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Multi-Phonon Relaxation of the $1s\,(T_2)$ Triplet of Neutral Magnesium Donors in Silicon

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Using adiabatic and one-electron approximations, the rate of multiphonon relaxation of the $1s\,(T_2)$ triplet of neutral magnesium donors in silicon is estimated. The dominant scattering processes associated with interaction with LO and LA phonons are taken into account. According to calculations, the rate of multiphonon relaxation at zero temperature is of the order of $10^{11}\,\text{s}^{-1}$.

Keywords: deep impurities, magnesium donors in silicon, multiphonon relaxation, adiabatic approximation.

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1. Introduction

Impurity centers have various physical applications; specifically, they may serve as active elements in lasers based on intracenter optical transitions (this was demonstrated in [1] for group-V donors in silicon). The deepening of levels in deep-lying impurities expands the range of potential radiation sources. An Mg^0 donor may be regarded as a candidate here [2].

Characterized as a substitutional impurity in silicon, magnesium is a double donor. The binding energy of singly charged and neutral donors is 256 and 107 meV, respectively [3–5]. Just as in shallow donors, the $1s$ level in magnesium is split by the short-range potential of a lattice with tetrahedral symmetry into $1s\,(A_1)$ singlet, $1s\,(T_2)$ triplet, and $1s\,(E)$ doublet. In addition to this, two ladders of states specified by the total spin of a system of two electrons (spin-singlet — parastates and spin-triplet — orthostates) emerge in a helium-like neutral Mg^0 donor. These ladders of weakly coupled (due to the weakness of spin-orbit interaction) states may induce various spin-dependent effects, expanding the range of possible applications of such centers in semiconductors.

Both the positions of first excited levels and the lifetime (relaxation time) of states need to be determined in order to examine the possibility of construction of such sources. Since transitions are allowed in the electric dipole approximation, direct measurements of relaxation times may normally be performed with resonance excitation of p-type states of donors in silicon in pump-probe experiments. In contrast, the examination of binding energies and lifetimes of excited s-states of donors is performed individually in each specific case. Specifically, the binding energy of $1s\,(E)$ and $1s\,(T_2)$ levels of magnesium in silicon has until quite recently been estimated only based on indirect data [4]. Spectroscopic studies of thermal filling of excited states coupled with measurements of Fano resonances in the photocurrent spectrum [2] provided an opportunity to identify the position of the $1s\,(T_2)$ parastate level: ~ 66 meV above the $1s\,(A_1)$ ground state energy. Since the energy difference between these levels is ~ 2 meV higher than the maximum optical phonon energy, single-quantum processes of electron relaxation from this level are forbidden by the energy conservation law. In the present study, we consider multi-phonon processes of relaxation of this level: transitions of electrons from level $1s\,(T_2)$ to the ground state of a donor with emission of phonons.

Several approximations and simplifications were used in calculations of the probability of these transitions. First, the problem was considered in the one-electron approximation: it was assumed that an electron of an impurity center moves in the field of an ion and a second electron, which is characterized by an overall positive unit point-like charge. Second, we limited ourselves to the effective mass approximation in calculations of wave functions of donor states. This mass was considered to be isotropic and equal to the effective mass of the density of states of Δ-valleys. The chemical shift of $1s\,(A_1)$ and $1s\,(T_2)$ levels was characterized using the quantum defect method. In this approximation, the localization radius is ~ 1 nm for $1s\,(A_1)$ state and ~ 1.7 nm (which is close to the Bohr radius of ~ 1.9 nm) for $1s\,(T_2)$. Comparing these values with the lattice constant (0.543 nm), we conclude that although the effective mass approximation is fairly crude (in particular, for the ground state), it still allows one to obtain estimates.

Third, the degeneracy of $1s\,(T_2)$ level was ignored in calculations of probabilities of non-radiative transitions: we used the adiabatic approximation and Born–Oppenheimer equations [6]. This approach disregards vibronic effects [7] that induce collective electron-vibration motion in which all electronic states of the $1s\,(T_2)$ triplet are actually involved (Jahn–Teller effect). In view of this, the adiabatic separation of motion into electron and vibration (phonon) parts used here with the corresponding factorization of wave functions is an approximation and a simplification. However, this approximation provides an opportunity to characterize the electron-vibration motion associated with the indicated triplet term qualitatively by analyzing such an important parameter of it as the scale of localization of electron states and specifying the relation between electron and vibration motions within the adiabatic approximation (with the specifics of Jahn–Teller dynamics neglected).

Taking the moderate level depth of neutral magnesium into account, we consider the interaction of electrons at an impurity with bulk phonon modes using literature data on deformation potential constants.

According to the obtained estimates, the rate of multi-phonon relaxation of $1s(T_2)$ state is on the order of $10^{11}\,\mathrm{s}^{-1}$, which is close to the results of pump-probe measurements of $2p_0$ and $2p_\pm$ relaxation times [8].

2. Calculation method

2.1. Energy and wave functions

An electron bound at an impurity and interacting with lattice vibrations may be characterized by wave function $\Psi(\mathbf{r},\eta)=\psi(\mathbf{r},\eta)\chi(\eta)$ that is governed by the system of Born–Oppenheimer equations:

$$(H_e(\mathbf{r})+H_{eL}(\mathbf{r},\eta))\psi(\mathbf{r},\eta)=W(\eta)\psi(\mathbf{r},\eta), \tag{1}$$

$$(H_L(\eta)+W(\eta))\chi(\eta)=E\chi(\eta), \tag{2}$$

where $\psi(\mathbf{r},\eta)$ and $\chi(\eta)$ are the wave functions of an electron and phonons, respectively; H_e is the Hamiltonian of an electron in the field of an impurity; H_{eL} is the electron–phonon interaction energy; H_L is the lattice vibration energy; $\mathbf{r}$ is the radius vector of an electron; and η is the set of coordinates of vibration motion of a crystal. Electron energy $W(\eta)$ depends parametrically on coordinates η, since interaction energy $H_{eL}(\mathbf{r},\eta)$ also depends on them. Eigen value E specified by Eq. (2) is the total energy of an electron-vibration system.

Nonadiabaticity operator H_{na} is neglected in Eqs. (1)−(2) [6]. This provides an opportunity to solve this system of equations independently for each impurity level. Total energies E and wave functions $\Psi(\mathbf{r},\eta)$ determined by solving these equations correspond to stationary states of the electron-vibration system, which are classified by their association with specific impurity levels (solutions of Eq. (1)). Transitions between different states may be interpreted as non-radiative transitions with emission or absorption of phonons. The perturbation energy inducing transitions between states is operator H_{na}, and common perturbation theory may be used to calculate transition probabilities [6].

Let us solve Eq. (1) in the first order of perturbation theory. We examine the zero-order approximation ($H_{eL}=0$) in more detail, since the end result is expressed in terms of matrix elements of wave functions of this approximation. The same designation $\psi(\mathbf{r})$ with the dependence on normal coordinates η omitted is used for these wave functions.

Let us examine Hamiltonian H_e in the one-electron approximation under the assumption that an electron in excited and ground states moves in the field of a singly charged ion. Therefore, it is assumed that the presence of a second electron is manifested in partial screening of the ion charge. The problem is considered in the effective mass approximation, which is regarded as isotropic and equal to the effective mass of the density of states $m=0.32m_0$ [9]. The wave function of a bound state of a Coulomb center in multi-valley semiconductors is a linear combination of wave functions of states of different valleys and is written as [10]

$$\psi_n=\sum_j C_{nj}F_{nj}(\mathbf{r})\varphi_j(\mathbf{k},r). \tag{3}$$

Here, $\varphi_j(\mathbf{k},r)$ is the Bloch wave function at the bottom of conduction band of the j-th valley and $F_{nj}(r)$ is the envelope wave function of the donor state of the n-th level of the j-th valley. Coefficients C_{nj} specify the distribution of the wave function over all six valleys of the conduction band of silicon in accordance with tetrahedral point-group symmetry T_d. The values of coefficients C_{nj} for the $1s(A_1)$ singlet state and one chosen state of the $1s(T_2)$ triplet are as follows [11]:

$$A_1:\quad \frac{1}{\sqrt{6}}(1,1,1,1,1,1),$$

$$T_2:\quad \frac{1}{\sqrt{2}}(1,-1,0,0,0,0). \tag{4}$$

The numbering of valleys here is the same as in [11].

We use the quantum defect method for envelope wave functions:

$$F_n=A_n(r/r_0)^{\nu_n-1}\exp\bigl(-r/(\nu_n r_0)\bigr), \tag{5}$$

$$A_n=\bigl[4\pi r_0^3(\nu_n/2)^{2\nu_n+1}\Gamma(2\nu_n+1)\bigr]^{-1/2},$$

$r_0=\hbar^2\varepsilon/(e^2m)$, $\nu_n=(E_H/|E_n|)^{1/2}$, E_n is the energy of level n (n assumes the values of 1 and 2 for $1s(A_1)$ and $1s(T_2)$ levels, respectively), $E_H=e^4m/(2\hbar^2\varepsilon^2)$ is the binding energy in the effective mass approximation, e is the electron charge, and ε is permittivity.

Energy H_{eL} is written under the assumption that an electron bound at a donor interacts with bulk phonon modes and that the electron–phonon coupling is linear:

$$H_{eL}=\sum_{\sigma,\lambda,\mathbf{q}}u_{\sigma\lambda\mathbf{q}}(\mathbf{r})\eta_{\sigma\lambda\mathbf{q}}, \tag{6}$$

σ is the number of a dispersion law branch, λ is the type of a standing wave of crystal vibrations (cosine- or sine-type), $\mathbf{q}$ is the wave vector of a phonon, $\eta_{\sigma\lambda\mathbf{q}}$ are real normal coordinates in units of $[\hbar/(M\omega_{\sigma\mathbf{q}})]^{1/2}$, $\omega_{\sigma\mathbf{q}}$ is the phonon frequency, and M is the lattice oscillator mass. Here and elsewhere, summation over $\mathbf{q}$ is performed for a half of the Brillouin zone (see *Appendix*).

With energy $W(\eta)$ in (1) determined in the first order of perturbation theory, Eq. (2) is easy to solve in the harmonic approximation for operator H_L. The wave function of a phonon corresponding to mode $(\sigma, \lambda, \mathbf{q})$ is the wave function of a harmonic oscillator with a shifted equilibrium position:

$$\eta^{(i)}_{\sigma\lambda\mathbf{q}} = -\frac{\langle\psi_i|u_{\sigma\lambda\mathbf{q}}|\psi_i\rangle}{\hbar\omega_{\sigma\mathbf{q}}}. \tag{7}$$

The following is the total energy of the electron-vibration system consisting of an electron in a state with wave function ψ_i and a phonon subsystem characterized by set $\{n\}$ of occupation numbers $n_{\sigma\lambda\mathbf{q}}$:

$$E_{i,\{n\}} = W_i^{(0)} + \sum_{\sigma,\lambda,\mathbf{q}} \hbar\omega_{\sigma\mathbf{q}}(n_{\sigma\lambda\mathbf{q}} + 1/2) + J_i, \tag{8}$$

where $W_i^{(0)}$ is the electron energy in the zero-order approximation (at $H_{eL} = 0$ in Eq. (1)) and J_i is the deformation energy:

$$J_i = -\frac{1}{2}\sum_{\sigma,\lambda,\mathbf{q}} \hbar\omega_{\sigma\mathbf{q}}(\eta^{(i)}_{\sigma\lambda\mathbf{q}})^2. \tag{9}$$

Energy E_T of a purely electron transition with a fixed state of the phonon subsystem is specified by the difference of energies $E_{i,\{n\}}$ at a constant set of occupation numbers $\{n\}$:

$$E_T = W_2^{(0)} - W_1^{(0)} + J_2 - J_1. \tag{10}$$

In contrast to, e.g., chalcogens in silicon [12–14], literature absorption or luminescence spectroscopy data for the $1s(A_1)-1s(T_2)$ transition in Mg^0 donors are lacking. However, the corresponding transition energy E_T was identified by examining Fano resonances in the photoconductivity spectrum [2] and found to be equal to ~ 66 meV. The difference in deformation energies (on the order of 10 meV) was neglected in calculations of wave functions (3) and (5); it was assumed that $E_T \approx W_2^{(0)} - W_1^{(0)} = E_2 - E_1$.

2.2. Phonons and electron–phonon interaction

Matrix elements of operator H_{eL} and, consequently, functions $u_{\sigma\lambda\mathbf{q}}(\mathbf{r})$ in electron wave functions (3) are required for calculations:

$$\langle\psi_n|H_{eL}|\psi_m\rangle = \sum_{\sigma,\lambda,\mathbf{q}} \langle\psi_n|u_{\sigma\lambda\mathbf{q}}|\psi_m\rangle\eta_{\sigma\lambda\mathbf{q}}. \tag{11}$$

In view of the multi-valley nature of electron wave functions, matrix elements $\langle\psi_n|u_{\sigma\lambda\mathbf{q}}|\psi_m\rangle$ contain three contributions that correspond to normal scattering processes and g- and f-type Umklapp processes:

$$\langle\psi_n|u_{\sigma\lambda\mathbf{q}}|\psi_m\rangle = d^{nm}_{\sigma\lambda\mathbf{q}} + g^{nm}_{\sigma\lambda\mathbf{q}} + f^{nm}_{\sigma\lambda\mathbf{q}}. \tag{12}$$

The contribution of normal (intravalley) processes $d^{nm}_{\sigma\lambda\mathbf{q}}$ is associated with matrix elements diagonal in valleys $\langle F_{ni}\varphi_i|u_{\sigma\lambda\mathbf{q}}|F_{mj}\varphi_j\rangle$ $(i = j)$, while „intervalley" contributions are associated with non-diagonal $(i \neq j)$ matrix elements induced by pairs of valleys positioned on their symmetry axis $(g^{nm}_{\sigma\lambda\mathbf{q}})$ and valleys positioned at an angle to each other $(f^{nm}_{\sigma\lambda\mathbf{q}})$.

The final expressions for the probability of non-radiative transitions contain sums with each their term being quadratic in matrix elements (12). This leads to the emergence of contributions bilinear in $d^{nm}_{\sigma\lambda\mathbf{q}}$, $g^{nm}_{\sigma\lambda\mathbf{q}}$ and $f^{nm}_{\sigma\lambda\mathbf{q}}$. It is appropriate in the effective mass approximation to neglect cross contributions of types $d^{nm}_{\sigma\lambda\mathbf{q}}g^{ps}_{\alpha\mu\mathbf{k}}$, $g^{nm}_{\sigma\lambda\mathbf{q}}f^{ps}_{\alpha\mu\mathbf{k}}$, etc. This is reasonable, since regions of the Brillouin zone wherein each different-type factor is appreciably different from zero are sufficiently separated for moderately deep centers. Thus, only „diagonal" contributions containing products of only same-type factors („intravalley" or g- and f-type „intervalley" ones) were taken into account in calculations.

The energy distance between levels $1s(A_1)$ and $1s(T_2)$ is ~ 66 meV, which is only slightly larger than the maximum energy of optical phonons (64.3 meV [9]). Since normal processes of electron scattering on optical phonons are forbidden by symmetry [11], they were disregarded. The maximum resonance energy among symmetry-allowed intervalley scattering processes corresponds to g-LO phonons (~ 62 meV) [9]. These phonons are also characterized by the maximum deformation potential [9]. The only optical phonons taken into account were g-LO ones, and the only acoustical phonons considered were LA ones (normal processes and g-type processes). Intervalley f-type processes were neglected.

Reference values from [9] were used for the deformation potentials of „intervalley" phonons, and data from [15] were used for deformation potentials in intravalley scattering.

The Brillouin zone was assumed to be spherically symmetric with radius $q_D = (6\pi^2 N/V)^{1/3}$ [16], where V is the crystal volume, N is the number of unit cells, $V/N = a_0^3/4$, and a_0 is the lattice constant. The phonon dispersion law was assumed to be isotropic, and the following approximations were used. It was considered to be quadratic for optical phonons (the index of a dispersion law branch is $\sigma = 1$):

$$\omega_{1\mathbf{q}} = \omega_1(q) = \omega_1(0)\left(1 - \frac{q^2}{q_1^2}\right), \tag{13}$$

$$q_1^2 = q_D^2/\big(1 - \omega_1(q_D)/(\omega_1(0)\big),$$

where the maximum and minimum frequencies correspond to phonon energies $\hbar\omega_1(0) = 64.3$ meV and $\hbar\omega_1(q_D) = 51.4$ meV [9] and the minimum energy corresponds to the energy of an LO phonon at X point in the Brillouin zone. The dispersion law of acoustical phonons $(\sigma = 2)$ was approximated with a linear fractional function:

$$\omega_{2q} = \omega_2(q) = \frac{vq}{1 + q/q_2}, \tag{14}$$

$$q_2 = \omega_2(q_D)/\big(v - \omega_2(q_D)/q_D\big),$$

where the maximum frequency corresponds to the energy of an LA phonon at X point: $\hbar\omega_2(q_D) = 51.4\,\text{meV}$. Parameter v is equal to the direction-averaged sound velocity [17]:

$$v = \langle v_{\text{LA}}\rangle = \sqrt{\frac{1}{\rho}\Big(\frac{2}{5}c_{12} + \frac{4}{5}c_{44} + \frac{3}{5}c_{11}\Big)},$$

where ρ is the crystal density and c_{11}, c_{12}, and c_{44} are elastic constants [9]; $v \approx 9 \cdot 10^5$ cm/s.

2.3. Transition probability

Probabilities of non-radiative transitions are written in the common first-order perturbation theory wherein the nonadiabaticity operator serves as a perturbation:

$$w = \frac{2\pi}{\hbar} Av(\{m\}) \sum_{\{n\}} \Big|\langle 1, \{n\}|H_{na}|2, \{m\}\rangle\Big|^2 \times \delta(E_{2,\{m\}} - E_{1,\{n\}}), \tag{15}$$

where $|i, \{n\}\rangle$ and $E_{i,\{n\}}$ are the wave function and energy (8) of the electron-vibration system in the initial ($i = 2$) and final ($i = 1$) states and $\{n\}$ is the set of occupation numbers of phonon modes. Symbol $Av(\{m\})$ denotes statistical averaging over the initial states of the phonon subsystem.

Within the first order of perturbation theory, matrix elements of nonadiabaticity operator H_{na} may be substituted with matrix elements of operator H_{eL} (6) with the zero-order approximation used for the electron wave function [18]. This substitution is well-warranted under the supplementary condition of equality of energies of electron-vibration motion in the initial and final states. The indicated condition is satisfied automatically in expression (15) due to the presence of a δ-function.

With this substitution introduced, formula (15) is identical to the expression obtained by R. Pässler within the static coupling scheme [19]. Summation over the final states and statistical averaging over the initial states in the expression for the probability of non-radiative transitions were performed in [19], and we use the obtained results here.

Let us set the temperature to zero and write the Pässler's formula in our notation:

$$w = \frac{\pi}{\hbar} \sum_{\sigma\lambda\mathbf{q}} |V_{\sigma\lambda\mathbf{q}}|^2 R(E_T - \hbar\omega_{\sigma\mathbf{q}}), \tag{16}$$

$$V_{\sigma\lambda\mathbf{q}} = \langle\psi_1|u_{\sigma\lambda\mathbf{q}}|\psi_2\rangle, \tag{17}$$

where $R(E)$ is the Franck–Condon factor. It may be expressed via the inverse Laplace transform [19]:

$$R(E) = \frac{1}{2\pi i}\int\limits_{-i\infty}^{+i\infty} r(\tau)e^{-\tau E}d\tau, \tag{18}$$

$$r(\tau) = \exp\big(s_N(\tau) - s_N(0)\big).$$

At zero temperature,

$$s_N(\tau) = \sum_{\sigma\lambda\mathbf{q}} S_{\sigma\lambda\mathbf{q}} \exp(\tau\hbar\omega_{\sigma\mathbf{q}}), \tag{19}$$

where Huang–Rhys factor $S_{\sigma\lambda\mathbf{q}}$ for phonon mode $(\sigma, \lambda, \mathbf{q})$ is expressed in terms of the difference of equilibrium position shifts (7):

$$S_{\sigma\lambda\mathbf{q}} = \frac{1}{2}\big(\eta^{(2)}_{\sigma\lambda\mathbf{q}} - \eta^{(1)}_{\sigma\lambda\mathbf{q}}\big)^2. \tag{20}$$

The values of $\eta^{(2)}_{\sigma\lambda\mathbf{q}}$ for the excited state were neglected in calculations, since they are much smaller than $\eta^{(1)}_{\sigma\lambda\mathbf{q}}$.

Terms containing products of diagonal and non-diagonal matrix elements (12) are omitted in formula (16). They may be neglected in the case of the considered transition, since they contain only „cross" contributions (see Section 2.2).

In practical calculations, it is convenient to present expression (16) as a sum of definite integrals corresponding to the contributions to adiabaticity violation of LO ($\sigma = 1$) and LA phonons ($\sigma = 2$):

$$w = \sum_{\sigma}\int w_\sigma(E)R(E_T - E)dE, \tag{21}$$

$$w_\sigma(E) = \frac{\pi}{\hbar}\sum_{\lambda\mathbf{q}} |V_{\sigma\lambda\mathbf{q}}|^2\delta(E - \hbar\omega_{\sigma\mathbf{q}}). \tag{22}$$

3. Results and discussion

Multi-phonon transition probability (21) is expressed in terms of integrals of the Franck–Condon factor, $R(E)$. Similar to the Dirac δ-function, this function is meaningful mostly in integrands (i.e., as a kernel of an integral operator). (Note that the infinite integral of $R(E)$ over energy E is equal to unity [19].) We used the following regularization for visual presentation of dependence $R(E)$ (Figure 1) and practical calculations. Factor $R(E)$ was substituted with function $R_\gamma(E)$, which is a convolution with a Gaussian distribution:

$$R_\gamma(E) = \frac{1}{\gamma\sqrt{2\pi}}\int R(W)\exp\Big(-\frac{(W-E)^2}{2\gamma^2}\Big)dW, \tag{23}$$

where broadening parameter γ should be sent to zero. It was assumed in calculations that $\gamma = 1.5\,\text{meV}$. Note that the maximum of function $R_\gamma(E)$ at $E = 0$ is broadened by the used regularization procedure.

Only intervalley scattering processes (terms $g^{12}_{\sigma\lambda\mathbf{q}}$ in formula (12) corresponding to g-processes) contribute to non-diagonal matrix element $\langle\psi_1|u_{\sigma\lambda\mathbf{q}}|\psi_2\rangle$ and, consequently, to functions $w_\sigma(E)$ (22). The contribution of normal (intravalley) processes of scattering ($d^{12}_{\sigma\lambda\mathbf{q}}$ in (12)) on LA phonons is zero for the chosen initial and final electron $1s(T_2)$ and $1s(A_1)$ states, and the corresponding contribution for optical phonons is, as was noted, zero in virtue of more general

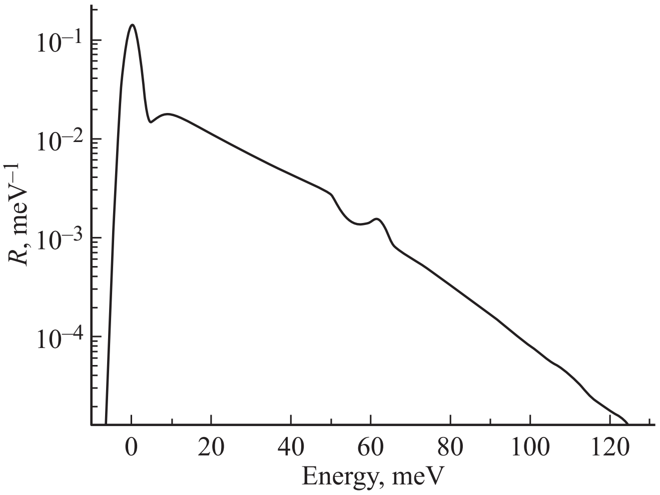

Figure 1. Energy dependence of the Franck–Condon factor for $1s(T_2)-1s(A_1)$ transition at zero temperature.

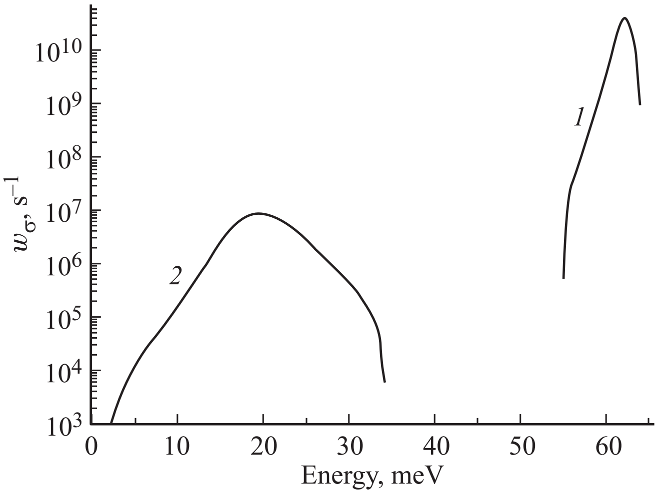

Figure 2. Functions $w_1(E)$ (curve *1*) and $w_2(E)$ (*2*) characterizing the degree of adiabaticity violation in the interaction of a donor electron with g-LO and g-LA phonons, respectively.

symmetry considerations. Functions $w_\sigma(E)$ for LO and LA phonons are shown in Figure 2. Their maxima correspond roughly to the resonance energies of g-LO (62 meV) and g-LA (18.5 meV) phonons.

At the same time, the „intravalley“ interaction with LA phonons actually contributes to the non-radiative transition probability. This is attributable to the dependence of the Franck–Condon factor on diagonal matrix elements for which the „intravalley“ contribution of LA phonons is dominant. The quantitative measure of this contribution is the sum over modes of Huang–Rhys factors. For a fixed branch σ of the dispersion law,

$$S_\sigma = \sum_{\lambda\mathbf{q}} S_{\sigma\lambda\mathbf{q}}.$$

The values corresponding to LO and LA phonons are $S_1 \approx 6 \cdot 10^{-3}$ and $S_2 \approx 0.65$. Intravalley processes produce a dominant contribution to S_2, while the contribution of g-processes $(9 \cdot 10^{-4})$ is significantly smaller. Huang–Rhys factors $S_{\sigma\lambda\mathbf{q}}$ characterize the variation of lattice deformation and the corresponding change in accumulated energy, which is specified by (9), in transition of an electron between impurity states. This change is reflected in the energy conservation law that is expressed by factor $R(E)$.

It is evident that the contribution of g-processes to the overall Huang–Rhys factor and, consequently, the Franck–Condon factor is small compared to that of „intravalley“ processes of interaction with LA phonons. In a similar fashion, the inclusion of intervalley f-processes of scattering should not affect function $R(E)$ in any significant way.

Having performed integration and summation in formula (21), we find that the overall rate of multi-phonon transitions is $w \approx 8 \cdot 10^{10}\,\mathrm{s}^{-1}$. The relaxation rate is fairly high due to the proximity of the transition energy and the one-quantum resonance at g-LO phonons. The contributions to transition probability w emerging due to the adiabaticity violation in interaction with LO and LA phonons (contributions from functions $w_1(E)$ and $w_2(E)$ (22)) are $\sim 8 \cdot 10^{10}$ and $\sim 7 \cdot 10^{7}\,\mathrm{s}^{-1}$, respectively. Since the deformation potential of g-LO phonons is at least 5 times higher than the other deformation potentials of g- and f-phonons, we believe that the inclusion of interaction with other „intervalley“ phonons should not alter the estimate of the multi-phonon transition rate in any significant way.

In order to determine the sensitivity of the relaxation rate to the inaccuracy of deformation potentials, probability w was calculated with deformation potentials varying within ±20% of their tabular values. The transition rate falls within the range from $5.1 \cdot 10^{10}$ to $1.1 \cdot 10^{11}\,\mathrm{s}^{-1}$ when the deformation potential of g-LO phonons is varied, while the variation of deformation potentials of LA phonons (both for g-type processes and for intravalley transitions) turned out to have little effect on the relaxation rate. Note that the error of calculation of transition probabilities attributable to electron–phonon coupling constants is specified not only by the inaccuracy of their tabular values, but also by the deviation of calculations from the effective mass approximation.

4. Conclusion

The relaxation rate of $1s(T_2)$ triplet at low temperatures was estimated with the use of the adiabatic approximation and the one-electron approximation for $\mathrm{Si:Mg}^0$ donor parastates. The multi-phonon relaxation rate is on the order of $10^{11}\,\mathrm{s}^{-1}$. Dominant scattering processes induced by the interaction with LO and LA phonons were taken into account in calculations.

Appendix

Let us express matrix elements (12) in terms of deformation potentials and matrix elements on envelope wave functions $F_{nj}(\mathbf{r})$. Following [20], we substitute phonon creation and annihilation operators with normal coordinates in the expressions for electron interaction with „intervalley" phonons.

Let us expand the electron–phonon interaction energy in a series in powers of displacements $\mathbf{z}_{\mathbf{n}\rho}$ of atoms in unit cells. The positions of cells is characterized by translation vectors $\mathbf{n}$, and index ρ denotes the number of an atom in a cell:

$$H_{eL} = \sum_{\mathbf{n}\rho} \mathbf{z}_{\mathbf{n}\rho} C_\rho(\mathbf{r}-\mathbf{n}),$$

$$\mathbf{C}_\rho(\mathbf{r}-\mathbf{n}) = \left(\partial H_{eL}/\partial \mathbf{z}_{\mathbf{n}\rho}\right)_{\{\mathbf{z}_{\mathbf{n},\rho}\}=0}. \qquad (A.1)$$

Displacements $\mathbf{z}_{\mathbf{n}\rho}$ may be presented as an expansion

$$\mathbf{z}_{\mathbf{n}\rho} = \sum_{\sigma\mathbf{q}} \frac{\mathbf{e}_{\sigma\rho\mathbf{q}}}{\sqrt{2NM\omega_{\sigma\mathbf{q}}/\hbar}} \left(a_{\mathbf{q}\sigma} + a^+_{-\mathbf{q}\sigma}\right)\exp(i\mathbf{q}\mathbf{n}), \qquad (A.2)$$

where $\mathbf{e}_{\sigma\rho\mathbf{q}}$ is a unit phonon polarization vector; summation over $\mathbf{q}$ is performed within the entire Brillouin zone. We isolate summations over two halves of the Brillouin zone differing in the sign of $\mathbf{q}$ in $(A.2)$ and introduce (via a linear transformation) new phonon creation and annihilation operators corresponding to standing waves and real normal coordinates:

$$b^+_{\mathbf{q}\sigma 1} = \frac{1}{\sqrt{2}}\left(a^+_{\mathbf{q}\sigma} + a^+_{-\mathbf{q}\sigma}\right),$$

$$b^+_{\mathbf{q}\sigma 2} = \frac{i}{\sqrt{2}}\left(-a^+_{\mathbf{q}\sigma} + a^+_{-\mathbf{q}\sigma}\right), \qquad (A.3)$$

where annihilation operators are derived from $b^+_{\mathbf{q}\sigma\lambda}$ $(\lambda = 1, 2)$ via Hermitian conjugation.

Assuming that envelope wave functions $F_{nj}(\mathbf{r})$ are sufficiently smooth, we calculate the matrix elements of operator H_{eL} on basis wave functions

$$\psi_{nj} = F_{nj}(\mathbf{r})\varphi_j(\mathbf{k}, \mathbf{r}), \qquad (A.4)$$

$$\varphi_j(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})\alpha_j(\mathbf{r}), \qquad (A.5)$$

where $\alpha_j(\mathbf{r})$ is the periodic part of the Bloch function of the j-th valley normalized by condition

$$\int_{\Omega_0} |\alpha_j|^2 d\mathbf{r} = \Omega_0,$$

where integration is performed over a unit cell with volume Ω_0. The envelope wave function is normalized to unity within the bulk of a crystal. Having introduced real normal coordinates $\eta_{\mathbf{q}\sigma\lambda} = (b_{\mathbf{q}\sigma\lambda} + b^+_{\mathbf{q}\sigma\lambda})/\sqrt{2}$, one may write matrix elements (12) on basis functions (A.4):

$$\langle\psi_{nj}|u_{\sigma\lambda\mathbf{q}}|\psi_{ml}\rangle = \left(\frac{2\hbar}{NM\omega_{\sigma\mathbf{q}}}\right)^{1/2}$$

$$\times A_{\sigma jl} \int F^*_{nj} \exp\big(i(\mathbf{k}_l - \mathbf{k}_j)\mathbf{r}\big) c_\lambda(\mathbf{q}\mathbf{r}) F_{ml} d\mathbf{r}, \qquad (A.6)$$

$c_1(\mathbf{q}\mathbf{r}) = \cos(\mathbf{q}\mathbf{r})$, $c_2(\mathbf{q}\mathbf{r}) = \sin(\mathbf{q}\mathbf{r})$, $\mathbf{k}_j$ is the wave number corresponding to the minimum of the j-th valley,

$$A_{\sigma jl} = \frac{1}{\Omega_0}\int_{\Omega_0} \varphi^*_j \xi_{\sigma\mathbf{q}} \varphi_l d\mathbf{r},$$

$$\xi_{\sigma\mathbf{q}}(r) = \sum_\rho \mathbf{e}_{\sigma\rho\mathbf{q}} \mathbf{C}_\rho(\mathbf{r}). \qquad (A.7)$$

The dependence of $A_{\sigma jl}$ on $\mathbf{q}$ was neglected, and the corresponding index in the designation of these constants was omitted. Magnitudes of constants $|A_{\sigma jl}|$ for matrix elements $(A.6)$ non-diagonal in valleys may be equated to the deformation potentials of „intervalley" phonons known from literature.

With these transformations taken into account, summation over $\mathbf{q}$ in (11) should be performed within one half of the Brillouin zone. Matrix elements (12) of arbitrary wave functions are determined from $(A.6)$ with account for the coefficients of expansion of (3) in basis functions. When calculating integrals with envelope wave functions in $(A.6)$, one should bear in mind that phonon wave vector $\mathbf{q}$ is defined accurately to within a reciprocal lattice vector.

In expressing intravalley part $d^{nm}_{\sigma\lambda\mathbf{q}}$ of matrix elements (12) in terms of deformation potentials, we take advantage of the fact that the electron–phonon interaction energy in the long-wavelength limit is proportional to the deformation tensor. Following, e.g., [21] and using expansion $(A.2)$ for displacements and transformation $(A.3)$ for operators, we obtain the following for a matrix element diagonal in valleys:

$$\langle\psi_{nj}|u_{\sigma\lambda\mathbf{q}}|\psi_{mj}\rangle = \left(\frac{2\hbar}{NM\omega_{\sigma\mathbf{q}}}\right)^{1/2} q\left(\Xi_d + \frac{(\mathbf{q}\mathbf{e}_j)^2}{q^2}\Xi_u\right)$$

$$\times \int F^*_{nj} s_\lambda(\mathbf{q}\mathbf{r}) F_{mj} d\mathbf{r}, \qquad (A.8)$$

where $\sigma = 2$ (LA phonons), $\mathbf{e}_j$ is a unit vector codirectional with the axis of the j-th valley, $s_1(\mathbf{q}\mathbf{r}) = -\sin(\mathbf{q}\mathbf{r})$, and $s_2(\mathbf{q}\mathbf{r}) = \cos(\mathbf{q}\mathbf{r})$. In calculations, we substituted $(\mathbf{q}\mathbf{e}_j)^2$ in $(A.8)$ with its value averaged over the solid angle; thus introducing averaged deformation potential $\Xi_d + \Xi_u/3$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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