated materials with concentration of the compensating A-centres ( $N_A$ ) exceeding that of donor impurities ( $N_D$ ). However, another approximation of the temperature dependence of  $E_A$  is given in the same paper for weakly compensated samples ( $N_A/N_D < 1$ )

$$\Delta E_A = 0.146 + 2 \times 10^{-4} T \text{ (eV)}. \quad (2)$$

A spread in experimental  $\Delta H_A$  values has also been observed for strongly compensated materials [11]. However, according to [8], Hall-effect measurements with materials of just this kind should have provided the most accurate ionization energy values for this defect, with the error in the case of strong compensation expected to be less than 2%.

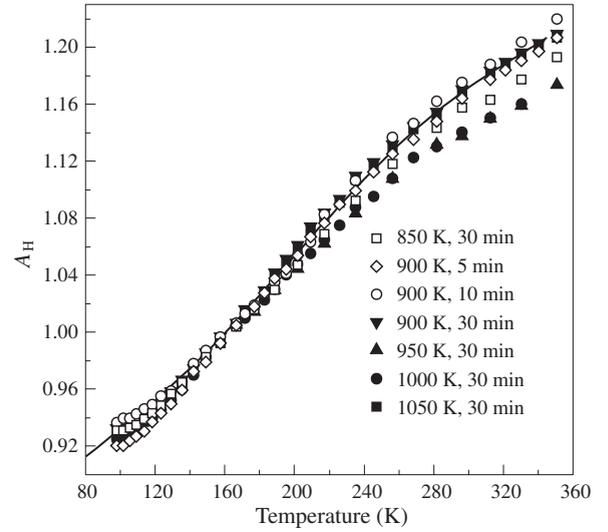
In [12, 13], the enthalpy of ionization of the A-centre was determined using capacitance measurements, with accuracy assumed to be rather high. This can be inferred from the rather great number of significant digits given for this value, e.g.,  $\Delta H_A = 0.169$  eV [12] and  $\Delta H_A = 0.164$  eV [13]. Seemingly, these numerical values could be accepted as more accurate than those furnished by Hall-effect measurements. However, the  $\Delta H_A$  values obtained in other studies by capacitance methods show much wider scatter, also exceeding, in our opinion, the expected value.  $\Delta H_A$  has been reported to be 0.15 eV [14] and 0.19 eV for detector-grade silicon [15]. Moreover, the interpretation of capacitance data is difficult, since the electric field in a p–n junction affects the rate of electron emission from the acceptor level of the A-centre [16, 17]. As a rule, this effect is not taken into account, which makes ambiguous comparison of  $\Delta H_A$  values obtained in studying various barrier structures.

Thus, prior to solving the problem of whether the V–O complex has a donor level in the lower half of the energy gap, it is necessary to obtain unambiguous data on the position of its acceptor level. In addition, the lack of consistent  $\Delta H_A$  data indicates that a single-level model cannot account for the characteristics of this defect. Therefore, the aim of the present study was to verify the validity of the model of a simple isolated point defect, as applied to describing the occupancy function of the acceptor state in the A-centre, and to determine the defect parameters necessary for constructing physically adequate models of recombination in irradiated silicon crystals.

## 2. Experimental details

Czochralski-grown single-crystal n-type silicon with resistivity of 20  $\Omega$  cm and carrier concentration  $n \approx 2 \times 10^{14}$  cm $^{-3}$  was studied. The oxygen and carbon concentrations were determined from IR-absorption spectra with calibration coefficients taken from [18, 19]: [O] =  $0.9 \times 10^{18}$  cm $^{-3}$  and [C] =  $5 \times 10^{16}$  cm $^{-3}$ .

The temperature dependences ( $T_{\text{meas}} = 78\text{--}320$  K) of the Hall coefficient ( $R_H$ ) were measured on a standard setup in a dc magnetic field ( $B = 0.21$  T) on bridge-type samples. The samples were approximately 15 mm long, 2 mm thick and 3 mm wide. They had three pairs of contact arms arranged along their length. The centre-to-centre distance between the arms was 3.5 mm, and the arm width, 0.8 mm. The central arms were used to measure the Hall voltage.



**Figure 1.** Temperature dependences of the Hall factor defined as  $A_H = R(T)/R(T_0)$  ( $T_0 = 160$  K) for silicon samples subjected to heat treatment at various temperatures. The full curve corresponds to the  $A_H(T)$  approximation obtained in [20].

The carrier concentration ( $n$ ) was calculated using the conventional expression

$$n = \frac{A_H(T)}{eR_H} \quad (3)$$

where  $A_H(T)$  is the temperature-dependent Hall factor. The temperature dependence of the Hall factor was determined in the same way as it was done in [9, 10, 20]. It is known that the carrier concentration in doped semiconductors is practically constant over a wide temperature range when the dopant is completely ionized [1, 2]. Therefore, the carrier concentration in the as-grown samples was considered to be temperature independent when the Fermi level ( $F$ ) was lower than  $E_c - 0.10$  eV and the change in the Hall coefficient with increasing temperature was related solely to changes in  $A_H$ . Since the as-grown material commonly contains thermal donors with levels lying close to  $E_c - 0.15$  eV [21], a preliminary heat treatment at  $T > 500$  °C, resulting in their annihilation, is necessary for this method to be adequate. It was expected that the approximation of  $A_H(T)$  for the material under study in the temperature interval 100–300 K would be close to the results of [20], since the  $A_H(T)$  dependence is determined at a relatively low doping level and  $T > 100$  K by the mechanism of scattering on thermal lattice vibrations [22–24] and must be practically independent of the phosphorus impurity concentration. The results obtained by applying the above-described procedure to determine  $A_H(T)$  are presented in figure 1.

Deviations of the  $A_H(T)$  dependence from that reported in [20], observed on some samples, may be due to the fact that it is not always possible to eliminate thermal defects. As follows from the obtained data (see figure 1), the change in the carrier concentration at  $T_{\text{meas}} \leq 280$  K, associated with the ionization of these defects, did not exceed 2% relative to the phosphorus impurity concentration even in the most unfavourable situation (heat treatment at 677–727 °C). Another factor that could distort the  $A_H(T)$  dependences in some samples is the not quite homogeneous distribution of the dopant throughout the ingot.

If this is the case, then, as is clear from the presented data, the inhomogeneity is rather weak and the resulting effect is negligible. The inhomogeneity can also be avoided by sample preselection.

To introduce A-centres, the samples were irradiated with  $^{60}\text{Co}$  gamma rays. A dose was chosen in accordance with the weak-compensation condition, so that the concentration of A-centres was less than that of the donor impurity ( $N_A/N_D < 1$ ).

The defect parameters were determined using the least-squares method, with the minimum of the following function found

$$Q(\mathbf{X}) = \sum_i \left( \frac{n_{\text{fit}}(T_i, \mathbf{X}) - n_{\text{exp}}(T_i)}{n_{\text{fit}}(T_i, \mathbf{X})} \right) \quad (4)$$

where  $\mathbf{X}$  is the vector whose components are defect parameters, including the entropy and enthalpy of ionization of various charge states of the defect, and, optionally, degrees of degeneracy and energies of excited states. The concentration  $n_{\text{exp}}(T_i)$  is an experimental concentration at temperature  $T_i$ , and  $n_{\text{fit}}(T_i)$  is the value calculated using the appropriate neutrality equation by setting  $T = T_i$  and the defect parameters to be  $\mathbf{X}$ . The details of the employed least-squares procedure were briefly described in [25].

A semiquantitative analysis of Hall-effect data can be conveniently made using the differential approach proposed in [26]. In this method, the dependence of the quantity

$$D_H^U = kT \frac{dn}{dF} \quad (5a)$$

on the Fermi energy  $F$  is studied. The maximum value  $D_H^U$  is proportional to the defect concentration; therefore, in comparing data obtained for crystals with different defect concentrations, it is preferable to use, instead of  $D_H^U$ , a normalized quantity

$$D_H = \frac{4D_H^U}{N_A} \quad (5b)$$

whose maximum value is practically unity for a monovalent defect with  $\Delta S_A = 0$  [26].

A numerical approximation for  $D_H^U$  was chosen in the present study as

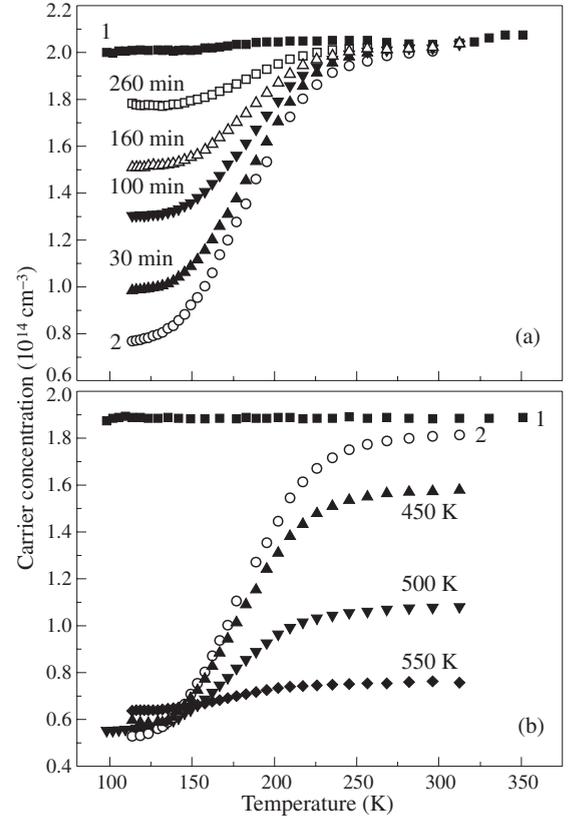
$$D_H^U \approx \Delta_H^U \equiv \frac{kT_i}{2} \left( \frac{\Delta n_i}{\Delta F_i} + \frac{\Delta n_{i+1}}{\Delta F_{i+1}} \right) \quad (6)$$

where  $\Delta n_i = n_{\text{exp}}(T_i) - n_{\text{exp}}(T_{i-1})$ ,  $\Delta F_i = F_{\text{exp}}(T_i) - F_{\text{exp}}(T_{i-1})$ ; and  $n_{\text{exp}}(T_i)$  and  $F_{\text{exp}}(T_i)$  are the experimental concentration and Fermi energy, determined at  $T = T_i$ . Such an approximation allows partial smoothing of  $\Delta_H$  fluctuations resulting from random experimental errors.

### 3. Experimental results

#### 3.1. Effect of residual thermal donors on the temperature dependence of carrier concentration

Experimental temperature dependences of the carrier concentration in Si crystals irradiated with  $^{60}\text{Co}$  gamma rays and annealed at various temperatures are shown in figure 2. Regions of slightly increasing (150–200 K) and decreasing



**Figure 2.** Temperature dependences of the carrier concentration in (a) as-grown Si crystals and (b) those subjected to preliminary heat treatment at 1050 K for 30 min after irradiation with  $^{60}\text{Co}$  gamma rays and at various stages of annealing. The dependences obtained before (■) and after (○) irradiation are also presented. The upper figure shows data obtained immediately after irradiation and upon subsequent isothermal annealing at 600 K for different times of annealing; the lower figure presents data obtained after isochronous annealing for 30 minutes at different temperatures.

(220–270 K) carrier concentration are observed for the as-grown crystals (figure 2(a), curve 1). Such a behaviour is due to the existence of bistable double thermal donors (TD) formed upon cooling of the silicon ingot after growth. Since one of the TD levels lies at  $E_c - 0.15$  eV [21], the presence of TDs can distort results of analysis of the curves for irradiated samples. The TDs were eliminated by preliminary heat treatment at temperatures above 500 °C. Measuring the temperature dependence of the carrier concentration after the heat treatment (figure 2(b), curve 1) allows determination of the TD concentration. Comparison of the first curves in figures 2(a) and (b) shows that practically all the TDs present in the as-grown crystals are bistable thermal donors of the first type (BTD-1). The characteristics of these centres were reported in [27].

The concentration of BTD-1 in the as-grown crystals is 5–7% of the donor impurity concentration. Since the equilibrium Fermi level lies at  $T \approx 300$  K somewhat above the BTD-1 occupancy level  $E(0/+ +) = E_c - 0.32$  eV, the TD concentration in the configuration with shallow levels does not exceed 1–2% of  $N_D$ . To reach the equilibrium occupation, BTD-1 needs a time of about 1 h after placing a sample in a light-tight measuring cell. This time corresponds to the time

of relaxation of the persistent photoconductivity induced by external illumination. Such measuring procedure provides the conditions when most of TDs in a crystal are in a configuration with deep levels and their effect on the  $n(T)$  behaviour is insignificant.

The lifetime of nonequilibrium carriers decreases by several orders of magnitude in irradiated crystals. Therefore, the intensity of illumination by scattered light is not enough to give rise to BTD-1 rearrangement into a configuration with shallow levels. The residual photoconductivity is small and  $n(T)$  measurements can be done immediately after placing a sample in the measuring cell.

To completely eliminate the effect of TDs on the results of Hall-effect data analysis, a preliminary heat treatment is necessary, removing the TDs. In order to prevent repeated introduction of TD after the heat treatment, samples should be cooled sufficiently fast. However, such cooling conditions were found to affect the behaviour of radiation-induced defects in silicon crystals.

### 3.2. Does the position of the A-centre level change in heat treated crystals?

As is clear from figure 2 (curves 2), irradiation gives rise to a radiation-induced defect that is ionized when the Fermi level lies close to  $E_c - 0.18$  eV. Henceforth this defect is referred to as  $E(0.18)$ . According to the results of capacitance measurements [12, 28, 29], this defect, known as the A-centre, is predominant in Czochralski-grown silicon crystals irradiated with  $^{60}\text{Co}$  gamma rays, with the concentrations of other centres, having levels located in the upper half of the energy gap, negligibly small.

As mentioned above, to correctly evaluate the position of the A-centre levels, it is necessary to use samples subjected to a short (3–30 min) preliminary heat treatment at  $T > 800$  K. Even though such a treatment makes the concentration of thermal donors lower, other thermal defects may be formed. Their presence in our crystals manifests itself in changes in the temperature and mechanism of  $E'(0.18)$  annealing, well seen from the  $n(T)$  curves shown in figure 2. While the temperature of  $E(0.18)$  annealing in the as-grown samples is  $T_{\text{ann}} \approx 300\text{--}350^\circ\text{C}$ , in pre-annealed crystals it decreases to  $150\text{--}250^\circ\text{C}$ . Raising the temperature of preliminary heat treatment results in lower annealing temperature of A-centres [30]. In addition, the annealing of  $E(0.18)$  in crystals subjected to preliminary heat treatment leads to a decrease in the carrier concentration at 300 K, which is not observed in the initial material (figure 2(a)). Annealing experiments will be considered in detail elsewhere.

It is important to elucidate how these thermal defects affect the parameters of the A-centres. As shown by DLTS studies [31], the experimentally determined level of the A-centre may change upon preliminary heat treatment at  $T > 600^\circ\text{C}$ . Therefore, before studying the applicability of one or another model to the description of the occupancy function of this level, it is necessary to make sure that this function is independent of the presence of other defects in the crystal.

For this purpose, let us consider in more detail the problem of the preliminary analysis of the occupancy function  $f(T, F, \mathbf{X})$ , which determines the number of electrons bound

to any centre. In the case of not very low temperatures, for a monovalent defect that can bind a single electron the vector  $\mathbf{X} = X_1$  has only two components: the enthalpy  $\Delta H_1$  and entropy  $\Delta S_1$  of ionization [12, 32, 33]. The entropy of ionization is given by

$$\Delta S_1 = \Delta S_1^v + \Delta S_1^c = \Delta S_1 + k \ln \frac{g_e}{g_f} \quad (7)$$

where  $\Delta S_1^v$  is the ‘vibrational’ ionization entropy, and  $\Delta S_1^c = k \ln (g_e/g_f)$  is the ‘configurational’ ionization entropy related to the quantum-mechanical degeneracy of an empty (degree of degeneracy  $g_e$ ) and occupied (degree of degeneracy  $g_f$ ) energy level of the defect. The corresponding occupancy level ( $E(1/0)$ ) is determined by the ionization potential of the defect,  $\Delta E_1 = \Delta H_1 - T \Delta S_1$ , as  $E(1/0) = E_c - \Delta E_1$ .

With increasing number of electrons that can be bound to the defect, the dimensionality of the vector  $\mathbf{X}$  becomes higher. For a divalent defect, which can bind two electrons, the vector  $\mathbf{X} = X_2$  must have at least four components  $\mathbf{X}_2 = \{\Delta H_1, \Delta S_1, \Delta H_2, \Delta S_2\}$ .

In  $n(T)$  measurements, we have two variables,  $F$  and  $T$ . The temperature dependence of the Fermi energy can be calculated from the neutrality equation. For the case when the occupation of only one of the defects changes during experiment, this equation can be written as

$$N_{\text{net}} = n + N_A f_A(F, T, \mathbf{X}) \quad (8)$$

where  $N_{\text{net}}$  is the total electron concentration at  $T = 0$  K at the level of the defect in question, having concentration  $N_A$ , and at higher local levels;  $f_A(F, T, \mathbf{X})$  is the occupancy function of the defect.

$N_{\text{net}}$  is found as the concentration of carriers on the high-temperature plateau in the  $n(T)$  dependence for irradiated samples (figure 2). When the degree of compensation is small,  $N_A < N_{\text{net}}$  and electrons are frozen out into free states of the defect with decreasing temperature. The electron concentration then becomes

$$N_{\text{low}} = n(f_A \rightarrow 1) = N_{\text{net}} - N_A. \quad (9)$$

which is the carrier concentration on the low-temperature plateau in the  $n(T)$  dependence for irradiated samples (figure 2). Having thus obtained  $N_{\text{low}}$  from the low-temperature regions of the temperature dependences of carrier concentration, we can readily calculate by means of equation (8) the numerical value of the occupancy function  $f_A(F, T, \mathbf{X})$  at any point of the measured  $n(T)$  curve.

If several dependences  $n(T)$  are obtained for different samples, then, using the above-mentioned procedure, we can determine the  $f_{ij}$  value for each experimental curve only at certain points ( $T_i, F_j$ ). Then, if it were always possible to calculate the occupancy function at points characterized by identical pairs of coordinates on the  $(T, F)$  plane, a defect could be identified on the basis of these  $f_{ij}$  values without taking any explicit expression for  $f_A(F, T, \mathbf{X})$ . Since measurements are commonly carried out under varied conditions (different concentrations of doping and compensating impurities, different defect concentrations), either  $T$  or  $F$  values will always differ from one another during measurements. Therefore, the occupancies obtained at the

same position of the Fermi levels but at different temperatures, will naturally differ. In this case, the defect is identified as follows. First, we specify an explicit occupancy function (or select a model of the electronic structure of the defect) and then find the vector  $\mathbf{X}$  in some way.

If the defect model is unknown, we can use simplified methods of analysis. The simplest method of defect identification on the basis of Hall-effect data can be applied if  $N_{\text{net}}$  and  $N_A$  can be found. This method consists in determining the defect level from the position of the Fermi level ( $F_{1/2}$ ) at a point where the occupancy function  $f_A(F, T, \mathbf{X})$  is 1/2. For irradiated samples,  $N_{\text{net}}$  and  $N_A$  can be readily determined from experimental curves with an error of no more than  $\pm 0.01 \times 10^{14} \text{ cm}^{-3}$  (see figure 2), which ensures that  $F_{1/2}$  is determined with high accuracy. In all the crystals studied here,  $F_{1/2} = E_c - (0.183 \pm 0.001) \text{ eV}$  for the A-centre. This value is very close to  $F_{1/2} = E_c - 0.185 \text{ eV}$  [20] obtained for lower-resistivity crystals in which the centre is ionized at higher temperatures. Thus, this test allows a preliminary conclusion that the parameters of the A-centre remain unchanged during various treatments of the crystals under study.

If finding  $N_{\text{net}}$ ,  $N_{\text{low}}$ , and hence  $N_A$  is difficult, the above-mentioned differential technique can be used for estimating the position of the defect level. Furthermore, applying this differential procedure imparts ‘spectroscopic appearance’ to Hall-effect data. According to [26], the position of the defect level can be estimated as that of the Fermi level ( $F_{\text{max}}$ ) at the point where  $D_H^U$  reaches its maximum. However, if it is possible to determine  $N_A$  from  $n(T)$ , the differential procedure can also be applied to analyse the occupation function of the defect without specifying its analytical model.

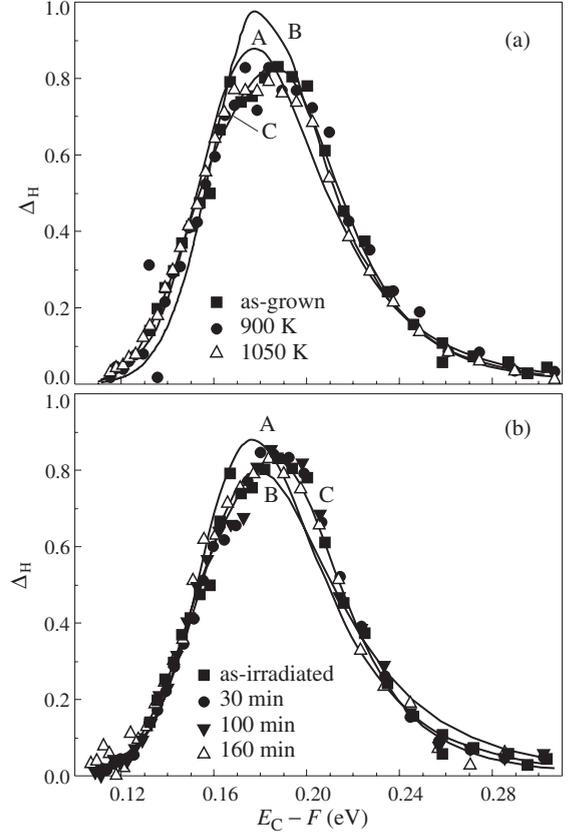
In this case, one needs to use  $D_H$ . As shown by numerical modelling [7] for the case of weak compensation and  $N_{\text{net}}$  varying by no more than a factor of two, the run of the  $D_H(F)$  curves does not change noticeably when the defect concentration is varied widely. This fact allows, already in preliminary stages of a study, a detailed comparison of the values of the  $E(0.18)$  occupancy function, obtained on samples with different concentrations of this centre and varied thermal prehistory.

Figure 3(a) shows  $D_H(F)$  dependences for crystals subjected to different kinds of preliminary heat treatment. It can be seen that the curves not only have a maximum at the same position, but also practically coincide with each other in a rather wide range of Fermi energies. Such an agreement shows that in both the initial and the preliminary annealed crystals, the behaviour and parameters of the occupancy function of the A-centre are practically unchanged immediately after irradiation and in the course of annealing. This confirms our preliminary conclusion made on the basis of the equality of  $F_{1/2}$  for different curves in figure 2. Furthermore, as is clear from figure 3(b), the occupancy function of the A-centre is also unchanged during annealing at  $T > 300^\circ\text{C}$ .

### 3.3. Model of monovalent defect

The relationship between the concentrations of a defect in the  $i$ th and  $(i - 1)$ th charge states is known [2] to be determined by the Gibbs factor [2]

$$\frac{N^i}{N^{i-1}} = \varphi_{\text{Gi}}(F, T) \quad (10)$$



**Figure 3.** Dependences of  $\Delta H$  on the distance between the conduction band bottom ( $E_c$ ) and the Fermi level ( $F$ ). Dots correspond to experimental data and lines are calculated curves. The upper figure (a) presents data obtained immediately after irradiation for as-grown (■) crystals and those subjected to preliminary heat treatment at 900 K (●) and 1050 K (△); the calculated curves were obtained in the framework of the single-level model for  $\Delta H_A = 0.160 \text{ eV}$  and  $\Delta S_A = -1.1 \times 10^{-4} \text{ eV K}^{-1}$  (curve A),  $\Delta H_A = 0.183 \text{ eV}$  and  $\Delta S_A = 0 \text{ eV K}^{-1}$  (curve B), as well as for the divalent defect model with parameters obtained for crystals heat treated at 900 K:  $\Delta S_1 = -0.6 \text{ eV K}^{-1}$ ,  $\Delta H_1 = 0.187 \text{ eV}$ ,  $\Delta S_2 = -1.05 \text{ eV K}^{-1}$ ,  $\Delta H_2 = 0.150 \text{ eV}$  (curve C). The lower figure (b) presents experimental data obtained for the as-grown crystal immediately after irradiation (■) and after the subsequent isothermal annealing at 600 K for different annealing times; calculated curves A and C are the same, as in the upper figure and curve B is plotted according to the single-level model with  $\Delta H_A = 0.146 \text{ eV}$  and  $\Delta S_A = -2 \times 10^{-4} \text{ eV K}^{-1}$  [10].

$$\begin{aligned} \varphi_{\text{Gi}}(F, T) &= \exp\left(\frac{F - E_i}{kT}\right) \\ &= \exp\left(-\frac{E_c - F}{kT}\right) \exp\left(\frac{\Delta E_i}{kT}\right) = \frac{n}{N_{ci}} \end{aligned} \quad (11)$$

where  $E_i$  is the  $i$ th occupancy level of the defect.  $N_{ci}$  is the effective density of states in the conduction band, reduced to the level  $E_i$  and usually defined by

$$N_{ci} = N_c \exp\left(-\frac{\Delta E_i}{kT}\right) = N_c \exp\left(-\frac{\Delta H_i - T \Delta S_i}{kT}\right). \quad (12)$$

By a monovalent defect is meant an isolated point defect that can bind only a single electron. Such a defect has only

one occupancy level in the energy gap, and the single-level model will be considered applicable to this case. For the monovalent defect,  $i = 1$ , and, designating the concentrations of its occupied and empty states as  $N^1$  and  $N^0$ , we have

$$N^1 + N^0 = N \quad (13)$$

where  $N$  is the defect concentration. Then it follows from expressions (10)–(13) that the electron occupancy of the defect level  $E_1$  is determined by the quasi-Fermi function

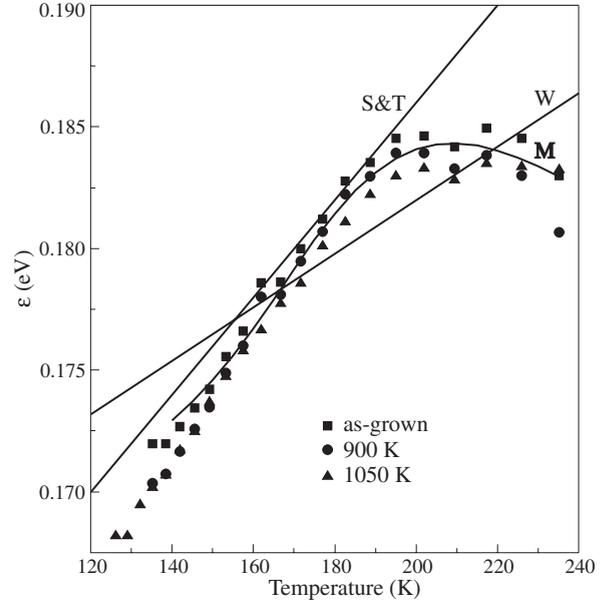
$$f_1 = \frac{\varphi_{G1}(F, T)}{1 + \varphi_{G1}(F, T)} = \frac{n}{n + N_{c1}} \quad (14)$$

For the A-centre,  $\Delta E_A = \Delta H_A - T \Delta S_A$  can be found from (10)–(12) by calculating  $N_A^- = N_{\text{net}} - n$  and  $N_A^0 = n - (N_{\text{net}} - N_A)$  using the neutrality equation (8). After appropriate transformations, we obtain the well-known expression  $\Delta E_A = \varepsilon(T)$  [1, 2], where

$$\varepsilon(T) \equiv kT \ln \frac{N_c}{n} \frac{N_{\text{net}} - n}{n - (N_{\text{net}} - N_A)} \quad (15)$$

If we try to describe the experimental dependences  $D_H(F)$  on the assumption that the A-centre has only one occupancy level in the energy gap, the following behaviour is revealed. For example, the curve calculated using (8) and (14) under the assumption that  $\Delta H_A = 0.183$  eV and  $\Delta S_A = 0$  demonstrates especially pronounced disagreement with experimental data at the maximum of the  $D_H(F)$  dependence. A somewhat better agreement between the calculated and experimental dependences is observed with increasing  $\Delta S_A$  and decreasing  $\Delta H_A$ , in accordance with the approximations (1) and (2) (figure 3). At the same time, it is impossible to state that any of the calculated curves shown in this figure describes the experimental data satisfactorily over the whole range of Fermi energies. Therefore, the validity of the single-level model for describing our experimental curves  $n(T)$  is to be analysed. However, the  $D_H(F)$  dependences are not very suitable for such an analysis. First, it is known that differentiation makes wider the scatter in experimental data. Second, the explicit expression for  $D_H(F)$  [7] is much more complicated than the initial neutrality equation (8) with the quasi-Fermi occupancy function (14). Therefore, detailed quantitative analysis of  $D_H(F)$  is inexpedient. We believe that direct analysis of  $\varepsilon(T)$  is more appropriate.

The experimental dependences  $\varepsilon(T)$  calculated using (15) are presented in figure 4. The same figure shows straight lines plotted according to equations (1) and (2). It can be seen that the S&T approximation is rather good for the low-temperature region of the experimental dependence  $\varepsilon(T)$ . The second line (W) is a linear approximation to this dependence over the entire temperature range studied. However, as is clear from figure 4, the dependence  $\varepsilon(T)$  is nonlinear. This nonlinearity is observed for all of the samples studied. It cannot be due to systematic errors in calculating the concentration by expression (3), since the  $A_H(T)$  dependence deviates from the approximation obtained on the basis of the data for non-irradiated samples. Theoretical estimations [22–24] show that the deviations of  $A_H$  from the employed approximation cannot exceed 1–2% over the whole temperature range 100–300 K. The fact that the temperature dependence of the carrier



**Figure 4.** Temperature dependences of  $\varepsilon(T)$ , plotted for the same crystals as in figure 3(a) (with the same designations). Also shown are the dependences  $\Delta E_A(T)$  plotted according to data reported in [9]:  $\Delta H_A = 0.160$  eV,  $\Delta S_A = -1.1 \times 10^{-4}$  eV K $^{-1}$  (line W) and in [10]:  $\Delta H_A = 0.146$  eV,  $\Delta S_A = -2.0 \times 10^{-4}$  eV K $^{-1}$  (line S&T) and the curve  $\varepsilon(T)$  calculated in terms of the divalent centre model (curve M) with the same parameters as in the previous figure.

mobility does not change significantly allows us to exclude from consideration the nonuniform distribution of impurities that could appear if the degree of compensation changed during irradiation and annealing.

Therefore, we can conclude that the single-level model can be applied to the description of the occupancy function of the A-centre only when the ionization energy of the centre,  $\Delta E_A(T)$ , depends on temperature essentially nonlinearly. Such a dependence is possible, in principle, if the entropy of ionization is temperature dependent, e.g., if the defect has excited states [1, 2, 32, 33]. Then the degrees of degeneracy  $g^-$  and  $g^0$  in expression (7) will vary with temperature as

$$g^{(i)} = g^{(i)} \left( 1 + \sum_{j=1}^N \delta_j \exp -\frac{\varepsilon_j}{kT} \right) \quad (16)$$

where  $i$  is the number of the charge state, and  $\delta_j$  is a factor taking into account the degeneracy of the  $j$ th excited state lying  $\varepsilon_j$  higher than the ground state.

However, to reveal a nonlinearity of this kind, it is necessary to carry out measurements either at  $T \rightarrow 0$  K or in a very wide temperature range. In the case in question ( $T_{\text{meas}} = 100$ – $300$  K), departures of  $\Delta E_A(T)$  from linearity, associated with a temperature-related change in  $\Delta S_A$ , are not observable experimentally.

Another indication that the single-level model is inapplicable is that  $\Delta H_A \approx 0.145$  eV, obtained using low-temperature approximation to  $\varepsilon(T)$ , disagrees with the higher values  $\Delta H_A \approx (0.17$ – $0.18)$  eV found from Hall-effect data for strongly compensated materials [10].

Thus, we can conclude that the single-level model fails to consistently account for the whole body of experimental Hall-effect data related to the electronic structure of the A-centre.

### 3.4. Analysis of the single-level model by the least-squares method

Thus, a more complex model is needed. Unfortunately, analysis of such models fails to provide explicit expressions, like equation (15), that could be used to determine the ionization energy of the defect. In this case, presumably the most effective technique for quantitative analysis of experimental data is the least-squares method. Further, we deal with a nonlinear objective function  $Q(\mathbf{X})$ , which requires a detailed analysis of the search algorithm employed to find the minimum of the objective function and the problem of error propagation and effect of systematic errors. A detailed quantitative analysis of these two problems requires a separate study that will be reported elsewhere.

Here, we use simple semiquantitative estimations of the efficiency of the least-squares procedure. As usually, the quantitative measure in least-squares analysis is the deviation of the experimental concentration  $n_{\text{exp}}(T_i)$  from the calculated value  $n_{\text{fit}}(T_i)$ . Let us define the relative uncertainty of measurements by  $\delta_i \equiv n_{\text{exp}}(T_i)/n_{\text{fit}}(T_i) - 1$ . To estimate the validity of the model used to analyse  $n(T)$ , we follow two criterions. First, the number of negative and positive  $\delta_i$  values is to be approximately the same and their distribution is to be random. Second, the root-mean-square error should not exceed essentially the estimated error of experiment.

The evaluation of the A-centre parameters can be affected by various factors. These may include instrumental errors associated with measuring the electric current through the sample, Hall voltage, magnetic field and sample thickness—Hall effect data used to determine the carrier concentration, and also errors related to simplification of the theoretical model. Changes in the Hall-factor, caused by variation of the ionized centre concentration in the course of sample irradiation may serve as an example. For further consideration, it is convenient to classify experimental errors into several groups, which need not be the same in different stages of error analysis made in determining the A-centre parameters.

First, let us consider a single temperature scan. In this case, all the errors can be classified into three groups: (i) random errors  $\delta_{\text{random}}$ , (ii) temperature-independent systematic errors  $\delta_{\text{bias}}$  and (iii) temperature-dependent systematic errors  $\delta_{\text{bias}}(T)$ . Then, the experimental carrier concentration at the  $i$ th experimental point can be expressed as

$$n_{\text{exp}}(T_i) = [1 + \delta_{\text{random}}(i) + \delta_{\text{bias}} + \delta_{\text{bias}}(T_i)] n(T_i) \quad (17)$$

where  $n(T_i)$  is the carrier concentration at temperature  $T_i$ , determined under certain idealized conditions, i.e. in the absence of any interfering factors.

Random errors are caused by fluctuations in measured currents, voltages and temperatures. Our set-up employed a current-stabilization circuit, so that the current was constant within 0.3% during the measurements. The voltage was measured with a voltmeter with standard deviation  $\delta_{HV} = 0.5\%$ . The operation mode of the instruments did not change significantly in measuring a single  $n(T)$  dependence ( $T = 78\text{--}300$  K). Therefore, the relative random error in determining the current and voltage in a single measurement cycle was, as a rule, less than above-mentioned values. The temperature fluctuations did not exceed  $\pm 0.2$  K.

Systematic errors of the first type may arise from (i) inaccuracy of Hall coefficient measurements, related to geometric characteristics of the sample, (ii) inaccuracy of magnetic field measurements and measuring device calibration. Systematic errors of the second type may result from (i) inaccuracy in calibration of the thermometric device, (ii) deviations of the  $A_H(T)$  dependence from the expected one and (iii) presence of background defects with levels in the range  $E_c - (0.10\text{--}0.20)$ . The error of temperature measurements did not exceed 0.7 K. The  $A_H$  deviations caused by a change in the ionized impurity concentration must be the greatest at low temperatures. The estimations made on the basis of Baranskii's data [24] indicate that for the crystals studied the change in  $A_H$  at  $T = 77.4$  K does not exceed 1% at the maximum fluence. As shown by the experiment, even though it is impossible to entirely eliminate various background defects, their concentration can be easily made less than 2% of the dopant concentration.

With the use of several samples subjected to different preliminary heat treatments, some systematic errors can be readily made random. In particular, this is the case for errors caused by the presence of background thermal defects. If a batch of samples is used instead of a single sample, then the random component in the error of defect parameter determination becomes greater, and the systematic component, smaller than the respective values for a single scan. Such a randomization of systematic errors makes it possible to improve the accuracy of determining the enthalpy and entropy of A-centre ionization.

Deviations of the experimental dependence  $n_{\text{exp}}(T)$  from a fitted curve  $n_{\text{fit}}(T)$  may be due only to a random error and a systematic error of the second kind. A systematic error of the first kind (temperature-independent) leads solely to a parallel shift of the curve  $n(T)$ , thus changing the defect concentration and the ionization entropy. At the same time, the occurrence of  $\delta_{\text{bias}}(T)$  changes the shape of the  $n(T)$  curve. We performed numerical experiments to estimate the effect of  $\delta_{\text{bias}}(T)$ . In these experiments, we started with calculation of the  $n(T)$  dependences in the framework of the single-level model. Then,  $\delta_{\text{bias}}(T)$  errors were set and  $n_{\text{exp}}(T)$  was calculated using expression (17). Then, the inverse problem was solved: defect parameters were estimated and used to calculate  $n_{\text{fit}}(T)$ . It was found that, e.g., a shift of the temperature calibration at the minimal measurement temperature ( $T_{\text{min}} = 100$  K) by  $\delta T_{\text{max}} = 1$  K results in simultaneous changes in the ionization entropy by less than 0.1 eV/K and in the ionization enthalpy by less than 0.002 eV. In this case, the deviation of  $n_{\text{fit}}(T)$  from  $n_{\text{exp}}(T)$  does not exceed 0.1%. Similar experiments were carried out to estimate the effect of background impurities and possible deviations of  $A_h(T)$  dependences from those used in this study. It was found that, for the expected  $\delta_{\text{bias}}(T)$  values, the maximum relative deviation does not exceed 0.15%.

Thus, we may conclude that the random error  $\delta_i$  determined from experimental curves must be less than 0.5%. This conclusion is confirmed by data for non-irradiated samples (figure 1), when the temperature dependences  $R_H(T)$  are approximated by a polynomial. The plot of the random error associated with such an approximation is presented in figure 5(a) (curve 1). For irradiated crystals, an increase in  $\delta_i$  would be expected because of the growing contribution from

**Table 1.** A-centre parameters estimated in terms of different models for samples subjected to preliminary heat treatment at different temperatures.

Samples	Preliminary heat treatment	Model of monovalent defect		Model of two independent defects				Model of divalent defect			
		$\Delta S_1/k$	$\Delta H_1$ (eV)	$\Delta S_\alpha/k$	$\Delta H_\alpha$ (eV)	$\Delta S_\beta/k$	$\Delta H_\beta$ (eV)	$\Delta S_1/k$	$\Delta H_1$ (eV)	$\Delta S_2/k$	$\Delta H_2$ (eV)
ED-5	none	-2.545	0.142	-0.306	0.148	0.355	0.202	-0.654	0.186	-1.000	0.151
ED-6	none	-2.382	0.146	-1.391	0.150	0.810	0.211	-0.453	0.191	-0.916	0.154
ED-7	none	-2.016	0.152	0.583	0.174	1.418	0.222	0.787	0.215	-0.114	0.166
EB-4	3 min at 800 K	-2.219	0.149	0.197	0.161	0.394	0.198	0.124	0.199	-1.158	0.151
EB-3 †	30 min at 800 K	-2.121	0.151	-1.213	0.149	1.112	0.214	0.110	0.200	-1.461	0.148
EA-3	30 min at 850 K	-2.860	0.135	-0.677	0.151	0.993	0.210	0.417	0.204	-0.869	0.149
EB-2	2 min at 900 K	-2.251	0.146	0.070	0.163	0.929	0.210	0.465	0.206	-0.175	0.161
EB-8	5 min at 900 K	-2.558	0.142	0.318	0.166	0.606	0.206	0.431	0.207	-0.066	0.163
EB-9	30 min at 900 K	-2.334	0.147	0.262	0.165	1.203	0.215	1.245	0.221	-0.450	0.160
EA-5 ‡	30 min at 950 K	-2.585	0.143	-2.313	0.137	0.113	0.196	-1.417	0.174	-2.006	0.140
EA-9 ‡	30 min at 1000 K	-2.666	0.142	-0.906	0.148	-0.496	0.184	-1.042	0.180	-1.639	0.143
EA-10	30 min at 1050 K	-2.377	0.146	-1.102	0.154	0.608	0.208	-0.458	0.192	-0.586	0.158

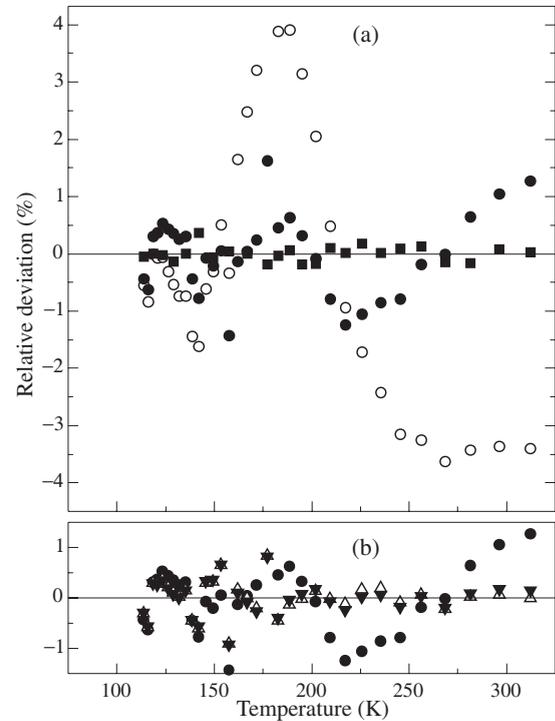
† According to [34], at  $T > 500^\circ\text{C}$  the content of thermal donors first decreases (as in sample EB-3) and then may increase. This was observed in sample EB-4 as an increase in the concentration of ( $E_c - 0.14$  eV) defects to  $1.4 \times 10^{13} \text{ cm}^{-3}$ . The A-centre parameters listed in the table were obtained using an estimator that takes into account the presence of such defects.

‡ As follows from figure 1, the greatest systematic error in A-centre parameters is possible for these two temperatures of preliminary heat treatment. Therefore, these data were disregarded in calculating the mean values.

$\delta_{\text{bias}}(T)$  and the increasing rate of Hall voltage decrease with temperature in measuring  $R_H(T)$  dependences.

Fitting to the experimental  $n(T)$  dependences was done with  $n_{\text{fit}}(T_i)$  calculated according to equations (8) and (14), under the conventional assumption that the ionization energy of the defect linearly depends on temperature  $\Delta E_A = \Delta H_A - T \Delta S_A$ . In the first place, it was of interest to verify the applicability of the Wertheim approximation to our experimental dependence  $n(T)$ . Therefore, at the start, solely minimization with respect to  $N_{\text{net}}$  and  $N_A$  was carried out,  $\Delta H_A$  and  $\Delta S_A$  being fixed and set in accordance with expression (1). As is clear from the plot (figure 5(a), curve 2),  $\delta_i$  values exceed the expected errors considerably and the dependence  $\delta(T)$  is not a random function. This confirms our conclusion that equation (1) cannot be used to describe experimental  $n(T)$  dependences.

If, however, we carry out minimization with respect to all four parameters ( $N_{\text{net}}$ ,  $N_A$ ,  $\Delta H_A$ ,  $\Delta S_A$ ), the function  $Q(\mathbf{X})$  has a minimum at the point  $\mathbf{X}_1^*$  with coordinates  $\Delta H_A^* = 0.146$  eV and  $\Delta S_A^* = -2.4k$  (where the ionization entropy is measured in Boltzmann constant units  $k = 8.62 \times 10^{-5} \text{ eV K}^{-1}$ ). The  $\Delta H_A$  and  $\Delta S_A$  values estimated for different samples are presented in table 1. The estimated values are close to those reported in [10] (see equation (2)), obtained for a sample with low degree of compensation. However, even in this case, the relative errors  $\delta_i$  are rather large and the temperature dependence (figure 5(a), curve 3) is not a random function, which is one more evidence of the inapplicability of the single-level model to describe the occupation function of the A-centre. So, to obtain an adequate description of  $f_A(T, F)$ , we have to assume that there are two levels lying close to  $E_c - 0.17$  eV and, therefore, a greater number of parameters are to be used to describe the experimental data. This can be done in two ways.



**Figure 5.** Comparison of relative carrier concentration deviations  $\delta_i = [n_{\text{exp}}(T_i) - n_{\text{fit}}(T_i)]/n_{\text{exp}}(T_i)$  calculated using (a) the single-level and (b) two-level models. The upper figure (a) shows errors (■) for experimental data (see figure 2(b), ■) with  $A_H(T)$  approximated by a polynomial and errors (○) for data (see figure 2(b), ○) with the use of a single-level model with fixed parameters  $\Delta S_A$  and  $\Delta H_A$  taken from equation (1); (●) the same as in the preceding case, but with all the parameters of the model ( $N_{\text{net}}$ ,  $N_A$ ,  $\Delta S_A$  and  $\Delta H_A$ ) determined by a least-squares procedure. The lower figure (b) shows the same as in the upper figure (●), errors (Δ) (see figure 2(b), ○) for the model of two independent defects and the same as in the preceding case but with the use of the model of a divalent defect (▼).

### 3.5. Model of two independent defects with closely lying levels

The first way to improve the fitting is to assume that there are two, rather than one, monovalent radiation-induced defects within the energy interval in question (near  $E_c - 0.18$  eV). In this case, the neutrality equation becomes:

$$N_{\text{net}} = n + N_{\alpha} f_{\alpha}(F, T; E_{\alpha}) + N_{\beta} f_{\beta}(F, T, E_{\beta}) \quad (18)$$

where  $f_i(F, T, E_i)$  is the occupancy function for  $i$ th defect with level  $E_i$  ( $i = \alpha, \beta$ ), defined by (14). Now seven, instead of four, parameters are used in fitting to experimental  $n(T)$  dependences:  $N_{\text{net}}$ ,  $N_{\alpha}$ ,  $\Delta S_{\alpha}$ ,  $\Delta H_{\alpha}$ ,  $N_{\beta}$ ,  $\Delta S_{\beta}$  and  $\Delta H_{\beta}$ . At the same time, the new objective function appears to have two maxima instead of one. One of these is located at a point  $X_2$ , such that  $\Delta H_{\alpha} = \Delta H_{\alpha}^* = 0.145$  eV and  $\Delta S_{\alpha} = \Delta S_{\alpha}^* = -2.3$  eV K<sup>-1</sup>, with the parameters  $\Delta S_{\beta}$  and  $\Delta H_{\beta}$  having no physical meaning [25]. Therefore, this is a subordinate minimum.

The mean coordinates of the second minimum are:  $\Delta S_{\alpha} = -0.3k$  (standard deviation  $s_{S_{\alpha}} = 0.7k$ ),  $\Delta H_{\alpha} = 0.158$  eV ( $s_{H_{\alpha}} = 0.009$  eV),  $\Delta S_{\beta} = +0.8k$  ( $s_{S_{\beta}} = 0.4k$ ) and  $\Delta H_{\beta} = 0.210$  eV ( $s_{H_{\beta}} = 0.007$  eV). The concentration ratio of these two defects was estimated to be  $N_{\alpha}/N_{\beta} = 0.5 \pm 0.15$ . The quality of fitting can be judged from figure 5(b). It can be seen that the relative errors and their distribution make it possible to adopt the proposed model of the distribution function.

### 3.6. Model of a single divalent defect

One more model, also characterized by a rather large number of parameters, is that of a divalent defect with two closely lying levels. For such a defect, the neutrality equation reads

$$N_{\text{net}} = n + N_A f(F, T, E_{A1}, E_{A2}) \quad (19)$$

where  $f(F, T, E_{A1}, E_{A2})$  is the average number of electrons located on both levels of the defect with concentration  $N_A$ . The function

$$f(F, T, E_{A1}, E_{A2}) = \frac{n^2 + 2nN_{cA2}}{n^2 + nN_{cA2} + N_{cA1}N_{cA2}} \quad (20)$$

can be readily obtained from the condition

$$N^2 + N^1 + N^0 = N \quad (21)$$

and equation (10).  $N_{cA1}$  and  $N_{cA2}$  are determined according to (13), where  $i$  takes the values  $A_1$  or  $A_2$ . The level  $E(2/1) = E_c - E_{A2}$  corresponds to a transition of the defect from the state with two bound electrons to that with a single electron, and the level  $E(1/0) = E_c - E_{A1}$ , to a transition to a state without bound electrons.

This model has one less parameter, compared with the preceding case; nevertheless, the fitting may frequently be even better (as a rule, the minimum value of the function  $Q(\mathbf{X})$  is 10–20% less than that achieved in the preceding case). The above experimental  $n(T)$  dependences gave the following mean values for the A-centre parameters:  $\Delta S_{A2} = -0.7k$  (standard deviation  $s_{S_{A2}} = 0.5k$ ),  $\Delta H_{A2} = 0.156$  eV ( $s_{H_{A2}} = 0.006$  eV),  $\Delta S_{A1} = +0.2k$  ( $s_{S_{A1}} = 0.6k$ ), and  $\Delta S_{A1} = 0.202$  eV ( $s_{H_{A1}} = 0.011$  eV). The correlation energy

( $U$ ) is positive ( $U = \Delta H_{A1} - \Delta H_{A2} > 0$ ). As seen in figure 4, the dependence  $\varepsilon(T)$  calculated using expressions (19) and (20) is also in close agreement with the experimental data.

Thus, on the basis of the fitting quality criterion, we can conclude that both the two-level models are acceptable for describing Hall-effect data. To estimate the validity of each of these models, it is necessary to consider their agreement with data concerning the A-centre, obtained using different experimental techniques.

## 4. Discussion

### 4.1. Model of two independent defects

In the first place, it should be noted that the model of two independent defects is, in principle, in agreement with ESR data [35, 36]. Moreover, just the hypothesis concerning the existence of two acceptor defects with levels lying close to  $E_c - 0.17$  was proposed in [36] to account for the variation of the ESR-signal intensity for the A-centre and phosphorus donors under irradiation. According to this hypothesis, the  $\beta$ -defect should be identified as the A-centre. The nature of the  $\alpha$ -defect cannot be understood on the basis of the available knowledge of radiation defect formation in silicon. It can only be stated that, since the carbon concentration in our material is small, the  $\alpha$ -defect can hardly be related to the  $C_i-C_s$  complex formed in silicon crystals with rather small concentration of oxygen. This conclusion is supported by the thermal stability of the  $\alpha$ -defect, its annealing temperature being equal to that for the A-centre and higher than that for  $C_i-C_s$  [37]. The assumption that the  $\alpha$ -defect is one more radiation-induced oxygen complex is the likeliest.

At the same time, there are several arguments against the model of two independent defects. First, two independent acceptor defects with levels  $\Delta H_{\alpha} = (0.15-0.16)$  eV and  $\Delta H_{\beta} = (0.19-0.20)$  eV would manifest themselves in capacitance measurements and be well resolved by DLTS. However, DLTS data show that the defect with a level at  $E_c - 0.20$  eV is practically lacking in silicon crystals irradiated with <sup>60</sup>Co gamma rays [12, 28, 29].

Second, as follows from the annealing data (figures 2 and 3), both these defects must be annealed out simultaneously. Such a behaviour would be expected for interacting radiation-induced defects. In this case, however, the ratio of their concentrations must be close to unity, instead of 2 : 1 found in our experiments. Third, oxygen complexes generated under irradiation and having the required properties were not detected by IR spectroscopy.

All these facts indicate that, most likely, the model of two independent defects cannot be used in our case and the second hypothesis is to be considered in more detail.

### 4.2. A-centre as amphoteric defect with closely lying levels

First of all, a model of the A-centre as a divalent defect should agree with ESR data. Since solely the acceptor state of this centre is paramagnetic [35], we have to identify its upper level  $E(2/1)$  as acceptor  $E_A(-/0) = E_c - (0.15-0.16)$  eV and lower level  $E(1/0)$  as donor  $E_A(0/+)$  =  $E_c - (0.19-0.20)$  eV. Thus, in this model, the A-centre is an amphoteric defect with closely lying levels.

Further, let us consider how changes in the amplitudes of ESR signals from phosphorus donors and A-centre are related in the case of increasing irradiation fluence. According to the proposed model, at a low degree of compensation the concentration of paramagnetic Si-B1 centres in Czochralski-grown silicon crystals must be  $(N_{\text{net}} - N_{\text{low}})/2$ , with the decrease in the ESR amplitude for phosphorus donors proportional to  $N_{\text{net}} - N_{\text{low}}$  (see figure 2(a)). Thus, if only a single charge state of the divalent defect is paramagnetic, it would be expected that the increase in the ESR intensity for the A-centre is half the decrease in the signal from the phosphorus donors. This prediction is in agreement with experimental data [35, 36].

One more result obtained from ESR measurements [38] is noteworthy, also counting in favour of the proposed model. If a silicon crystal is subjected to uniaxial pressure, the A-centre level changes in different ways for defects having different orientations with respect to the direction of the applied pressure. In this case, those defects have mainly occupied levels, whose orientation ensures the lowest energy of the ground state of a bound electron. After the external pressure is removed, the electron occupancies of defects with arbitrary orientations relax to the equilibrium value. In [38], the time constant of the relaxation process was found to vary with temperature according to the Arrhenius law with activation energy  $\Delta E_{\text{relax}} = 0.20$  eV. Such a redistribution is observed only in strongly compensated crystals with  $N_{\text{D}}/N_{\text{A}} \approx 0.1$ . That is why the observed relaxation process was considered to result from the emission and recapture of electrons by A-centres [38]. Since the emission rate is determined by the ionization energy, then, in accordance with the model proposed in [38], it would be expected that  $\Delta E_{\text{relax}} = \Delta H_{\text{A}} \approx (0.16-0.17)$  eV if the A-centre is a simple acceptor. The authors of [38] accounted for the higher experimental value of  $\Delta E_{\text{relax}}$  by assuming the existence of an activation barrier for electron capture to the level related to this centre. However, later studies [39] demonstrated that there is no barrier for electron capture by the A-centre. Thus, in terms of the single-level model, the data of [38] contradict the Hall-effect data [9, 10]. At the same time, according to the proposed model, the relaxation time obtained in [38] must be determined at strong compensation mainly by the rate of emission from the lower level and must have an ionization energy characteristic of a donor state,  $\Delta E_{\text{A1}} \approx (0.19-0.20)$  eV. Thus, only the hypothesis that the A-centre is an amphoteric defect allows a consistent interpretation of the above ESR and Hall-effect data. Certainly, for an unambiguous verification of the proposed model, it would be desirable to obtain an ESR spectrum that could be attributed to a positively charged A-centre. However, as experience shows, the presence of an unpaired electron at the centre does not guarantee its detection by ESR spectroscopy [40].

It is also necessary to consider the question as to whether capacitance technique data (mainly DLTS data) agree with the proposed model. Therefore, we analyse the behaviour of the divalent defect under conditions of transient capacitance measurements. Let the emission rate from donor and acceptor levels be

$$e_1(T) = \sigma^+ \langle v \rangle N_c \exp\left(\frac{\Delta S_{\text{A1}}}{k}\right) \exp\left(-\frac{\Delta H_{\text{A1}}}{kT}\right) \quad (22)$$

$$e_2(T) = \sigma^0 \langle v \rangle N_c \exp\left(\frac{\Delta S_{\text{A2}}}{k}\right) \exp\left(-\frac{\Delta H_{\text{A2}}}{kT}\right) \quad (23)$$

where  $\sigma^+$  and  $\sigma^0$  are the electron capture cross-sections for the positive and neutral states of the defect, and  $\langle v \rangle$  is the mean thermal velocity of charge carriers. If  $e_2 \gg e_1$  over the entire temperature range studied, then, after a p-n structure is reversely biased, we shall observe a decay of the nonequilibrium capacity with two well-resolved components: fast and slow. The DLTS spectrum will have two peaks, from which  $\Delta H_{\text{A1}}$  and  $\Delta H_{\text{A2}}$  are readily obtained. If  $e_2 = e_1$  within the temperature range in question, the decay will have only a single component, with only one DLTS peak observed. A similar situation occurs if  $e_2 \ll e_1$ , with the capacitance decay determined by the time constant  $\tau = 1/e_2$ . In this case, only the enthalpy of ionization of the upper level  $\Delta E_{\text{A2}}$  can be found from the temperature dependence of the emission rate.

The condition  $e_2 \leq e_1$  can be satisfied for an amphoteric defect with closely lying levels at  $\sigma^+ > \sigma^0$ . Then at a certain temperature

$$T_{\text{eqv}} = \frac{\Delta H_1 - \Delta H_2}{k \ln(\sigma^+/\sigma^0)} \quad (24)$$

the equality  $e_2 = e_1$  holds. If DLTS measurements are carried out at  $T > T_{\text{eqv}}$ , an amphoteric defect will behave in capacitance measurements as a monovalent centre with the enthalpy of ionization  $\Delta H_{\text{A2}}$ . If  $T_{\text{eqv}}$  is within the temperature interval at which measurements are carried out, we find from experiment some effective enthalpy of ionization  $\Delta H_{\text{eff}}$ , where  $\Delta H_{\text{A2}} \leq \Delta H_{\text{eff}} \leq \Delta H_{\text{A1}}$ .

Apparently, just this is the case for the A-centre. As a rule, the capture cross-section of an attracting centre,  $\sigma^+$ , much exceeds that for a neutral centre,  $\sigma^0$ . Assuming that  $\sigma^+/\sigma^0 = (10-1000)$ , we estimate  $T_{\text{eqv}}$  to be  $50 \leq T_{\text{eqv}} \leq 200$  K, using expression (25). Thus,  $T_{\text{eqv}}$  may fall within the temperature interval 80–130 K in which DLTS measurements are commonly carried out. If  $80 \leq T_{\text{eqv}} \leq 130$  K, we can determine from capacitance measurements the effective enthalpy of ionization of the A-centre:  $0.15 \leq \Delta H_{\text{Aeff}} \leq 0.20$  K. Therefore, the fact that the A-centre behaves in DLTS measurements as a monovalent defect with the enthalpy of ionization  $\Delta H_{\text{A}} = 0.18$  eV [28, 41–43] can be accounted for by the closeness of  $T_{\text{eqv}}$  to 100 K.

As is known, the emission rate of an attracting centre increases in an external electric field  $E$  (see, e.g., review [44]). If the A-centre is studied by capacitance methods either in heavily doped materials or at rather great reverse biases, the emission rate  $e_{\text{A1}}$  will exceed the value given by equation (23). While  $e_{\text{A1}}(0) \approx e_{\text{A2}}(0)$  in zero field, we have  $e_{\text{A1}}(E) < e_{\text{A2}}(E)$  at non-zero electric fields, and, hence,  $\Delta H_{\text{Aeff}}$  decreases with increasing  $E$ , tending to  $\Delta H_{\text{A2}}$ . We believe that it is this increase in the emission rate and decrease in  $\Delta H_{\text{Aeff}}$  that were observed in [16, 17]. Although the above-mentioned analysis is preliminary, we can conclude on its basis that capacitance data may also be in agreement with the model of the A-centre as an amphoteric defect. Moreover, this model accounts for the scatter in experimental  $\Delta H_{\text{A}}$  values obtained in different studies.

The change in our concepts concerning the charge states and energy levels of the A-centre must mainly affect the recombination statistics in irradiated semiconductors. However, some concepts of radiation defect formation in silicon should also be modified.

### 4.3. Pair correlation of radiation-induced defects in silicon

In considering the problem of ESR data interpretation, the additional decrease in the intensity of the ESR signal from a phosphorus impurity with increasing irradiation dose should be accounted for. In other words, it is necessary to explain why the carrier concentration in the irradiated samples remains practically unchanged at temperatures at which the A-centre is completely ionized (figure 2). Had the A-centre possessed a donor level,  $N_{\text{net}}$  would increase to a value  $N_{\text{net}} = N_{\text{P}} + N_{\text{A}}$  upon irradiation, and, after complete ionization of the A-centre, we would observe an increase in the carrier concentration by  $N_{\text{A}}$ , compared with the initial concentration of the phosphorus impurity. Since no such increase is observed, we have to assume that one more acceptor defect with practically the same incorporation efficiency is generated under irradiation, simultaneously with the A-centre. Moreover, as follows from figure 2, this acceptor centre must be annealed in entirely the same manner as it occurs with the A-centre. Although such a correlated behaviour seems to be improbable at first glance, it would be expected for genetically related radiation-induced defects. Moreover, it is this behaviour that follows from the DLTS data for  $E(0.18)$  and a hole trap  $H(0.42)$  [41]. It is assumed, that the trap  $H(0.42)$  is related to the  $C_i-O_i$  complex [45, 46]. In this case, it is necessary to take into account that the concentration of V–O and  $C_i-O_i$  complexes is much less than that of other impurities (in particular, oxygen and carbon). Therefore, their simultaneous annealing is possible solely as a result of direct interaction between two closely located vacancy-type and interstitial complexes. Such a pair correlation in the arrangement of A-centres and  $C_i-O_i$  complexes agrees with the results obtained in a study of direct electronic transitions between these centres [5].

Thus, the data presented suggest that, changing our concepts of the electrical activity of the A-centre, we also have to change our interpretation of data on interactions between impurities and radiation-induced defects in silicon in order to explain the formation of pairs of impurity–defect complexes at small doses of  $\gamma$ -irradiation.

## 5. Conclusion

The temperature dependences of carrier concentration in n-type Czochralski-grown silicon crystals irradiated with  $^{60}\text{Co}$  gamma rays have been studied. The applicability of the model of a monovalent defect with a level lying close to  $E_c - 0.17$  eV for describing the properties of the A-centre in silicon crystals is analysed. This model is shown to contradict the available experimental data.

Two suggestions are made. Firstly, two independent defects with levels at  $E_c - 0.17$  eV are formed upon irradiation of Czochralski-grown silicon crystals, and, secondly, the A-centre is a divalent defect having two levels in the upper half of the energy gap. Experimental data obtained by other methods are analysed. A conclusion is made that ESR, DLTS and Hall-effect data can be consistently accounted for under the assumption that the A-centre has two levels: an acceptor located at  $E_c - (0.15-0.16)$  eV and a donor at  $E_c - (0.19-0.20)$  eV.

Verification of the proposed hypotheses concerning the properties of the oxygen–vacancy complex in silicon needs additional experimental data. These may be Hall-effect data obtained in n-Si crystals strongly compensated by irradiation or in p-Si crystals in which the energy levels of the  $C_i-O_i$  complex in the lower half of the energy gap have been studied. Apparently, to construct a reliable model of the electronic structure of the A-centre, Hall-effect and ESR spectroscopic measurements are to be carried out on the same silicon crystals subjected to various preliminary heat treatments.

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