PHYSICAL REVIEW B VOLUME 30, NUMBER 6 15 SEPTEMBER 1984

Search for fractional-charge impurities in semiconductors with photothermal ionization spectroscopy

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(Received 2 December 1983; revised manuscript received 1 May 1984)

The detection of possible fractional-charge impurities (FCI's) in semiconductors with photothermal ionization spectroscopy (PTIS) at low temperatures is analyzed. Existing formulas for the PTIS signal strength and for the minimal concentration of normal shallow majority impurities, detectable with PTIS, are extended to the case of majority FCI's. Account has been taken of semiconductor material constants, as well as temperature, background radiation, and degree of compensation. A conventional experimental setup for the detection of normal shallow impurities with PTIS is described. It is shown that this configuration can detect down to 10^7 FCI's cm^{-3}—if present—in ultrapure germanium, depending on the concentration of minority impurities. Modifications to the experiment are proposed which release this dependence and which lower this limit down to 10^5 cm^{-3}, i.e., one fractional charge per 10^{19} nucleons. From measured PTIS spectra of an ultrapure Ge sample it is deduced that the sample contained less than about 1.5×10^{11} cm^{-3} acceptorlike FCI's.

I. INTRODUCTION

In 1964 Gell-Mann[1] and Zweig[2] independently suggested that particles with fractional charges—called quarks by Gell-Mann—might be the basic constituents of nucleons. The quark model provided the impetus for numerous experimental searches for free quarks, reviewed, e.g., by Kim,[3] Jones,[4] Lyons,[5] and Marinelli and Morpurgo.[6] Quantum chromodynamics, however, postulates that free quarks do not exist in nature but are confined in colorless neutral triplets (for a review on confinement see, e.g., Ref. 7). In the literature many speculations about fractionally charged particles other than free quarks have appeared, such as, e.g., diquarks,[8] constituents of quarks and leptons,[9–11] and hadronic color singlets.[12,13] In 1977 LaRue, Fairbank, and Hebard[14] reported the first successful observation of third-integral charges on superconducting niobium balls. The technique applied was a modification of the original Millikan oil-drop experiment.[15] After their publication, suggestions in the literature about possible systematical errors were ruled out by additional measurements, confirming their original results.[16] But up to now they are the only group that claims to have observed fractional charge. Therefore, it may be desirable to check their results in a different experimental environment.

Fractional charge in stable matter may be found in the form of fractionally charged atoms. These atoms then are composed of a central nucleus of small size with positive fractional charge surrounded by a cloud of electrons of normal atomic dimensions.[17] This central nucleus may be a single fractionally charged particle or a fractionally charged particle attached to a conventional nucleus. Such fractionally charged particles could, for example, be free quarks which were left over from the "big bang."[12,17–19] As put forward in 1980 by Chaudhuri, Coon, and Derkits,[20] fractional charge may be found in semiconductors in the form of fractional-charge impurities (FCI's) which should behave much like shallow donors or acceptors. Looking at semiconductors has the advantage that much knowledge exists about its crystal growth, characterization techniques, and impurities. In addition, the shallow donor and acceptor energy levels of such FCI's are calculable.[20]

FCI's, if present, can be expected to manifest themselves in very low concentrations. For the detection of extremely low concentrations of normal shallow donors and acceptors, photothermal ionization spectroscopy (PTIS) has proved to be a very sensitive technique. This technique, also called photoelectric spectroscopy, was originally developed by Lifshits and Nad' in 1965.[21] Extensive reviews on PTIS and its application to ultrapure germanium have been given by Kogan and Lifshits,[22] and Haller, Hansen, and Goulding.[23] Whereas conventional absorption spectroscopy fails to detect impurity concentrations below 10^{13} cm^{-3}, PTIS has demonstrated its usefulness even for impurity concentrations down to 10^8 cm^{-3}. For that reason the application of PTIS in the search for FCI's, first proposed in Ref. 20, seems a very straightforward idea. Using PTIS has the advantage that it can also give an estimate for the concentration of FCI's, if present, whereas a Millikan type of experiment can only prove the existence of fractional charge.

The nature of FCI's in semiconductors and the shallow energy levels associated with them will be discussed in Sec. II. In addition, the influence of the chemical history of a sample on the occurrence of the FCI's is discussed. Kogan and Lifshits[22] analyzed the PTIS method for normal impurities only. The main results of an extension of this analysis to FCI's are given in Ref. 24. A more detailed treatment of this extended analysis will be given in Sec. III, where we will follow closely the notations of Kogan and Lifshits. The influence of temperature, background radiation, and degree of compensation is discussed in detail for a semiconductor with one type or two types of majority impurities. An expression for the minimal detectable concentration of FCI's will be given for a semi-

conductor with one type of majority impurity. In Sec. IV the experimental arrangement necessary for PTIS is shown and the results of a search for FCI's in one particular sample are given. In Sec. V we shall calculate the lower limit on the concentration of detectable FCI's with this particular experimental setup. In addition, we shall discuss the modifications of the experimental arrangement, which makes it possible to detect FCI's with the same sensitivity as fractional charges were detected in the successful experiment of LaRue, Fairbank, and Hebard.

II. FCI'S IN SEMICONDUCTORS

An impurity in a crystal is by definition any element which deviates from the regularly ordered building blocks constituting the crystal lattice. If such an element has a net fractional charge we will call it an FCI. An FCI, if existing, is thought to consist of a fractionally charged nucleus surrounded by an electron cloud of ordinary atomic dimensions.[17] This nucleus can be a single particle of positive fractional charge, or a fractionally charged particle bound to strongly interacting particles with a resulting net positive charge. The size of such a composite nucleus is much smaller than the Bohr radius of the electron, if one assumes that the fractionally charged particle has a mass much larger than that of an electron and that its nonelectromagnetic interaction with nuclear matter is negligible at atomic distances.[17] The nature of such a fractionally charged particle is not necessarily a single quark, but might also be a diquark,[8] a constituent of quarks and leptons,[9–11] or a hadronic color singlet.[12,13]

FCI's can in principle be present in all types of solids. Following the proposal of Chaudhuri, Coon, and Derkits[20] we will focus our attention on FCI's in semiconductors. FCI's, if present, are expected to manifest themselves in very low concentrations only. The characteristics of impurities in very low concentrations in semiconductors—especially tetrahedral structures such as, e.g., germanium, silicon, and gallium arsenide—are well known. Impurities in semiconductors are very sensitive to crystal treatments such as, e.g., the chemical-purification process (that discriminates against ions, which FCI's always are), zone refining, and crystal growth. The chemistry of fractionally charged atoms has gained much interest.[17,25,26] Lackner and Zweig[17,25] composed a periodic table for elements of third-integral charge with values for chemical factors such as electronegativity, oxidation numbers, and crystal radii. Chaudhuri, Coon, and Derkits[27] deduced segregation coefficients of FCI's with hybridized sp^3 bonds in tetrahedrally coordinated crystals, such as, e.g., Ge, Si, and GaAs. A segregation coefficient can be used to describe the distribution of impurities in a crystal after growth from the melt or after zone refining. This coefficient k^0 is the ratio of the concentration of an impurity in the just solidified material and the concentration in the remaining liquid during nonequilibrium solidification. A value of k^0 of the order of 1 indicates that impurities most likely survive these selective processes. A value of $k^0>1$ for a particular impurity offers the possibility to enrich a sample with this type of impurities. For example, for germanium as a semiconducting host material, Chaudhuri *et al.* found several possible FCI's with $k^0>0.1$ in the second, third, and fourth row of the Periodic Table. In the second row the nuclear charge of such FCI's should equal that of a boron atom $\pm\frac{1}{3}e$. For instance, quark-nucleon complexes consisting of a combination of a Be nucleus (positive charge $4e$) with a u quark ($\frac{2}{3}e$), a B nucleus ($5e$) with a d quark ($-\frac{1}{3}e$), a B nucleus with a $\bar{d}$ quark ($\frac{1}{3}e$), and a C nucleus ($6e$) with a $\bar{u}$ quark ($-\frac{2}{3}e$) would obey this demand. In the third and fourth row the FCI's should have nuclear charges between those of Al and P and of Ga and As, respectively. Of the FCI's mentioned several even have a value for k^0 substantially higher than 1. This means that such FCI's—if present in a Ge ingot—would be retained during the zone-refining process, and be concentrated in the top of the crystal after growing from the melt. In an earlier paper[20] Chaudhuri *et al.* also suggested that, in view of the high diffusion rates of interstitial H, He, and Li^+ in common semiconductors, small FCI's could be introduced from FCI-rich contiguous matter by standard doping and drifting techniques.

Many of the FCI's with $k^0>0.1$ are situated in the Periodic Table between the columns of the conventional shallow donors and acceptors of the semiconducting host material. Such FCI's can be expected to give rise to localized, shallow donorlike or acceptorlike energy states. Shallow donors and acceptors energetically resemble an isolated atom, consisting of an electron bound in the Coulomb field of a nucleus with charge Ze ($-e$ is the charge of an electron). Such an isolated atom gives rise to a hydrogenlike energy-level scheme with an ionization energy $E_{0,Z}$ given by

$$E_{0,Z}=Z^2\frac{m}{2}\left[\frac{e^2}{4\pi\epsilon_0\hbar}\right]^2, \tag{1}$$

where m is the rest mass of an electron, ϵ_0 the permittivity of free space, and $\hbar$ is Planck's constant divided by 2π. In a semiconductor an electron (or hole) is bound in the Coulomb field of a localized donor (or acceptor) impurity similarly. This idea was worked out in the effective-mass theory originally developed by Kittel and Mitchell[28] and Kohn and Luttinger.[29] Replacing the mass of the free electron with an appropriately averaged effective mass m^* and taking into account the dielectric constant ϵ of the semiconductor, one obtains as a good estimate for the ionization energy

$$E_{i,Z}=\frac{m^*}{m}\frac{1}{\epsilon^2}E_{0,Z}\ . \tag{2}$$

The associated Bohr radius is enlarged by a factor $(m/m^*)\epsilon$ with respect to that of a hydrogenlike atom. In this context Z denotes the difference in valence of the donor (acceptor) impurity and the atoms of the host material. In germanium, for instance, this leads to an ionization energy of about 10 meV for shallow (i.e., $Z=1$) donors and acceptors, a value more than a thousand times smaller than the ionization energy of a hydrogen atom (13.6 eV). The quark-nucleon complexes in germanium with a $\bar{d}$ quark attached to a Ge nucleus and a d quark attached to an As nucleus were examples of $Z=\frac{1}{3}$ and

$Z=\frac{2}{3}$ donorlike FCI's, respectively. Similar combinations of a u quark with an Al nucleus and of a $\bar{u}$ quark with a Ge nucleus are examples of $Z=\frac{1}{3}$ and $\frac{2}{3}$ acceptorlike FCI's, respectively.

The energy-level schemes of shallow donorlike and acceptorlike FCI's are calculable. The excited states of normal ($Z=1$) shallow donors and acceptors are described quite well by the effective-mass theory.[30] This is because in these states the bound electron or hole moves through a volume much larger than that occupied by the central impurity and it "feels" mainly the valence charge Z. For $Z=\frac{1}{3}$ or $\frac{2}{3}$ FCI's this argument is even stronger, since the size of the wave functions of the corresponding states is larger. For the lowest states of normal shallow donors and acceptors central-cell corrections are necessary,[30] but these will again be less for the $Z=\frac{1}{3}$ or $\frac{2}{3}$ FCI's. As pointed out in Ref. 20, the binding energies in the energy-level schemes of normal ($Z=1$) shallow donors are reduced by a factor of Z^2 for $Z=\frac{1}{3}$ or $\frac{2}{3}$ donorlike FCI's. In addition, the multivalley orbit ground-state splitting is reduced by a factor of Z^4. In semiconductors such as Ge and Si the ground-state level of normal ($Z=1$) acceptors is not splitted because of the single (degenerate) band extremum at wave vector $\vec{k}=0$. As an illustration, Fig. 1 shows the energy-level schemes for acceptorlike FCI's and the shallow boron acceptor in germanium. The binding energies of the FCI's are deduced from those of the boron acceptor by means of Eq. (2). The notation for the energy levels has been taken from the corresponding spectral transition lines, as given by Haller and Hansen.[31]

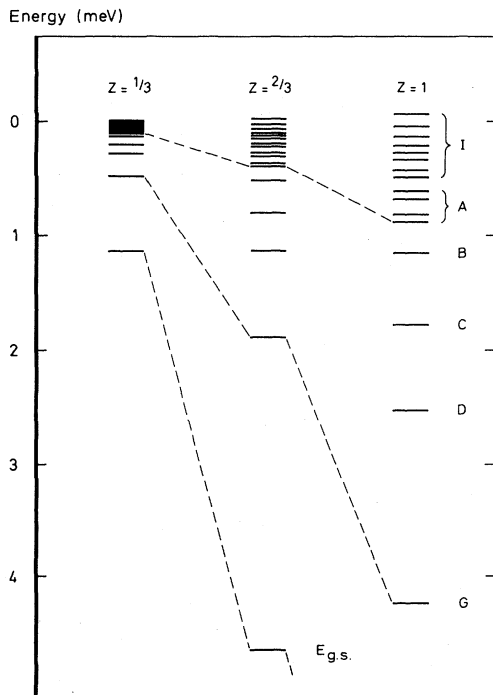

FIG. 1. Energy-level schemes for two acceptorlike FCI's and a normal shallow acceptor in germanium. The nomenclature has been taken from Ref. 31.

III. ANALYSIS OF DETECTION OF FCI'S BY PTIS

A. The critical concentration β/α

PTIS is a spectroscopic technique which measures the change in electrical conductivity of a semiconducting sample, caused by a change in number of free electrons (holes) in an energy band due to ionization of a donor (acceptor) in a two-step process. The bound electron (hole) is raised from the ground state to an excited state by the absorption of a photon and is subsequently thermally promoted into the conduction (valence) band. The PTIS spectrum of an impurity consists of a series of photoconductivity peaks, situated on the low-energy side of a broad continuum. This continuum originates from direct optical ionization of a donor (acceptor).

Detailed understanding of the PTIS signal formation first of all requires knowledge of the occupation of the ground state of impurities. Moreover, the number of equilibrium free carriers in the band should be known, as well as the time response of this system of free carriers after the injection of additional free carriers. The relevant processes depend on temperature, background radiation, and degree of compensation.

Consider a semiconductor with free carrier concentration n and one type of majority impurity with concentration N. Let N^0 and N^i denote the concentration of neutral and ionized majority impurities, respectively, and KN the concentration of compensating minority impurities, where K is the degree of compensation; then this system is described by the set of rate-of-change equations

$$\frac{dn}{dt}=\beta N^0-\alpha n N^i\,,\qquad \frac{dn}{dt}=-\frac{dN^0}{dt}=\frac{dN^i}{dt}\,. \tag{3}$$

Here β is the coefficient of impurity ionization by thermal phonons and by background radiation, expressed in units of $\sec^{-1}$ and α is the trapping rate coefficient expressed in units of $\text{cm}^3\sec^{-1}$. In equilibrium, expressions can be derived for N^0, N^i, and n, containing terms K, N, and β/α

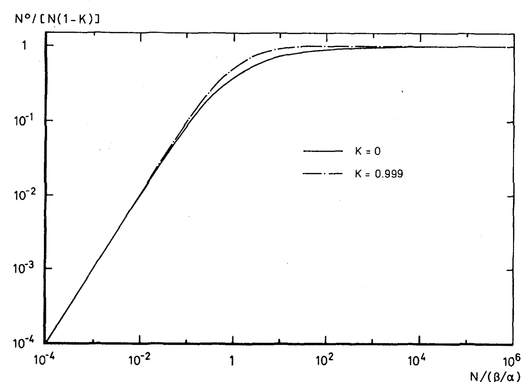

FIG. 2. Normalized occupation of the ground state of a majority impurity as a function of $N/(\beta/\alpha)$ for the situation of one type of majority impurity for the two limiting cases of compensation.

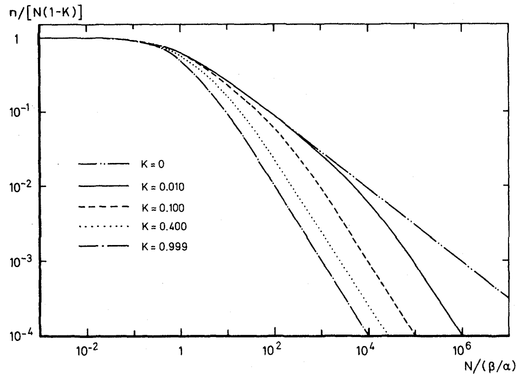

FIG. 3. Normalized concentration of free majority carriers as a function of $N/(\beta/\alpha)$ for the situation of one type of majority impurity for several degrees of compensation.

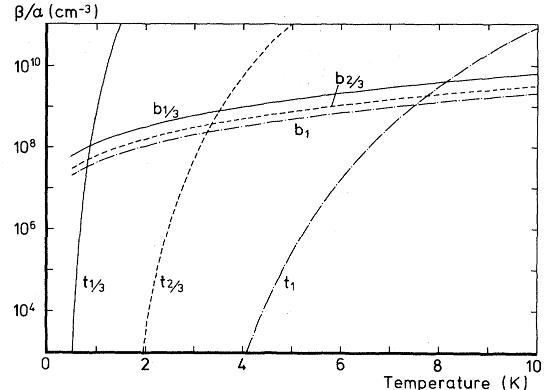

FIG. 4. Temperature dependence of the critical concentration β/α for normal acceptors ($Z=1$) and acceptorlike FCI's ($Z=\frac{1}{3},\frac{2}{3}$) in germanium, for the limiting cases of thermal ionization (curves $t_{1,\,1/3,\,2/3}$) and ionization by background radiation (curves $b_{1,\,1/3,\,2/3}$).

only. This can be done by using the obvious relation $N=N^0+N^i$, the condition of electrical neutrality $N^i=n+KN$ and $dn/dt=0$ because of the equilibrium situation. The resulting normalized concentrations $N^0/[N(1-K)]$ and $n/[N(1-K)]$ are shown in Figs. 2 and 3, respectively, as a function of the dimensionless quantity $N/(\beta/\alpha)$ for several values of K. These figures show that the quantity β/α, having dimensions of cm^{-3}, acts as a critical impurity concentration: For impurity concentrations N much higher than β/α almost all majority impurities are in the ground state (except those which are ionized because of the presence of compensating minority impurities), and hence the concentration of free carriers is very low. For impurity concentrations well below this critical concentration β/α nearly all majority impurities are ionized and n approaches its maximum value $N(1-K)$. The quantity β/α also acts as a critical concentration for the strength of the PTIS signal; therefore we will study β/α in detail.

1. *Thermal ionization*

First we assume that the influence of background radiation on the ionization of the majority impurities is negligible with respect to thermal ionization at temperature T. Although for this case β and α can be evaluated separately,[32,33] there also exists one simple expression for β/α:[34]

$$\left[\frac{\beta}{\alpha}\right]_Z(T)=\frac{2}{g}\left[\frac{2\pi m^*kT}{h^2}\right]^{3/2}e^{-E_{i,Z}/kT} . \tag{4}$$

Here g denotes the degeneracy of the ground state of the majority impurity and k is the Boltzmann constant.

The temperature dependence of β/α in case of thermal ionization is shown in Fig. 4 for two acceptorlike FCI's and one shallow acceptor in germanium. The curves are calculated by taking $g=4$, $m^*/m=0.38$, and $E_{i,1}=10$ meV, and using Eq. (2). The temperature range and the values of β/α are chosen according to the interesting range of values for the search for FCI's.

2. *Ionization by background radiation*

Now we assume thermal ionization of the majority impurities to be negligible with respect to the ionization by background radiation. For this situation no simple expression for $(\beta/\alpha)_Z$ exists. Therefore, it is necessary to consider β and α separately. We will confine ourselves to the case of acceptorlike impurities in germanium. First β will be evaluated and subsequently α.

The quantity β is totally determined by the broadband background radiation, and is independent of temperature. In practice, when applying the PTIS technique, low-pass optical filters are always used, thus limiting the range of energies of the radiation reaching the semiconducting sample below a maximum energy $E_{\max,Z}$. The additional subscript Z indicates the possibility that one chooses the filtering according to the type of impurity—characterized by Z—one searches for.

The quantity β is given by the expression

$$\beta_Z=\int_{E_{i,Z}}^{E_{\max,Z}}\frac{\sigma_{i,Z}(E)}{A}F(E)dE . \tag{5}$$

Here A is the area of the illuminated surface of the sample and $F(E)dE$ the number of photons per second with energies between E and $E+dE$, reaching the sample. The symbol $\sigma_{i,Z}(E)$ denotes the cross section for optical ionization of a carrier from the ground state of an impurity, characterized by Z, for light with energy E.

To find an expression for $\sigma_{i,Z}(E)$ we first look at the solution of the problem for an isolated one-electron atom with a nucleus with charge Ze. For such an atom the cross section is an explicit analytic formula, expressed in units of a_0^2, a_0 being the Bohr radius of the ground state of the hydrogen atom (see, e.g., Sobel'man[35]). This expression exhibits the property

$$\sigma_{i,Z}(E_{i,Z})=\frac{1}{Z^2}\sigma_{i,1}(E_{i,1}) . \tag{6}$$

Extrapolating Sobel'man's solution for the one-electron

atom to the case of acceptors in germanium, one has to correct for the different Bohr radius of the ground state of an acceptor as well as for the fact that the host material is a dielectric. In Fig. 5 the solid curve represents this extrapolation as a function of E/E_i. As noticed by Kogan and Polupanov,[36] experiments revealed a quite different $E/E_{i,1}$ dependence for $\sigma_{i,1}$, but a correct value for $E=E_{i,1}$. They recalculated the cross section, using the detailed forms of the wave functions of the acceptors and of the light- and heavy-hole valence bands. The results of their calculations for the shallow boron acceptor in germanium are also shown in Fig. 5, indicated by crosses. Fortuitously, Kogan and Polupanov's calculations can be described with an $(E/E_i)^{-1}$ dependence, when ignoring the detailed structure below $E/E_i=1.2$, as illustrated in Fig. 5 by the dashed line. Hence we obtain

$$\sigma_{i,Z}(E)=\frac{f}{Z^2}\frac{E_{i,Z}}{E} \tag{7}$$

for the energy-dependent cross section of acceptors in germanium in a very good approximation, the factor f being about 1.1×10^{-14} cm^2.

Assuming the background radiation consists of (room-temperature) blackbody radiation, $F(E)dE$ is given by

$$F(E)dE=C\frac{E^2}{e^{E/kT_e}-1}dE\ , \tag{8}$$

where C is a quantity in units of $\mathrm{J}^{-3}\,\mathrm{sec}^{-1}$, depending on the experimental arrangement, and T_e the temperature of the blackbody. For the range of energies of interest here, we can approximate the denominator in Eq. (8) by E/kT_e, and $F(E)$ is simply proportional to E. With this approximation Eqs. (5)–(8) finally lead to the relation

$$\beta_Z=\frac{E_{\max,Z}-E_{i,Z}}{E_{\max,1}-E_{i,1}}\beta_1\ . \tag{9}$$

Our next step is to consider the trapping rate coefficient α. We will use the results of Abakumov, Perel', and Yassievich,[33] who used an improved version of the original cascade theory of Lax.[37] In this cascade model the capture of a carrier occurs through a continuous fall of the carrier in energy space from band-state levels with positive energy into higher impurity states with negative energies. It is assumed that the energy relaxation of the carrier during its fall is entirely due to interaction with acoustic phonons. A carrier is considered to be practically bound if it has descended into an impurity state with a binding energy greater than kT. This model also takes into account that a carrier cannot lose all its kinetic energy in the emission of a single acoustic phonon because of the laws of conservation of energy and momentum.

The expression for the temperature dependence of α (Ref. 33) contains several parameters, depending on the semiconductor material and type of charge carriers, such as ϵ, m^*, and, because acoustic phonons are involved, the velocity of sound, and the mean free path of the carrier. It shows the property

$$\alpha_Z=Z^3\alpha_1\ . \tag{10}$$

The temperature dependence of α_1 for shallow acceptors in germanium is shown in Fig. 6, where we used parameter values given in Ref. 33. This temperature behavior is also confirmed by experiment.[33]

Several factors, however, can influence this T dependence for α_1. Such factors are the overlap of impurity states at high impurity concentrations, the freezing out of recombination centers by the formation of donor-acceptor dipole pairs, and the capture of carriers in potential wells because of potential fluctuations. Nevertheless, in ultrapure germanium these factors are unimportant at temperatures above 0.5 K,[33] just as the possible influence of

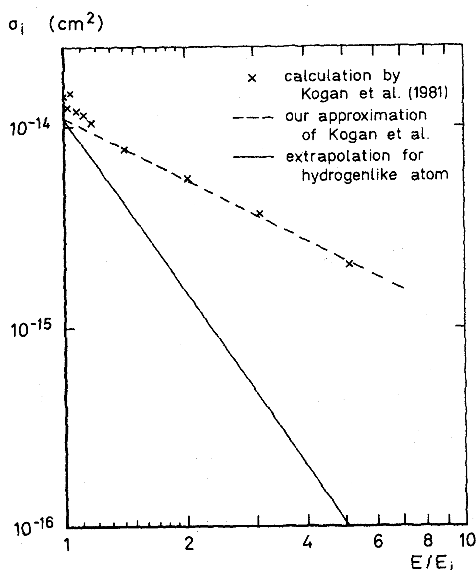

FIG. 5. Theoretical values for the cross section for optical ionization of a shallow acceptor impurity in germanium as a function of E/E_i (for details, see text).

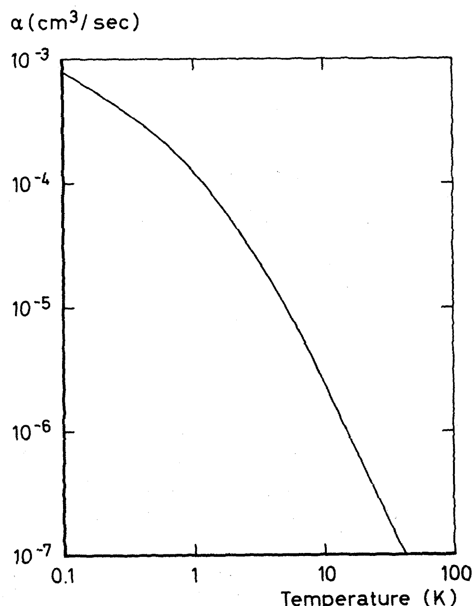

FIG. 6. Temperature dependence of the theoretical values for the capture cross section of holes for shallow acceptors in germanium.

optical phonons.[38] The most serious factor is the application of an electric field, necessary for recording PTIS spectra. An electric field distorts higher levels of impurity states and causes extra heating of carriers, but in ultrapure germanium these effects are small for electric field strengths lower than 100 mV/cm at temperatures above 0.5 K.[39]

Having considered β and α separately, we can write, from Eqs. (9) and (10),

$$(\beta/\alpha)_Z=\frac{1}{Z^3}\frac{E_{\max,Z}-E_{i,Z}}{E_{\max,1}-E_{i,1}}(\beta/\alpha)_1 \ . \tag{11}$$

Thus knowing $(\beta/\alpha)_1$ for ionization purely by background radiation for shallow acceptors, β/α for acceptor-like FCI's simply follows from this equation. As will appear in the next section, a low value for $(\beta/\alpha)_Z$ enhances the PTIS signal strength. Because of Eq. (2), the optimal cutoff energy, when searching for FCI's, is much lower than when searching for shallow acceptors. Regarding the optical cross section, shown in Fig. 5, the optimal choice is $E_{\max,Z}\simeq 2E_{i,Z}$.

Figure 4 shows the temperature dependence of $(\beta/\alpha)_Z$ in case of ionization by background radiation for different values of Z. For the determination of the $(\beta/\alpha)_1$ curve we used $\beta=5\times10^3$ sec^{-1} (see the Appendix) and α according to Fig. 6. The curves for $Z=\frac{1}{3}$ and $\frac{2}{3}$ were calculated by assuming that optical filtering was used with $E_{\max,Z}=2E_{i,Z}$.

B. PTIS signal strength

With PTIS one essentially measures the change in concentration of free carriers in the band, Δn, with regard to the equilibrium concentration of free carriers, n, as a function of the energy of the light irradiated onto the semiconducting sample. In practice this can be done in two fundamentally different ways: measuring the changes in voltage across the sample, using a constant current source, or measuring the changes in current, using a constant voltage. An elementary analysis demonstrates that both methods basically measure the quantity $\Delta n/n$. By considering this quantity, the PTIS signal will be analyzed for a semiconductor with one type and with two types of majority impurities, respectively.

Consider a semiconductor with one type of majority impurity. If the number of impurities is very low, the flux of photons can be regarded as constant throughout the sample and mutual shielding of impurities can be neglected. Assuming monochromatic radiation (apart from broadband background radiation, if present) is incident on the sample with energy E and with photon flux $I(E)$, then $\Delta n/n$ is given by[22,40]

$$\frac{\Delta n}{n}=\frac{I(E)\sigma_i(E)}{A}\frac{N^0\tau}{n} \ , \tag{12}$$

where τ is the lifetime of the nonequilibrium carrier.

This equation indicates that the dependence on temperature and on background radiation of $\Delta n/n$ occurs via the quantity $N^0\tau/n$. To illustrate this we will evaluate the dependence of the dimensionless quantity $\beta N^0\tau/n$—being proportional to $\Delta n/n$—on β/α. The quantities N^0 and n have already been considered before. The nonequilibrium lifetime τ is defined as the time response of the system of free carriers, after the equilibrium is disturbed by an additional number of free carriers. By means of Eq. (3), an expression for τ can easily be obtained by using a linear relaxation-time approximation. Figure 7 shows the resulting dependence of $\beta N^0\tau/n$ on the dimensionless quantity $N/(\beta/\alpha)$. This figure demonstrates the remarkable properties and strength of PTIS. The different behavior of the curves for $N/(\beta/\alpha)>0.1$ basically originates from the strong dependence of n and τ on the degree of compensation K in this region. If $N\gg\beta/\alpha$, the signal strength $\beta N^0\tau/n$ becomes independent of $N/(\beta/\alpha)$ and the degree of compensation K. For $K\neq0$, the PTIS signal strength is even twice as large as the corresponding PTIS signal for $K=0$. With conventional absorption spectroscopy, however, the signal exhibits a linear dependence on impurity concentration.

Now consider a semiconductor with two types of majority impurities, denoted by 1 and 2, respectively. For this situation we want to be able to deduce the relative concentration N_1/N_2 from the measured PTIS spectrum. Therefore, assume that the semiconducting sample, apart from possible background radiation, is irradiated with monochromatic light with energy E_1 and photon flux $I(E_1)$, which ionizes impurity 1 and which causes a signal $\Delta n_1/n$. Assume the same for impurity 2. Under the condition that the system is only slightly distorted by this additional radiation, we can write the following formula for the relative signal strength S_1/S_2 (Ref. 22):

$$\frac{S_1}{S_2}=\frac{N_1}{N_2}\frac{\alpha_{Z_2}}{\alpha_{Z_1}}\frac{I(E_1)}{I(E_2)}\frac{\sigma_{i,Z_1}(E_1)}{\sigma_{i,Z_2}(E_2)}\left[\frac{N_1^0/N_1}{N_2^0/N_2}\right]^2 . \tag{13}$$

If minority impurities are present with concentration N_c, they are preferably compensated by carriers originating from the majority impurities with the lowest ionization energy. If, e.g., impurities 1 and 2 denote an FCI and a normal shallow impurity, respectively, and if $N_1<N_c$, the consequence is that $N_1^0=0$ and hence these FCI's cannot be detected by PTIS at all.

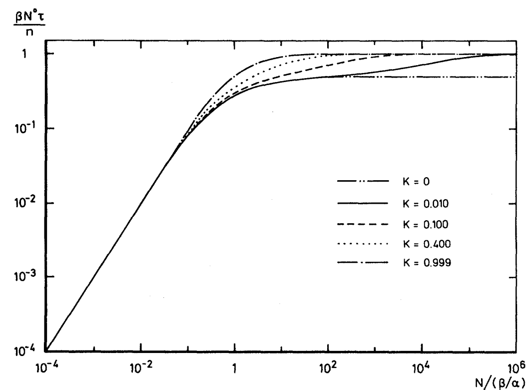

FIG. 7. Normalized strength of the PTIS signal for the situation of one type of majority impurity as a function of $N/(\beta/\alpha)$ for several degrees of compensation.

C. Minimal detectable concentration

We will now determine the minimal detectable concentration of impurities $N_{\min}$ for a semiconductor with one type of majority impurity. We assume an impurity can be detected by PTIS if its corresponding signal-to-noise ratio exceeds 1. At low impurity concentration the Johnson noise is dominated by the generation-recombination noise.[40] Assuming we are in the low-concentration area where N^0 is proportional to $N/(\beta/\alpha)$ (see Fig. 2), $N_{\min}$, corresponding to a signal-to-noise ratio of 1, is given by[40]

$$N_{\min}(Z)=(\beta/\alpha)_Z \frac{2A}{I(E)\sigma_{i,Z}(E)} \left[\frac{\alpha_Z \Delta f}{V(1-K)} \right]^{1/2} . \quad (14)$$

Here V is the volume of the sample and Δf denotes the frequency bandwidth of the amplifier.

IV. EXPERIMENTAL SEARCH FOR FCI'S WITH PTIS

In this section we will describe an experimental search for FCI's on an ultrapure germanium sample with PTIS. For that purpose we used the experimental setup, shown in Fig. 8. The far-infrared light, produced by a Grubb Parsons Michelson interferometer, enters the light pipe via a black polyethylene window, which blocks out all visible and near-infrared radiation. From there it passes through a cooled crystalline quartz filter with cutoff energy 27 meV into a semispherical, integrating cavity. The sample is clamped onto the base of the cavity and its temperature can be raised above the temperature of the surrounding helium bath by means of a heater. Using the electric circuit, shown in Fig. 8, photoconductivity interferograms are recorded with phase-sensitive detection

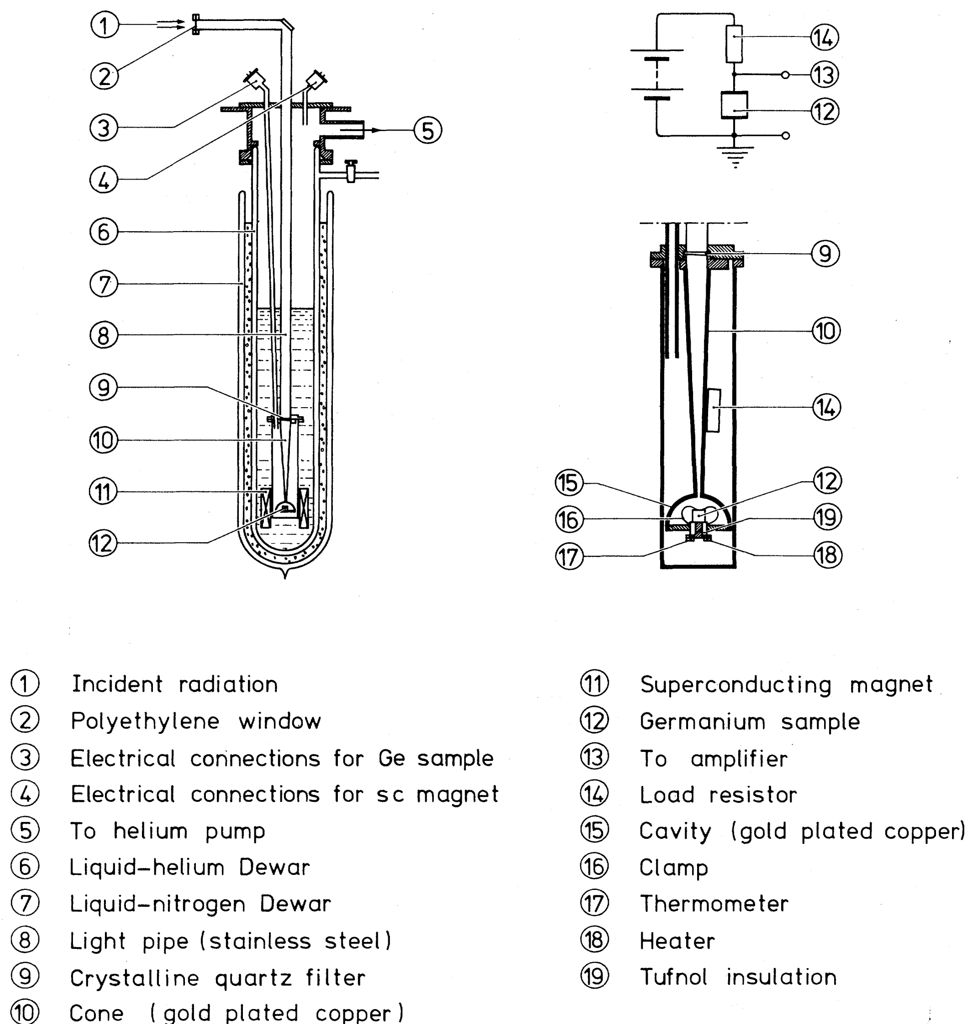

FIG. 8. Cryostat for photothermal ionization measurements.

techniques and subsequently Fourier-transformed on a PDP-11 computer.

The investigated sample—with dimensions $1\times1\times1$ cm^3 and weight 5.3 g—was *p*-type material with net impurity concentration $N_A - N_D = 2\times10^{11}$ cm^{-3} and with a degree of compensation of about 0.4, containing boron as the dominating majority impurity. Electric contacts were made by pressing flat copper disks against two opposite faces of the sample, wetted with a Ga-In eutectic. In order to avoid thermal ionization of possible FCI's and hence a reduction in the PTIS signal (see Sec. III), the spectra were recorded at low temperature, 1.2 K being the lowest temperature which can be achieved with the given experimental arrangement.

Figure 9 shows two PTIS spectra of this sample, measured at temperatures 1.2 and 2.0 K, respectively. Also indicated are the transitions belonging to the shallow $Z=1$ boron acceptor and the expected positions of the transition lines of the $Z=\frac{1}{3}$ and $\frac{2}{3}$ acceptorlike FCI's, using the energy-level schemes of Fig. 1. There is no evidence for a photoconductivity signal, originating from FCI's, above the noise level. Using this negative result, we want to derive an upper limit on the concentration of $Z=\frac{1}{3}$ or $\frac{2}{3}$ acceptorlike impurities in this particular sample.

In the preceding section it was demonstrated that an FCI concentration lower than the concentration of compensating impurities would explain the absence of a PTIS signal, originating from FCI's. For this sample this would yield an upper limit for FCI's of 1.3×10^{11} cm^{-3}. In principle it is possible, however, that the concentration of FCI's exceeds the concentration of compensating impurities, but that the corresponding PTIS signal is below the noise level visible in Fig. 9. This possibility can be numerically analyzed by means of Eq. (13), by assuming that, e.g., impurities 1 and 2 denote acceptorlike FCI's and shallow $Z=1$ impurities, respectively. This yields new upper limits of 1.5×10^{11} cm^{-3} and 1.6×10^{11} cm^{-3} for $Z=\frac{1}{3}$ and $\frac{2}{3}$ acceptorlike impurities, respectively. Together with Eqs. (7) and (10), we used the form of the spectral intensity distribution of the radiation from the interferometer, as determined by van der Werf,[41] and we assumed that nearly all shallow impurities are in the ground state.

Therefore, we conclude that this particular sample contained less than about 1.5×10^{11} acceptorlike FCI's, corresponding to less than one fractional charge per 2×10^{13} nucleons. This number cannot easily be related to the cosmic abundance of fractional charge,[4] since one does not *a priori* know the influence of the chemical purification process, zone refining, and crystal growth on the concentration of possibly present FCI's (Sec. II).

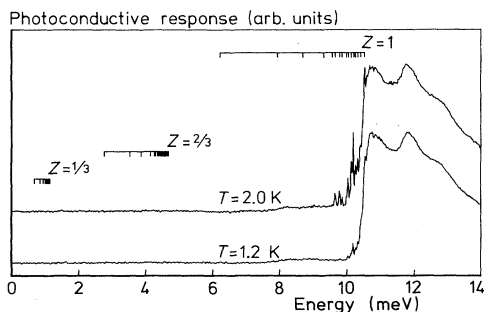

FIG. 9. Measured photoconductivity spectrum of a monocrystalline germanium sample ($N_A - N_D = 2\times10^{11}$ cm^{-3}, $K=0.4$) at 1.2 and 2.0 K.

V. MINIMAL DETECTABLE CONCENTRATION OF FCI'S BY PTIS

We want to discuss now the limits of the detectable concentration of FCI's by PTIS. First this will be done for the typical experimental arrangement as described in the preceding section. Then we will discuss possibilities to lower this limit.

If we want the FCI's to be detectable by PTIS at all, the concentration of majority FCI's should exceed the concentration of compensating impurities. If this condition is fulfilled, the minimal detectable concentration N_{min} is determined by the generation-recombination noise, originating from transitions of carriers from and towards normal ($Z=1$) shallow majority impurities, D^- or A^+ centers, or majority FCI's. The first type of noise can be reduced to a large extent by the application of an absorption filter with a cutoff energy E_{max} well below $E_{i,1}$ and the choice of a low enough temperature. Then all the normal shallow majority impurities can be considered to be in their ground state. The second type of noise is associated with D^- or A^+ centers, where an extra electron or hole is attached to a neutral shallow donor or acceptor, respectively. The degree of ionization of these centers can also be described by a critical concentration β/α and, more specifically, the critical concentration associated with thermal ionization is described by a formula just like Eq. (4). At certain T the actual value of this concentration is mainly determined by the ionization energy of the D^- or A^+ center. The analogy with the H^- ion predicts for the ionization energies $0.055E_{i,1}$, which implies about 0.5 meV in germanium.[42] The actual binding energies depend on the concentration and the chemical identity of the centers, the temperature, background radiation, and, e.g., electric field applied.[43–45] From the results of experimental work[43,44,46] we estimate the binding energies of A^+ or D^- centers in ultrapure germanium to be about 0.5—0.75 meV at low temperatures. Hence only a small fraction of the D^- or A^+ states remains in the ground state at temperatures above 0.75 K. Therefore, in a small temperature range—around 1 K—the problem of finding N_{min} for FCI's is reduced to that for a semiconductor with one type of majority impurity, which was dealt with in Sec. III.

For this situation N_{min} for $Z=\frac{1}{3}$, $\frac{2}{3}$, and 1 acceptorlike impurities is calculated for three different temperatures, the result of which is given in Table I. Here, in Eq. (14), we used the typical set of parameters $A=1$ cm^2, $V=1$ cm^3, $K=0.5$, and $\Delta f=0.1$ Hz. For each value of Z the additional monochromatic light was assumed to have an energy $E=E_{i,Z}$ and an associated photon flux I at that energy, typical for our spectrometer within a bandwidth of 0.1 meV.[41] The values for $\sigma_{i,Z}$ and α_Z were tak-

TABLE I. Minimal detectable concentrations of normal acceptors and FCI's with $Z=\frac{1}{3},\frac{2}{3}$ in p-type germanium for several temperatures under experimental conditions, described in Sec. IV.

T (K)	$N_{\min}(Z=1)$ (cm^{-3})	$N_{\min}(Z=\frac{2}{3})$ (cm^{-3})	$N_{\min}(Z=\frac{1}{3})$ (cm^{-3})
0.75	5×10^{6}	7×10^{6}	3×10^{7}
1.0	6×10^{6}	9×10^{6}	3×10^{8}
2.0	1×10^{7}	1×10^{7}	3×10^{11}

en from Figs. 5 and 6, taking into account their particular Z dependence. From Fig. 4 the highest of two possible values for β/α was chosen, corresponding to the dominating ionization mechanism, thermal or by background radiation, for a certain value of Z and T.

The values for $N_{\min}$, given in Table I, have to be considered as to give only an order of magnitude, in view of the approximations made. For $Z=\frac{2}{3}$ and 1 $N_{\min}$ is determined by ionization by background radiation. For $Z=\frac{1}{3}$ and temperatures above 1 K, however, $N_{\min}$ is determined by the process of thermal ionization. For the situation where background radiation is the dominating cause of ionization all values of $N_{\min}$ have the same order of magnitude, which is surprising in view of the different Z dependence of the components of Eq. (14). We can conclude that at temperatures that are low enough—under the conditions outlined above—one should be able to detect about 10^{7} acceptorlike majority FCI's per cm^{3} in germanium with PTIS, using a conventional Michelson interferometer. In view of the similar behavior of shallow donor impurities this should also apply to majority donor FCI's.

If one believes that the successful observation of third-integral charge in little niobium balls at helium temperatures by LaRue, Fairbank, and Hebard was caused by one fractional charge only, this corresponds to a concentration of fractional charge of 1 in 5×10^{19} nucleons. Assuming the same concentration in Ge, this would correspond to 6×10^{4} FCI's per cm^{3}. Therefore, it would be preferable to lower the limit of 1×10^{7} detectable FCI's with PTIS.

Ultrapure germanium, probably the purest substance produced by man, can easily be produced nowadays with shallow impurity concentrations down to 10^{9} cm^{-3}, but going to lower concentrations one meets technical problems.[23] Any normal purification method in a semiconductor will also reduce the number of FCI's. Chemical techniques in the early stages of purification strongly select against ions which FCI's always are. As already mentioned in Sec. II the least removal of FCI's may be accomplished by melt-segregation techniques such as zone refining. In view of this it would be preferable to relax the condition that the concentration of majority FCI's should exceed the concentration of minority impurities if one wants to be able to detect the FCI's with PTIS. This can be achieved by illuminating the semiconductor sample continuously with additional intrinsic light, i.e., radiation containing energies greater than the gap energy of the semiconductor.[47] A fraction of the minority impurities will return to the ground state again. This means that the minority impurities, and thus also minority FCI's, if present, can also be detected by PTIS! Moreover, a fraction of the formerly ionized majority FCI's becomes detectable by PTIS. Application of intrinsic light, however, gives rise to additional noise, due to electron-hole recombination and also influences the free carrier lifetime, making a new estimate for $N_{\min}$ too complicated.

At very low temperatures the values of $N_{\min}$ are determined by the intensity of the background radiation. The application of an optical bandpass filter, which transmits only radiation with energies around $E_{i,Z}$, reduces the value of β/α, associated with background radiation. Then substantial improvement can be achieved if the Fourier spectrometer with its low-intensity broadband source (typically ≤ 0.01 μW within a bandwidth of 0.1 meV) is replaced by a more intense monochromatic source. With, e.g., a far-infrared laser or a harmonic generator[48] this can lead to detectable concentrations of FCI's of 10^{5} cm^{-3} (corresponding to one fractional charge per 10^{19} nucleons) or even lower. If, in addition, intrinsic light is applied simultaneously, the constraint posed by the minority impurities is also released.

VI. CONCLUSIONS

We can conclude that the PTIS technique is a very useful tool for the detection of possible FCI's in semiconductors. If the number of compensating impurities is smaller than the number of FCI's, PTIS can detect down to 10^{7} FCI's per cm^{3}—if present—with the experimental arrangement used, including a far-infrared Michelson interferometer. The application of intrinsic light, which releases the condition concerning compensating impurities, and the use of, e.g., a far-infrared laser source can lower the concentration of detectable FCI's down to 10^{5} FCI's cm^{-3} (i.e., one fractional charge per 10^{19} nucleons) or even lower. From the absence of a PTIS signal, originating from FCI's in a p-type germanium sample, we conclude that this sample contained less than 1.5×10^{11} acceptorlike FCI's per cm^{3}.

ACKNOWLEDGMENT

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

APPENDIX: DETERMINATION OF A NUMERICAL VALUE FOR β

In germanium the concentration of ionized impurities N^{i} at temperatures below 10 K is in principle determined by three factors: the concentration of compensating impurities KN, thermal ionization, and ionization by background radiation. In this appendix a numerical value for

β will be derived for the situation that N^i, apart from its dependence on KN, is mainly determined by the intensity of the background radiation reaching the sample through a filter with cutoff energy $E_{\max,1}=2E_{i,1}$. This value will be obtained for the experimental arrangement, described in Sec. IV, and a p-type sample with $N=3.3\times10^{11}$ cm^{-3} and $K=0.4$.

For this purpose we determine the free carrier concentration n at 4.2 K, by measuring the resistance R_s of the sample and using the relation $n=G/e\mu R_s$, where μ is the mobility for holes and G a geometrical factor. From $G=1.0$ cm^{-1} for this sample, $R_s=640$ Ω and $\mu=1.1\times10^5$ cm^2 V^{-1} sec^{-1} (Ref. 49) at 4.2 K, one obtains $n=4.4\times10^8$ cm^{-3}. From Fig. 3 one can see that this corresponds to $\beta/\alpha=5\times10^8$ cm^{-3}. Using the value for α at 4.2 K, obtained from Fig. 6, this finally leads to $\beta=7.5\times10^3$ sec^{-1}.

In our experimental arrangement we used a crystalline quartz filter with a cutoff energy $E_{\max}=27$ meV. For this experimental situation $E_{\max,1}=2.6E_{i,1}$, using the ionization energy 10.5 meV for the boron impurity. Therefore, $\beta=5\times10^3$ sec^{-1} for $E_{\max,1}=2E_{i,1}$. Regarding the approximations we feel this value to be right within a factor of 2.

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