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# Enhanced Diffusion of Impurities and Defects in Crystals in Conditions of Ultrasonic and Radiative Excitation of the Crystal Lattice

By

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On the basis of the quantum theory of diffusion the influence of crystal lattice excitations (ultrasonic, nuclear irradiation) on the diffusion of impurity atoms is analysed. The effects considered in the paper are determined by two factors: the change of population of the impurity oscillator levels due to interaction with nonequilibrium excitations of the crystal lattice, and the change of the probability of diffusion transitions on the given level. The effects are qualitatively different for heavy impurity atoms whose diffusion is enhanced in nonequilibrium conditions and for light impurity atoms for which the effect of additional localization is possible.

На основе квантовой диффузии проведен анализ влияния возбуждений кристаллической решетки (ультразвук, ядерное облучение) на диффузию примесных атомов. Рассмотренные в работе эффекты определяются двумя факторами: изменением заселенностей уровней примесного осциллятора, благодаря взаимодействию с неравновесными колебаниями кристаллической решетки, и изменением вероятности диффузионного перехода по данному уровню. Эффекты качественно различны для тяжелых примесных атомов, диффузия которых ускоряется в неравновесных условиях, и для легких примесей, для которых возможен эффект дополнительной локализации.

## 1. Introduction

The problem of the influence of crystal lattice excitations on the diffusion of impurities and other point defects was considered in several theoretical and experimental papers [1 to 8]. Convincing evidences of the essential influence of crystal lattice excitations (ultrasound (US), nuclear irradiation (NI), laser irradiation, and others) on point defect diffusion in crystals were obtained in experiments [1, 7, 8]. In spite of this, the theoretical works, in our opinion, suffer from serious shortcomings and, in general, do not describe the experimental results.

The general conception of interaction of impurity atoms and point defects, which move under the influence of US, with dislocations was developed in [1]. Such a mechanism of US influence on diffusion can occur, without any doubts, in sufficiently strong US waves. In spite of this, such a mechanism is not realized in a relatively weak US wave when the strain in the wave does not exceed the limit of fluidity of the material.

Paper [6] devoted to the study of the influence of relatively weak US on impurity atom migration assumes that the system of impurity atoms is an equilibrium bath with respect to the phonon subsystem which is removed from the equilibrium state. The impurity atoms absorb the energy of nonequilibrium phonons, and this energy is identified with a decrease

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of the activation energy of migration. The estimations of [6] show that this decrease is essential and can lead to a noticeable acceleration of impurity diffusion.

The real situation is contrary to that: the phonon system is a nonequilibrium bath, and the impurity atom continuously exchanges energy with phonons. We cannot identify the energy transferred to the impurity atom with the decrease of activation energy because this energy returns to the phonon thermostat in a time of the order of $10^{-12}$ s. Moreover, one cannot introduce the term 'activation energy' which is defined by the height of the barrier, because the distribution function of impurity atoms on vibration levels in the well is no more a Boltzmann function. Only the part of activation energy connected with the energy transfer of lattice deformations [9, 10] is maintained. However, this part of activation energy is also modified by the presence of nonequilibrium phonons, and one can introduce the concept of an effective temperature for this part of the activation exponent. cf. [3 to 5].

The problem of the influence of nonequilibrium lattice vibrations, which are excited under the influence of irradiation of different types [2 to 5] (laser or nuclear radiation), on point defect diffusion is closely connected with the question of US effects. The difference between these processes consists in intensity and shape of the spectra of excited nonequilibrium phonons.

In this paper, in the framework of the quantum theory of diffusion, we are considering the influence of nonequilibrium lattice vibrations on the point defect diffusion in crystals and the degree of this influence for the case of US waves will be estimated.

According to the general theory of diffusion [9, 10] the coefficient of diffusion of impurity atoms is written in the form

$$D = \sum_l P(l)\, D_l, \tag{1}$$

where $P(l)$ is the population of vibration level $l$ in the initial site and $D_l$ is the 'partial' diffusion coefficient on level $l$. At high temperatures the term with $l = l_m$, where $l_m$ is the number of the level nearest to the barrier top, plays the main role in $\sum_l$, so that in equilibrium conditions the activation energy is defined by the sum of the energy of level $l_m$ (the height of the barrier) and the 'polaron' activation energy connected with the lattice deformation transfer energy. Both values, $P(l)$ and $D_l$, change in the presence of nonequilibrium lattice vibrations. The following account is devoted to the analysis of these changes.

## 2. The Excitation of an Impurity Oscillator by Nonequilibrium Lattice Vibrations

The problem of the parametric excitation of an oscillator in a thermostat, and of the oscillator which interacts with an external force, was discussed extensively in the literature [11, 12]. The strict consideration of the interaction of an impurity atom with long-wave and short-wave vibrations of the crystal lattice leads to the problem of the excitation of an impurity oscillator interacting with an alternating external force and a nonequilibrium thermostat. In order to obtain the level populations of such an oscillator it is necessary to solve the equation for the density matrix of the system. The solution of this equation is different for the cases of quasilocal and local oscillators, i.e. for heavy and light impurities [13, 14]. Assuming that the phonon representation number has the form $N(\omega_s) = n(\omega_s) + N^{(1)}(\omega_s)$, where $n(\omega_s) = (\exp{(\hbar\omega_s/kT)} - 1)^{-1}$ and $N^{(1)}(\omega_s)$ is some

addition to the equilibrium value, one can obtain the following formulae for level populations of a quasilocal oscillator:

$$P(l) = \frac{1 - \xi}{1 + \delta} \frac{(\xi + \delta)^l}{(1 + \delta)^l} \exp\left(-\frac{(1 - \xi)|a|^2}{1 + \delta}\right) L_l\left(-\frac{|a|^2(1 - \xi)^2}{(1 + \delta)(\xi + \delta)}\right), \qquad (2)$$

where

$$\xi = \exp\left(-\hbar\omega_\tau/kT\right), \qquad \delta = \frac{N^{(1)}(\omega_\tau)}{n(\omega_\tau) + 1},$$

$$a = \lim_{t \to \infty} \frac{i\beta}{\hbar\sqrt{2M\omega_\tau}} \int_0^t dt'\, \varepsilon(t')\, e^{\frac{\Gamma}{2}t' + i\omega_\tau t'}\, e^{-\frac{\Gamma}{2}t},$$

$L_l(x)$ is the Laguerre polynomial, $\beta$ is defined by the linear terms of the series expansion of the interaction energy between impurity atom and matrix atoms in displacements of the impurity atom from equilibrium positions [13], $\varepsilon(t)$ is the time dependent crystal strain due to the US wave, $\Gamma$ the relaxation rate of the oscillator, $M$, $\omega_\tau$ are mass and vibration frequency of the impurity atom.

One can see from (2) that the level population of the quasilocal oscillator is defined by the degree of excitation of nonequilibrium phonons with frequency equal to that of the oscillator (to the frequency of quasilocal vibrations). One can achieve a noticeable increase of higher excited level populations (which determine the diffusion coefficient at high temperatures) under the condition $N^{(1)}(\omega_\tau) > n(\omega_\tau)$. This effect is especially noticeable at low temperatures when the above condition can be achieved at lower intensity of excitation and when the rate of oscillator relaxation is decreased appreciably. The dependence of several level populations on the values $|a|^2$ and $\delta$ are presented in Fig. 1. One can see from this figure that the 'thermostat pumping' is more effective than the pumping by the external force in the sense of a quicker increase of high level populations. The second important moment is the impossibility to obtain an inverse population of the levels in the presence of 'thermostat pumping' only.

Let us consider in detail the possibility of excitation of impurity vibrations by US waves excited in the crystal by an external force. The influence of an US wave on the phonon subsystem is reduced to the change of the phonon distribution function. Phonon–phonon interaction leads to a relaxation of the distribution function to a new distribution which is characterized by a local temperature $T'$ and by a displacement in the space of phonon wave vectors in the case of $N$-processes. Detailed calculations of these values were performed in [15] where the absorption of US by dielectrics is considered.

Let us use the results of that paper. Assuming that $\Omega\tau \ll 1$, where $\tau$ is the relaxation time, and $\tau_n/\tau_u \gg 1$, where $\tau_n$ and $\tau_u$ are the relaxation times for normal and umklapp processes, respectively (so that $\tau \approx \tau_u$), within the Debye approximation one can obtain

$$\delta = \frac{N^{(1)}(\omega_\tau)}{n(\omega_\tau) + 1} = n(\omega_\tau)\,\gamma l_0 \sigma \frac{\hbar\omega_\tau}{kT}, \qquad (3)$$

where $\gamma$ is the Grüneisen parameter, $l_0$, $\sigma$ are the amplitude and wave vector of the US wave, respectively. The value $l_0\sigma \approx 10^{-3}$ corresponds to intensity of the US wave, approximately equal to 10 to 100 W/cm$^2$. At $1 < \hbar\omega_\tau/kT < 10$, which corresponds to real parameters at moderate temperatures, $\delta \approx \xi\gamma l_0\sigma(\hbar\omega_\tau/kT) \ll \xi$.
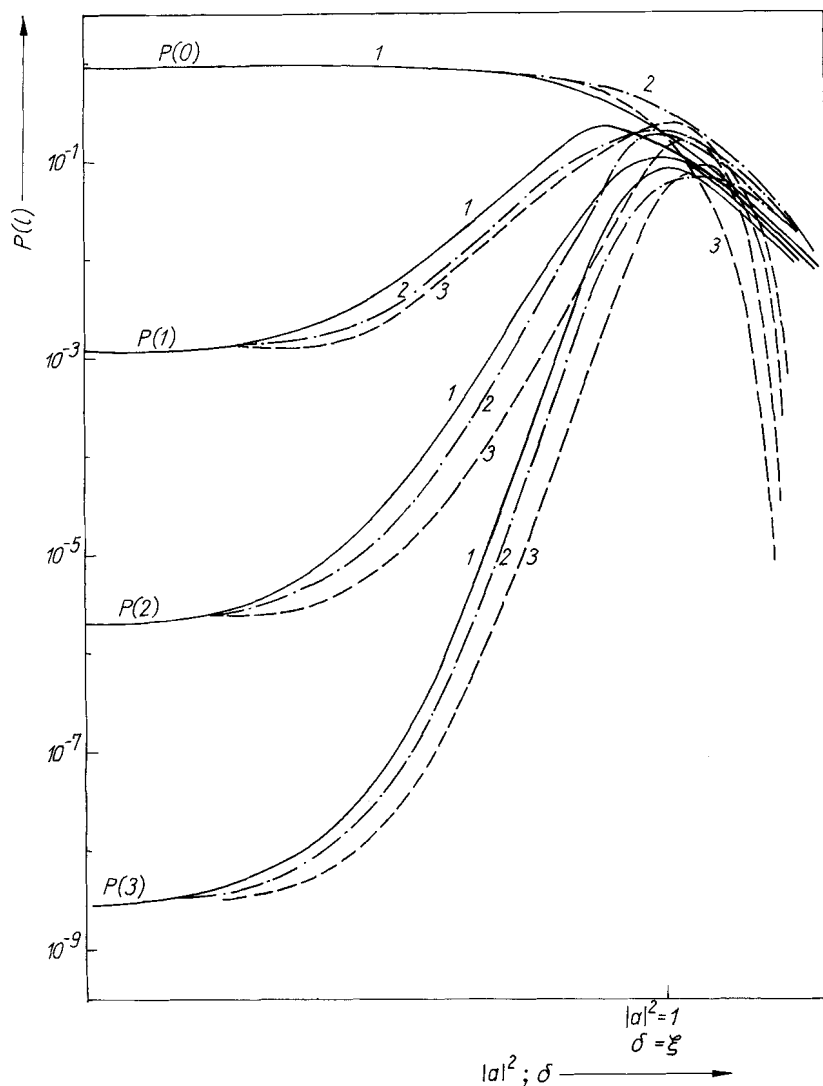
Fig. 1. Dependences of several quasilocal oscillator level populations on the external force intensity $Q$. (1) $a, \delta = f(Q)$, (2) $a = 0$, (3) $\delta = 0$

One can estimate the value $|a|^2$ for a particular model of interatomic interaction. Assuming that the interatomic potential is the screened Coulomb potential with the parameters $\chi r_0 \approx 1$, where $1/\chi$ is the screening radius, $r_0$ the interatomic distance, at $\omega_\tau \approx 10^{13}\ \mathrm{s}^{-1}$, one obtains $|a|^2 \approx 10^4 (l_0 \sigma)^2 / A$, where $A$ is the mass number of the impurity.

Thus, the estimations show that for sufficiently intensive US (of order of 10 to 100 W/cm$^2$), $\delta \ll \xi$ and $|a|^2 \ll 1$, so that mean energy of the oscillator practically does not differ from the equilibrium energy. However, the diffusion coefficient, according to (1), is determined by the population of the level nearest to the barrier top. The detailed calculation of the

populations shows that the conditions $\delta \approx \xi$ and $|a|^2 \approx 1$ are sufficient to obtain practically equally probable populations of several lowest levels (see Fig. 1). However, the growth of the population of the highest levels begins much earlier than these conditions are reached. For example, at $l_0\sigma \approx 10^{-3}$, $\delta \approx 10^{-4}$, $|a|^2 \approx 10^{-3}$, the population of the fifth level is 15% larger than the equilibrium one, and the population of the tenth level is 3% larger; $l_0\sigma \approx 2 \times 10^{-3}$, the populations of the fifth and tenth levels exceed the equilibrium values by 117% and 8%, respectively, and at $l_0\sigma \approx 10^{-2}$ by $\approx 1000\%$ and 51%, respectively.

One can conclude from this that, firstly, the influence of US on the diffusion of impurities depends considerably on the depth of the well in which the impurity vibrates, or, in other words, on the migration activation energy. The lower activation energy, the less US power is required to produce a greater probability of noticeable diffusion acceleration. Therefore, it should be expected that the impurities diffusing in interstices (and having smaller activation energy than that of substitutional impurities) should be more effectively accelerated than the substitutional impurities. Secondly, the estimations show that an US intensity of the order of 10 to 100 W/cm$^2$ is critical in the sense of its influence on diffusion, and at smaller intensity a noticeably enhanced diffusion due to the above mechanism of impurity excitation should not be expected.

The above results are valid for sufficiently heavy impurities which create quasilocal vibrations in the crystal vibrational spectrum. The results are considerably changed for the case of light impurity atoms which form local vibrations in the crystal vibrational spectrum. Since the disintegration of local vibrations is possible only by two (or more) phonons which satisfy the conservation laws of quasimomentum and energy, the populations of local oscillator levels should be determined by the sum of all nonequilibrium phonons satisfying the conservation laws [14],

$$P(l) = \frac{\xi^l}{N} \sum_s (1 - \xi A_s) A_s^l, \tag{4}$$

$$A_s = \frac{\left(1 + \dfrac{N^{(1)}(\omega_s)}{n(\omega_s)}\right)\left(1 + \dfrac{N^{(1)}(\omega_\tau - \omega_s)}{n(\omega_\tau - \omega_s)}\right)}{\left(1 + \dfrac{N^{(1)}(\omega_s)}{n(\omega_s) + 1}\right)\left(1 + \dfrac{N^{(1)}(\omega_\tau - \omega_s)}{n(\omega_\tau - \omega_s) + 1}\right)}. \tag{5}$$

One can make some conclusions from (5). At high temperatures when $n(\omega_s) \gg 1$, $A_s \to 1$ independently of the degree of nonequilibrium phonon excitation. Thus, the populations of local oscillator levels at high temperatures do not differ practically from the equilibrium Boltzmann values for arbitrary degree of nonequilibrium phonon excitation.

However, at sufficiently low temperatures ($A_s \to \infty$ at $T \to 0$) the populations of high excited levels can essentially exceed the equilibrium values both for the given temperature and for higher temperatures. This effect depends considerably on the frequency of excited nonequilibrium phonons. Fig. 2 shows the dependence of local oscillator level populations on the central frequency $\omega_1$ of the Gaussian nonequilibrium phonon distribution $N^{(1)}(\omega) = N_0^{(1)} \exp(-((\omega - \omega_1)/\Delta\omega)^2)$. The sharp maximum at $\omega_1 = \omega_\tau/2$ is seen in the figure. It is clear that such resonant behavior is characteristic of the bell-shaped spectrum of nonequilibrium phonons, because the populations are determined by the values $N^{(1)}(\omega)$ and $N^{(1)}(\omega_\tau - \omega)$.
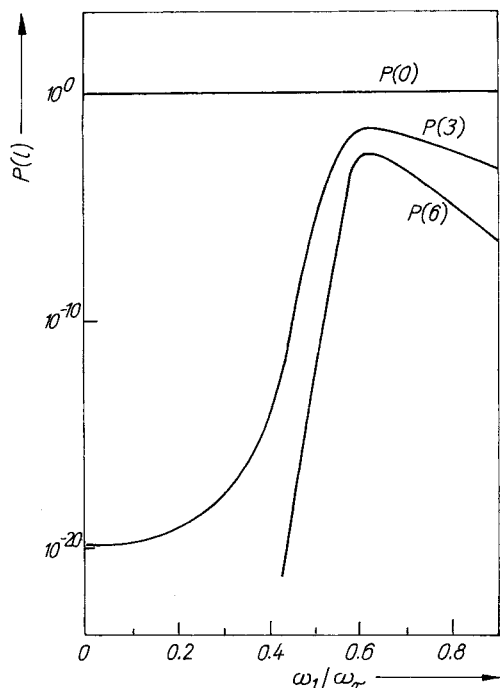
Fig. 2. Dependences of several local oscillator level populations on the central frequency $\omega_1$ of the Gauss nonequilibrium phonon distribution ($\omega_\tau$ is the frequency of a local vibration)

The more detailed analysis shows that for a local oscillator interacting nonlinearly with the thermostat the opposite effect to impurity oscillator excitation is possible. Namely, in an intermediate area of temperature, under conditions of nonequilibrium phonon excitation, the population of the ground level is increased, and the population of high excited levels is decreased compared to the equilibrium values. One can get the condition of the increase of ground level population from the inequality $\partial P(0)/\partial N^{(1)} > 0$. This condition can be fulfilled at moderate and high temperatures. This is reduced roughly to the inequality $T \ln 4 > \omega_\tau$. Really the condition $\partial P(0)/\partial N^{(1)} > 0$ is fulfilled at lower temperatures. Fig. 3 shows the dependence of level populations of a local oscillator on the degree of thermostat excitation $N_0^{(1)}$ at different temperatures calculated within Debye approximation with a Gaussian spectrum of nonequilibrium phonons. In the figure the decrease of higher level populations with increasing $N_0^{(1)}$ is clearly seen at $T = 100$ K. At lower temperatures the populations of high levels are essentially increased with increasing $N_0^{(1)}$ and can exceed the equilibrium populations calculated at higher temperatures by several orders of magnitude. Thus, the nonequilibrium phonon excitation in crystals (due to US waves or NI) can lead to additional localization of light impurities and to the decrease of the diffusion coefficient at moderate temperatures.

One can conclude from (5) that one can achieve a noticeable change of $P(l)$ if $N^{(1)}(\omega_s)$ is comparable in magnitude with $n(\omega_s)$. However, like the case of heavy impurities the increase (decrease) of high level populations begins at smaller values of $N^{(1)}$ and therefore at smaller values of US intensity. The calculation shows that an intensity of the order of 10 to 100 W/cm$^2$ is the threshold intensity in the sense of its influence on impurity diffusion.

Concluding this section we shall present some notes about the nonequilibrium phonon excitation by nuclear irradiation. It fast charged particles pass through matter, nonequilibrium phonons are created due to different physical processes: creation and annihilation of Frenkel pairs, stopping and Cherenkov emission of phonons, thermalization of hot electrons, and annihilation of other electronic excitations. All these excess phonons are summed up and diffusing particles interact with the phonon thermostat with a new distribution function which differs essentially from the equilibrium one. The determination of this distribution function is a suffciently complex problem which requires separate research.
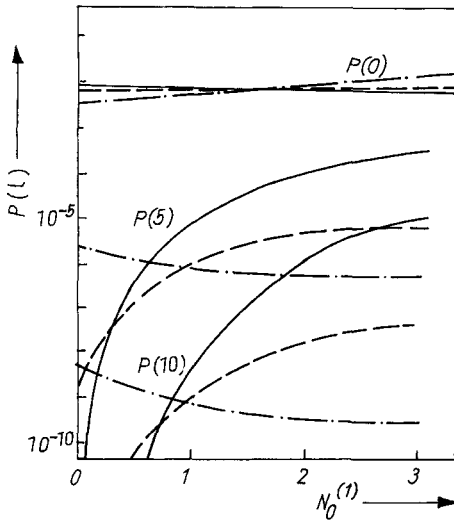
Fig. 3. Dependences of several local oscillator level populations on the degree of excitation of nonequilibrium phonons at different temperatures.
——— $T = 10$, — — — $50$, — · — $100$ K

However, the qualitative picture does not differ in principle from the above one: localization of light impurities at moderate temperatures and essential diffusion acceleration at low temperatures are possible. It is quite possible that the anomalous mobility of intrinsic defects in silicon at low temperatures is due to such "radiation shaking".

## 3. The Probability of Diffusion Jumps

Till now, we considered the influence of US waves and the nonequilibrium phonon thermostat on populations of impurity atom vibrational levels. It is expedient to consider also the influence of crystal lattice perturbations on the probability of the diffusion jump itself, i.e. on the value $D_l$ in (1).

We shall calculate the diffusion coefficient by computing the probability of diffusion jumps in unit time, i.e. neglecting the 'tunnel' contribution to diffusion [16]. Therefore, the result will be correct only at not very low temperatures. In order to be concrete we shall speak about US vibrations only, and in order to obtain the Hamiltonian of the system, we use the reasoning which are considered in [16, 17] to calculate the populations. Then, considering the US wave of a displacement as a plane wave, and deformation in the US wave as small, one can represent the interaction energy of an impurity localized in interstice $\chi$ with the crystal atoms in the form

$$V_\chi(r, R) = V_\chi^0(r, R) + \varepsilon(t) V_\chi'(r, R). \tag{6}$$

According to results of [10, 16, 17] the transition of an impurity to the neighbor interstice is defined by the difference operator between the full Hamiltonian with a migrating impurity and the local Hamiltonian. This operator depends on time according to (6), and the transition probability in unit time should be calculated taking into account these circumstances. In addition, one should calculate the correlation functions taking into account the nonequilibrium thermostat. Then, it is not difficult to show that the terms proportional to $\varepsilon(t)$ do not practically contribute to diffusion, and the diffusion coefficient on level $l$ at high temperatures can be presented in the form

$$D_l = \frac{g d^2 \sqrt{\pi} |M_{\chi\chi'}^l|^2}{\hbar^2 \sqrt{4 E_a kT (1 + b) + b\hbar\bar{\omega}}} \exp\left(-\frac{E_a}{kT(1 + b) + b\hbar\bar{\omega}}\right), \tag{7}$$

where $b = \frac{1}{2}\gamma l_0 \sigma$, $E_a = \sum_s \zeta_s^2 \omega_s$ is the 'polaron' activation energy connected with the transfer of the lattice deformation around the impurity during the diffusion transition, $M_{\chi\chi'}^l$, is the matrix element of the transition calculated with the localized wave functions of the impurity

[17], $\bar{\omega}$ is some characteristic frequency of the vibrational spectrum of the crystal. Thus, the influence of US on the probability of diffusion transitions consists in an increase of the effective temperature of the crystal and in an effective decrease of the 'polaron' activation energy. A change of such a kind occurs also if one takes into account the general nonequilibrium of the thermostat not due to US.

The calculation shows that the pre-exponential factor affects the temperature dependence of the diffusion coefficient in the region of very high temperatures only. This leads to the deviation from an activation dependence in the area of decrease of diffusion coefficient. The influence of US intensifies this tendency, and also decreases the pre-exponential factor due to the term $bh\bar{\omega}$ in the denominator of $D_0$. It should be noted that the deviation from an Arrhenius dependence in the region of high temperatures is not observed usually. This is connected probably with the crystal melting in the temperature region required for such a deviation.

The greatest change of the diffusion coefficient is due to the exponential factor. However, the full change of diffusion coefficient due to US should be considered taking into account the results of the previous section. The general behavior of the temperature dependence of the diffusion coefficient should be different for light and heavy impurity atoms.

For light impurities in the presence of US the impurity atom distribution on the vibrational levels at high temperature practically does not differ from a Boltzmann distribution. Therefore, the change of diffusion coefficient is determined by (7) and consists in an increase of the effective temperature and a decrease of deformation activation energy. The temperature dependence remains an activation dependence. For impurities which weakly distort the crystal lattice $\left[ \sum_s \xi_s^2 \omega_s \ll 1 \right]$ one cannot expect any change.

Since (7) is valid and can be used in a sufficiently wide temperature region, the effect of light impurity localization considered in the previous section should begin to be effective with decreasing temperature. This effect can be more noticeable for impurities which weakly distort the crystal lattice, since it is not masked by the increase of effective temperature and the apparent decrease of deformation activation energy.

At low temperatures all effects should be determined by the value $P(l)$, since the transition probability between the given levels and the 'tunnel' term also in real crystals tend to constant values at $T \to 0$. Thus, at low temperatures in the presence of US or another excitation of the crystal lattice an increase of the diffusion coefficient of light impurities should be observed.

For heavy impurity atoms the temperature dependence of the diffusion coefficient is less exotic. Namely, in the presence of US the diffusion coefficient of heavy impurities exceeds the equilibrium value at any temperature. The temperature dependence of $D$ is close to the activation dependence at high temperature with smaller activation energy, and $D$ tends to a constant value at $T \to 0$ exceeding in all regions the equilibrium value.

In conclusion we shall represent some comments about the experimental observation of the considered effects. Most experiments devoted to the US influence on diffusion were carried out with stress in US waves exceeding the fluidity strength of the material. Therefore, one cannot make a conclusion from these experiments about the magnitude of the effects considered above. One can obtain a trustworthy answer about the influence of the above mechanisms on impurity diffusion by investigating diffusion processes at low temperatures, but the author does not know such works. The high mobility of intrinsic point defects in silicon could serve as an indirect justification of the considered effects, although another explanation of this effect is possible.

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