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The role of impurity correlation in Auger recombination in heavily doped semiconductors

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Abstract. A theory has been developed for describing the influence of correlation in the impurity distribution on Auger processes in heavily doped semiconductors. The case when correlation exists because of Coulomb interactions between charged donors and acceptors as well as free carriers during the thermal preparation of the sample is considered. Taking into account both high-temperature ionic correlation and low-temperature electronic screening, the analytic dependence of the mean square of the impurity potential fluctuations on experimental conditions such as the doping concentration, compensation and excitation levels, temperature and growth condition of the sample is obtained. It is shown that for strongly compensated semiconductors the Auger coefficient may be, owing to the impurity correlation, diminished considerably by up to several orders of magnitude at heavy doping ($5 \times 10^{18} \text{ cm}^{-3}$ or above) and low excitation (below 10^{16} cm^{-3}). Moreover, the correlation effect in wide-band-gap materials is found to be far larger than that in narrow-band-gap materials.

1. Introduction

Auger recombination seems to be one of the most effective radiationless recombination mechanisms of carriers in semiconductors (Beattie and Landsberg 1959, Landsberg 1970, Robbins 1980a, b, c), especially in heavily doped semiconductors (Benz and Conradt 1977, Takeshima 1981, 1982, 1983, Quang 1990b). The heavy-doping region is of practical interest in view of the current use of high impurity concentrations in semiconductor devices. The theoretical investigations by Takeshima (1981) and Quang (1990b) have shown that the random field created by chaotically spaced impurities may give rise to strong enhancement of the Auger recombination in these materials.

However, it should be remarked that in the above-mentioned theories of Auger recombination it was usually assumed that the impurities are absolutely randomly spaced in the sample, i.e. their sites are independently distributed (Kohn and Luttinger 1957). In fact, it is well known that this assumption is not always realized, e.g. when the sample undergoes thermal treatment. Indeed, Keldysh and Proshko (1964) have indicated that there does exist some correlation in the distribution of impurities due to Coulomb interactions in the plasma consisting of ionized impurities and free carriers in the melt prior to solidification of the sample. This high-temperature correlation has been shown to be able to change significantly the characteristics of the random impurity field present in the system (Keldysh and Proshko 1964, Rogachev and Sablina 1966). This leads to an appreciable change in the electronic energy spectrum and, in particular, to a different

asymptotic behaviour of the density of states compared with the case of a random impurity distribution (Shklovskii and Efros 1970, Galpern and Efros 1972). It is also well known that the correlation-induced modification of the electronic energy spectrum is essential for quantitative interpretation of experimental data on the observable properties of heavily doped semiconductors, e.g. optical properties (Keldysh and Proshko 1964, Rogachev and Sablina 1966) and transport phenomena (Galpern and Efros 1972, Arnaudov *et al* 1979, Yanchev *et al* 1979). On the other hand, according to the theoretical considerations of Quang (1989, 1990a, b), Auger recombination taking place in non-crystalline systems is, in general, influenced strongly by the random field causing the disorder, depending exponentially on the mean square of the potential fluctuations. So the impurity correlation is expected to be of great importance in connection with this radiationless transition.

The goal of the present paper is to study the effect of the impurity correlation on Auger processes in heavily doped semiconductors. The consideration will be restricted to the case of high-temperature correlation. In section 2, the formulae to be used for calculating the influence of a random impurity field on Auger processes are gathered. Evaluation of the potential correlation function of interest proceeds in section 3, taking account of the ionic correlation and the electronic screening as well. In section 4, a discussion of the role of the impurity correlation in Auger transition is given for the case of strongly compensated samples. Plots and conclusions are presented in section 5. Finally, some concluding remarks are given in section 6.

2. Basic relations

We are dealing with Auger processes of non-equilibrium carriers in a heavily doped semiconductor. The condition for heavy doping is

$$N_I^{-1/3} \ll a_B \quad (1)$$

where $N_I = N_D + N_A$ means the total impurity concentration, $a_B = \kappa \hbar^2 / m e^2$ is the Bohr radius in the host crystal, with e being the electron charge, m the effective mass, and κ the static dielectric constant. It was pointed out (Bonch-Bruevich 1966, Bonch-Bruevich *et al* 1984) that, if the inequality (1) is fulfilled, the total impurity field varies slowly on the average in space so that a semiclassical approach to it may be applicable.

Then, by developing a Green function formalism, Quang (1989) has been able to prove that in the purely classical approximation the reciprocal lifetime of Auger recombination in a random field may be represented in the form of the volume and configuration average of a local reciprocal lifetime:

$$\frac{1}{\tau} = \left\langle \frac{1}{V} \int dR \frac{1}{\tau(R)} \right\rangle \quad (2)$$

with V as the sample volume. Here $\tau(R)$ is the lifetime of a local Auger transition occurring at the point R and is given by the expression of the Auger lifetime for the appropriate crystalline material, however, now with the band edges of the conduction and valence bands being bent because of random potential fluctuations. This means that, in order to get $\tau(R)$, we need only to replace in the no-field expression of the Auger lifetime (Haug 1972, Haug *et al* 1978) the usual dispersion relation $\epsilon_i(k)$ for an electron in the Bloch state $\lambda = |k\rangle$ by

$$E_\lambda(R) = \epsilon_i(k) + U(R) \quad (3)$$

where $U(R)$ is the potential energy of an electron moving in the total impurity field.

The impurity potential is known to be independent of the band index so that the band gap still remains as constant over all the sample despite random fluctuations of the band edges of the conduction and valence bands. This potential is, as usual, normalized by the charge neutrality condition of the sample:

$$\langle U \rangle = 0. \quad (4)$$

The angular brackets stand for ensemble averaging over all impurity configurations.

Equation (2) was found to be taken as the basis for study of Auger recombination in those disordered semiconductors that can be described by the smooth random field model (Quang 1990a, b, c).

In what follows, we shall confine the discussion to the case of small fluctuations in impurity concentrations. Then, the field in question is Gaussian irrespective of whether an impurity correlation exists or not (Galpern and Efros 1972). Accordingly, the random field can be completely characterized by the binary correlation function of the impurity potential (Bonch-Bruевич *et al* 1984):

$$\Psi(\mathbf{r} - \mathbf{r}') = \langle U(\mathbf{r})U(\mathbf{r}') \rangle. \quad (5)$$

Thus, the configuration average in (2) is well known to be given in terms of the mean square of the impurity potential:

$$\psi_1 = \Psi(0) = \langle U^2 \rangle. \quad (6)$$

As a result, for various recombination processes in heavily doped semiconductors, analytic expressions of the Auger coefficients may be derived whose form is found to depend upon the compensation degree and the excitation level of the sample as well (Quang 1990b). Therefore, to be specific we shall consider a closely compensated sample for which both electrons and holes make up non-degenerate gases with Boltzmann statistics. Then, we may arrive at the following relationship between the Auger coefficients C and C_0 for a strongly compensated heavily doped semiconductor with and without the random impurity field, respectively (Quang 1989):

$$C/C_0 = \exp(\psi_1/2T^2) \quad (7)$$

T being the sample temperature in units of energy.

The ratio of Auger coefficients may be clearly referred to as a measure of the impurity-field effect on the Auger transition in the sample. It is worthwhile noting that in the case under consideration this ratio is evidently seen to be independent of the band structure of the semiconductor. It has been indicated that the band-structure dependence of the Auger coefficient ratio can be obtained if at least one of the carrier gases becomes degenerate (Quang 1990b) or the band gap of the material fluctuates when the band edges of the conduction and valence bands are differently bent (Quang 1990a). Moreover, equation (7) is valid both for conduction band processes due to electron-electron collision as well as valence band processes due to hole-hole collision.

3. Correlated impurity distribution

Now let us turn to calculating the binary correlator of the impurity potential $\Psi(\mathbf{r})$, taking explicitly into account correlation in the distribution of impurities. We assume that heavily doped semiconductors are obtained by pulling from the melt. So, prior to solidification of the sample, it may be viewed as a plasma consisting of the following

charged particles: ionized donors and acceptors of average concentrations N_D and N_A , respectively, intrinsic electrons and holes of equal average densities $n_i = p_i$ and finally, extrinsic free carriers of density $n_e = |N_D - N_A|$ arising from doping. In the high-temperature plasma, these particles screen each other via Coulomb interactions, which obviously exerts a great influence on the probability of formation of impurity configurations. After solidification, there are in the sample at lower temperatures, besides the extrinsic carriers, also excess electrons and holes created by sample excitation and of equal average densities $\delta n = \delta p$. The total density of non-equilibrium carriers is then

$$n = n_e + 2 \delta n. \quad (8)$$

Only these carriers undergo Auger recombination and, at the same time, screen the electron potential energy produced by a given configuration of impurities.

Therefore, our underlying assumptions concerning the screening of the impurity field are as follows.

(i) *High-temperature screening.* According to the idea of Keldysh and Proshko (1964), the impurity distribution in the sample may be considered as a snapshot of the distribution in the plasma consisting of ionized impurities and free carriers which existed at the temperature T_0 when the impurity diffusion had been frozen out. Then, the probability that the fluctuations of the charge densities associated with ionized impurities and free carriers have a given configuration $\{\xi(r), \varphi(r)\}$ is proportional to $\exp(-\Omega\{\xi, \varphi\})$. For the case of Gaussian distribution, the following holds (Galpern and Efros 1972):

$$\Omega\{\xi, \varphi\} = \frac{1}{2(N_D + N_A)} \int dr \xi^2 + \frac{1}{2(2n_i + n_e)} \int dr \varphi^2 + \frac{e^2}{2kT_0} \int dr dr' \frac{[\xi(r) + \varphi(r)][\xi(r') + \varphi(r')]}{|r - r'|} \quad (9)$$

where the charge-density fluctuations of impurities and of free carriers are such that

$$\xi(r) = N_D(r) - N_D - [N_A(r) - N_A] \quad (10)$$

$$\varphi(r) = p_i(r) - n_i(r) \pm [n_e(r) - n_e]. \quad (11)$$

Hereafter, the upper sign refers to a p-type sample, and the lower to an n-type sample. It is to be noted that the last term in equation (9) describes the above-quoted correlation in the high-temperature plasma. This term is suggested to result in a significant decrease in the probabilities of large fluctuations in the impurity concentration (Rogachev and Sablina 1966).

The configuration-averaged value of any observable quantity may be represented by the use of equation (9) in terms of a path integral, i.e.

$$\langle A \rangle = \int \mathcal{D}\xi \mathcal{D}\varphi \exp(-\Omega\{\xi, \varphi\}) A\{\xi, \varphi\} / \int \mathcal{D}\xi \mathcal{D}\varphi \exp(-\Omega\{\xi, \varphi\}) \quad (12)$$

where $\mathcal{D}\xi \mathcal{D}\varphi$ means the Feynman measure on the functional space of charge-density fluctuations of impurities and free carriers $\{\xi, \varphi\}$.

(ii) *Low-temperature screening.* For a given configuration of the impurities, the electron potential energy is to be determined in accordance with the semiclassical treatment by the usual Poisson equation (Shklovskii and Efros 1972):

$$\Delta U = (4\pi e^2/\kappa) \{\xi(r) + \delta p(r) - \delta n(r) \pm [n_e(r) - n_e]\} \quad (13)$$

in which the field source consists of both the fluctuation of the charged-impurity concentration and that of the non-equilibrium carrier density as well. This implies that the Fourier transform of the impurity potential is to be taken in the form

$$u_q = (4\pi e^2/\kappa) [\xi_q / (q^2 + r_0^{-2})]. \quad (14)$$

Here ξ_q means the corresponding Fourier transform of the excess impurity charge

density, and r_0 is the electronic screening length due to the non-equilibrium carrier density.

Now recall that the correlator of the impurity potential can be given in terms of its Fourier transform (Bonch-Bruевич *et al* 1984) as

$$\Psi(\mathbf{r} - \mathbf{r}') = \frac{1}{2} \sum_q \langle u_q^2 \rangle \cos[\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')]. \quad (15)$$

Next, on the basis of equation (12), we are in a position to evaluate the Fourier transform of the density correlator $\langle \xi(\mathbf{r}) \xi(\mathbf{r}') \rangle$ with the aid of the standard method applying to Gaussian functionals (see, e.g., Itzykson and Zuber 1985). The result is (Galpern and Efros 1972) that

$$\langle \xi_q^2 \rangle = (2N_I/V) [(q^2 + r_c^{-2}) / (q^2 + r_c^{-2} + R_c^{-2})]. \quad (16)$$

Here we have introduced the correlation lengths R_c and r_c connected with the ionized impurities and the free carriers, respectively, which existed in the sample at the freeze-out temperature T_0 for impurity diffusion:

$$R_c = (\kappa T_0 / 4\pi e^2 N_I)^{1/2} \quad (17)$$

$$r_c = (\kappa T_0 / 4\pi e^2 (2n_i + n_c))^{1/2} \quad (18)$$

with n_i depending on T_0 : $n_i = n_i(T_0)$.

Now, inserting equations (14) and (16) into (15) we may write the following Fourier representation for the impurity potential correlator:

$$\Psi(\mathbf{r}) = \int \frac{d\mathbf{q}}{(2\pi)^3} \psi(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) \quad (19)$$

with

$$\psi(\mathbf{q}) = N_I (4\pi e^2 / \kappa)^2 [1 / (q^2 + r_0^{-2})^2] [(q^2 + r_c^{-2}) / (q^2 + r_c^{-2} + R_c^{-2})]. \quad (20)$$

It is interesting to note that the Fourier transform of the potential correlator given by equation (20) involves two factors: the first term associated with the electronic screening of the random field created by a given impurity configuration, and the second term connected with the influence of impurity correlation on the probability for this configuration. This equation differs from the relevant expressions adopted by Galpern and Efros (1972) and Yanchev *et al* (1979) in the explicit presence of the electronic screening length r_0 in the first factor. Consequently, the integral (19) turns out to be convergent at small wavevectors ($\mathbf{q} \rightarrow \mathbf{0}$) so that we ought not to invoke any cut-off in wavevector space. Then, the evaluation of the potential correlator is straightforward, yielding

$$\Psi(\mathbf{r}) = \Psi_R(\mathbf{r}) - \Psi_c(\mathbf{r}). \quad (21)$$

Here the first term stands for the potential correlator in the case of random impurity distribution and is, as usual, given by (Bonch-Bruевич *et al* 1984)

$$\Psi_R(\mathbf{r}) = (2\pi e^4 N_I r_0 / \kappa^2) \exp(-r/r_0) \quad (22)$$

and the second term is the correction owing to impurity correlation:

$$\Psi_c(\mathbf{r}) = \{\Psi_R(\mathbf{r}) / [1 + (R_c/r_c)^2 - (R_c/r_0)^2]\} \times [1 - \{2(R_c/r_0)/(r/R_c)[1 + (R_c/r_c)^2 - (R_c/r_0)^2]\} [1 - \exp(r/r_0 - r\sqrt{1 + (R_c/r_c)^2}/R_c)]]]. \quad (23)$$

Finally, we return to the mean-square potential fluctuation ψ_1 defined by equation (6). With the help of equations (21)–(23), we get the following relation:

$$\psi_1 = \psi_1^R - \psi_1^c \quad (24)$$

in which ψ_1^R and ψ_1^c , respectively, denote the correlationless value and the correlation-induced correction to the random parameter:

$$\psi_1^R = 2\pi e^4 N_I r_0 / \kappa^2 \quad (25)$$

$$\psi_1^c = \psi_1^R / [(R_c/r_0) + \sqrt{1 + (R_c/r_c)^2}]^2. \quad (26)$$

It is clear from equation (24) that the impurity correlation is found to decrease the mean-square potential fluctuation $\psi_1 < \psi_1^R$. The reason lies in the fact that, as indicated before, this correlation decreases the probability of large fluctuations in the impurity concentration and, therefore, in the electron potential energy as well. In addition, according to equation (26) the effect of the impurity correlation depends on its relative comparison with the electron correlation and the electronic screening as well.

To end this section, we shall consider the two opposite limiting cases.

(a) *Strong impurity correlation.* If the impurity correlation length is small compared both with the electronic screening length and with the electron correlation length:

$$R_c \ll r_0 \quad R_c \ll r_c \quad (27)$$

then $\psi_1^c = \psi_1^R$, and hence $\psi_1 = 0$. This means that in the present case the correlation between impurities becomes so strong that it screens almost completely the long-range fluctuations in impurity concentration, which lead to a vanishingly small value of the random parameter. Furthermore, the second inequality in (27) implies that

$$n_c \ll N_I \quad n_i(T_0) \ll N_I \quad (28)$$

i.e. the strong correlation may be realized only in closely compensated heavily doped samples with wide band gap.

(b) *Weak impurity correlation.* In the opposite case, the impurity correlation length is large in comparison with at least one of the screening and correlation lengths due to free carriers:

$$R_c \gg r_0 \quad R_c \gg r_c. \quad (29)$$

Then $\psi_1^c \ll \psi_1^R$, and hence $\psi_1 \approx \psi_1^R$. So, the correlation can simply be neglected. Thus, we are able to generalize the statement made by Galpern and Efros (1972) in a sense that participation of the free carriers in not only high-temperature correlation but also low-temperature screening will extend the applicability domain of the theory based on random impurity distribution. It is worth noting that, contrary to our above considerations, the correlated value of the mean-square potential energy used by Yanchev *et al* (1979) (their equation (7)) cannot be reduced to the conventional correlationless value when neglecting the impurity correlation ($R_c \gg r_0$). Moreover, the second condition in (29) implies that

$$n_i(T_0) \gg N_I \quad (30)$$

i.e. the correlation becomes of less importance in moderately doped samples with narrow band gap.

4. Effect of impurity correlation on Auger transitions

Now we apply the theory developed in the preceding sections to study the role played by impurity correlation in recombination processes occurring in heavily doped semi-

Table 1. Material parameters used.

Parameter (units)	GaAs	InSb
Band gap at 300 K (eV)	1.426	0.180
Temperature coefficient (10^{-4} eV K $^{-1}$)	-3.90	-2.75
Effective mass, electron (m_0)	0.067	0.014
Effective mass, heavy hole (m_0)	0.45	0.4
Static dielectric constant	13.18	17.72
Freeze-out temperature (K)	1000	700

conductors. As quoted above, we shall be concerned with a strongly compensated sample: $n_c \ll N_1$, for which the effect of the random impurity field on Auger transitions is described by equation (7).

Upon putting equation (24) into equation (7), we may immediately derive the following expression for the Auger coefficient when the correlation is taken into consideration:

$$C^R/C = \exp(\psi_1^c/2T^2) \tag{31}$$

where C and C^R denote the Auger coefficients for the sample in question with correlated and random impurity distributions, respectively, and ψ_1^c is, as before, the correlated part of the mean-square potential fluctuation provided by equation (26).

From the equation just obtained, we can easily come to the conclusion that impurity correlation reduces the recombination rate compared with the case of uncorrelated impurity distribution. This is clear if we bear in mind that the correlation causes a decrease in the mean-square potential fluctuation. The Auger coefficient is shown to fall exponentially with increase in the correlated part ψ_1^c . In addition, the correlation effect will evidently be of more importance at low temperatures.

Next, we recall that, for non-degenerate carrier statistics, r_0 is given as the Debye-Hückel screening length:

$$r_0 = (\kappa T/4\pi e^2 n)^{1/2} \tag{32}$$

with n defined by equation (8).

By replacing the screening lengths R_c , r_c and r_0 entering equation (26) with equations (17), (18) and (32), respectively, and then inserting the resulting equation into (31), we can finally find the following expression:

$$\frac{C^R}{C} = \exp((\pi^{1/2} e^3/2\kappa^{3/2}) \llbracket N_1/n^{1/2} T^{3/2} \{ (nT_0/N_1 T)^{1/2} + [1 + (2n_i/N_1)]^{1/2} \}^2 \rrbracket). \tag{33}$$

This describes the influence of impurity correlation on Auger processes in a closely compensated heavily doped semiconductor. So, it follows from equations (33) and (8) that the correlation effect is, in general, found to depend strongly on such experimental conditions as the doping concentration, compensation and excitation levels, temperature and growth condition of the sample as well.

5. Numerical results and conclusions

In order to get quantitative estimates, we chose GaAs and InSb as testing substances with material parameters compiled in table 1 (Neuberger 1971). There, to estimate

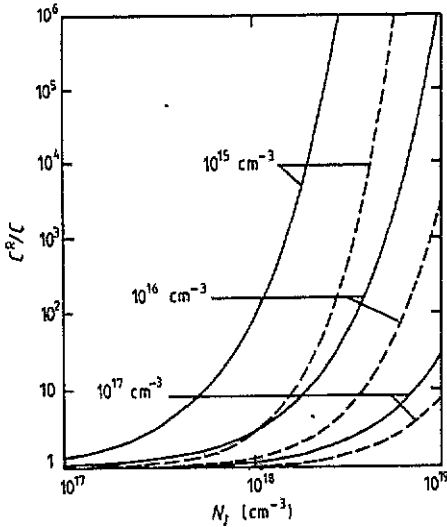


Figure 1. Ratio C^R/C of the Auger coefficients corresponding to the random and correlated distributions of impurities in GaAs (—) and InSb (---) against impurity concentration N_I at a temperature of 300 K for the various excitation densities δn indicated on the curves.

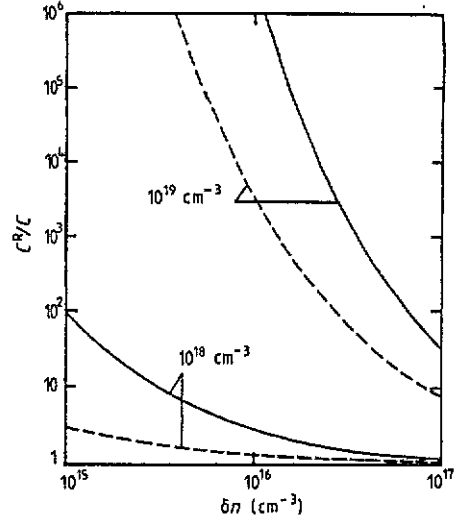


Figure 2. Ratio C^R/C defined as in figure 1 versus excitation density δn at temperature of 300 K for the different impurity concentrations N_I indicated on the curves.

the density $n_i(T_0)$ of intrinsic free carriers at the freeze-out temperature for impurity diffusion, we took account of the temperature dependence of the band gaps by linear extrapolation of their values at room temperature with the experimental values of the temperature coefficients found in Camassel and Auvergne (1975). The freeze-out temperature was reported by Arnaudov *et al* (1979) for GaAs (doped with Te and Ge), and by Galpern and Efros (1972) for InSb.

We have carried out numerical calculations of the Auger coefficient ratio C^R/C determined by equation (33) for the case when the compensation becomes so strong that the extrinsic carrier density is small compared with the excitation density, giving $n = 2 \delta n$. This ratio was plotted as a measure of the impurity correlation effect on the Auger recombination at room temperature ($T = 300$ K) in the impurity concentration range from 10^{17} to 10^{19} cm^{-3} and the excitation density range from 10^{15} to 10^{17} cm^{-3} . Figure 1 shows the dependence of the ratio C^R/C on impurity concentration for various excitation levels (10^{15} , 10^{16} and 10^{17} cm^{-3}), whilst in figure 2 it is sketched against excitation density for different doping levels (10^{18} and 10^{19} cm^{-3}). The full curves refer to the sample based on GaAs, and the broken curves to that on InSb.

From the results thus obtained, we may draw the following conclusions

(i) As seen from figure 1, the influence of impurity correlation proves to increase rapidly when elevating the doping level, and the Auger coefficient may be reduced by up to several orders of magnitude at high impurity concentrations (about $5 \times 10^{18} \text{ cm}^{-3}$ or above) and, in particular, with low excitation (less than 10^{16} cm^{-3}). On the contrary, at lower impurity concentrations $N_I \leq 10^{17} \text{ cm}^{-3}$, the impurity correlation is almost completely eliminated by free carriers with the densities used.

(ii) Following figure 2, the ratio C^R/C is shown to exhibit a rapidly decreasing function of excitation level. At high excitation levels (about 10^{17} cm^{-3} or above), the correlation effect is considerably diminished owing to a drastic increase in the electronic screening of the impurity field; in particular it may be almost omitted with moderate doping (about 10^{18} cm^{-3} or less).

(iii) A comparison of the full and broken curves indicates that, at equal levels of doping and excitation, the impurity correlation effect in GaAs is, generally, considerably stronger than that in InSb. This can be allowed for as follows. InSb is well known to have a remarkably narrower band gap so that the density of intrinsic free carriers in the plasma existed prior to solidification of the sample becomes much larger, which is far more efficient in reducing the impurity correlation as quoted above.

6. Concluding remarks

It is well known that, in the classical approach adopted here to the random impurity field when all forces arising from the field are neglected, the electron momentum conservation requirement does not break down and the influence of the field is reduced simply to gradual random bending of the band edges of the conduction and valence bands as seen evidently in equation (3) (Bonch-Bruевич 1973). Accordingly, in equation (2) for the reciprocal Auger lifetime, which has been derived from a general equation containing the Green functions for electrons moving in the field by dropping all derivatives of the impurity potential, only the energy-conserving δ -function and the carrier distribution functions are found to be modified, whereas the overlap integrals and the momentum-conserving δ -function still remain unaffected (Quang 1989). If the quantum corrections involving these derivatives are to be taken into account, e.g. when both electron and hole gases become degenerate (Quang 1990b), the electron momentum is no longer a good quantum number and the overlap integrals could be considerably altered by the impurity field. As a consequence, they could be significantly modified by the presence of impurity correlation so that taking the ratio of Auger coefficients may not cancel this out as in the case of classical approximation.

It should be emphasized that our calculation of the effect of impurity correlation on Auger recombination has been performed for the case of closely compensated semiconductors. This correlation is also believed to exert some influence on Auger transitions in slightly compensated samples and will be examined in a forthcoming paper (Quang 1991).

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