

Process of an acceptor center μB^- formation in diamond crystals

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Abstract. A formation process of an acceptor center μB induced by negative muon in a diamond crystal is considered in this work. It is shown that the process under consideration could be represented as three consecutive stages: a kinetic stage, connected with a capture of track electrons, a chemical stage, connected with establishing of chemical bounds of the radiation defect with lattice atoms, and a formation phase of the ionized negatively charged acceptor center. Quantitative estimates of characteristic times are obtained for every stage. It is shown that the total time necessary for the acceptor center formation is of the order 10^{-8}s . So this fact should be taken into account when experimental results are interpreted.

1. Introduction

It is well known, that a negative muon is captured on a lattice nuclear forming the so called μ -atom. But just after the muon capture in a lattice arises a positively charged radiation defect. Neutralization process of radiation defects induced by negative muons in crystals with diamond structure (Diamond, Silicon and Germanium) was considered in works [1, 2]. There was shown that this process could be considered as four consistent stages. At the first stage positively charged radiation defect with a charge equal to $Z - 1$, where Z is the charge of a host nuclear, captures electrons of the radiation track. At the second stage a neutral defect restores broken chemical bounds with lattice atoms. At the third stage an ionized acceptor center is formed. And at the final stage is formed a neutral (usual) acceptor center induced by the μ -atom. Only the last stage is studied well for the present. In [2] was considered a neutralization kinetics as a result of a capture of electrons from the radiation trace. There was shown that the capture process strongly differs in diamond crystal and in crystals of silicon and germanium. Namely, in a diamond crystal the radiation defect has not a time to be neutralized in a muon life-time $\tau_\mu \approx 2.2 \cdot 10^{-6}\text{s}$. So, the formation process of a chemically bounded radiation defect differs in crystals under consideration. Chemical bounds are restored in silicon and germanium for the neutral impurity μA (muonic atom), but in diamond for the positively charged ion μB^+ . A chemically bounded impurity μB^+ is neutralized in a diamond lattice. Estimation of a formation time of a neutral chemically bounded defect caused by a radiation transition was obtained in [1]. Because of this difference in neutralization processes a formation rate of chemically bounded neutral defect μA in a diamond almost two order higher than in silicon and germanium. In the following a neutral chemically bounded radiation defect μA forms an acceptor center in a lattice. At the first step of an acceptor center formation one need to consider a capture of an additional electron to fill an empty chemical bound around μA . After the capture of an electron an ionized



acceptor center μA^- is formed. This process is not studied yet, but the following step of a positive hole capture at the ionized acceptor center is well known. A process of an ionized acceptor center μB^- formation in a diamond crystal is studied in this work.

Experiments with Si and Ge was carried out more than 20 years ago [3]-[7]. Acceptor centers μAl and μGa was observed and hyperfine structure of μAl was studied in these experiments. Recent experiments with μ^- in synthetic diamond [8, 9] showed unusual behaviour of a muon spin polarization. A negative shift of a precession frequency and slow temperature dependence of a damping rate at temperature $T > 20K$ were observed. Full polarization (100%) was observed. Thus, in these experiments no neutral acceptor center μB was observed. The experimental results show that kinetic processes of a formation of the neutral acceptor center μB demand more detail theoretical examination.

2. Phonon spectrum changing caused by a neutral center μB

A neutral center μA enters into a chemical bound with nearest atoms of a lattice and forms a cluster in the first coordination sphere. This cluster possesses a local symmetry C_{3v} and a rather large electric dipole moment [1]. This electric dipole moment gives rise to an interaction necessary to capture a lattice electron and form of an ionized acceptor center. The neutral center μA has unsaturated chemical bounds because of that a crystal lattice turns out to be deformed. This deformation is a reason to change a phonon spectrum and a local phonon mode appearance. Chemical bounds are saturated after the missing electron capture. The new cluster is an ionized acceptor center and possesses a local crystal symmetry. When the ionized acceptor center is formed an appropriate phonon of the local mode is radiated and crystal deformations disappear. So, the problem is very similar to the problem of a thermalization of molecular ions in molecular crystals and cryocrystals of noble atoms (see e.g. [10, 11, 12]).

An exact solution of the problem taking into account a crystal symmetry is scarcely possible. But we can obtain qualitative results to get an estimation of a formation rate of the ionized acceptor center μB^- in diamond.

To solve the problem we will carry out some simplifications. They will make our model rather crude but describing qualitatively all necessary effects nevertheless. First of all we will accept an approximation of an elastic continuous media to describe a phonon spectrum changing. In this case a displacement vector $\mathbf{u}$ satisfies the wave equation in an elastic media at the presence of the electric field [13]:

$$\rho \ddot{u}_i = \frac{\partial \sigma_{ik}}{\partial x_k}, \quad (1)$$

where ρ is the density of a media. A tension tensor will be represented as a sum

$$\sigma_{ik} = \sigma_{ik}^{el} + \sigma_{ik}^E. \quad (2)$$

Here σ_{ik}^{el} is determined by constants of the elastic media as usual. The second term in the expression (2) is the tension tensor of the electromagnetic field in a media [14]:

$$\sigma_{ik}^E = \frac{1}{8\pi} (E_i D_k + E_k D_i), \quad (3)$$

where $\mathbf{E}$ and $\mathbf{D}$ are the average (macroscopic) electric field and the induction created by the dipole moment of the cluster $\mathbf{d}$ respectively. We are taking a simplification to determine the electric field $\mathbf{E}$, namely $\varepsilon_{ik} = \varepsilon(\mathbf{r})\delta_{ik}$

$$\mathbf{E} = \frac{1}{\varepsilon} \mathbf{D}. \quad (4)$$

So, for the force acting on the media from the side of the electric field created by the dipole moment we are obtaining

$$F_i = \frac{\partial \sigma_{ik}^E}{\partial x_k} = -\frac{1}{4\pi\varepsilon^2} \frac{\partial \varepsilon}{\partial x_k} D_i D_k. \quad (5)$$

Here was taken into account that outside the first coordinative sphere in the lattice $\text{div} \mathbf{D} = 0$.

Let's place the coordinate beginning at the center of the nuclear ${}_{\mu}\text{A}$ and consider that the dielectric susceptibility possesses a spherical symmetry, i.e. $\varepsilon(\mathbf{r}) = 1 + 4\pi\kappa(r)$, where $\kappa(r)$ is the dielectric susceptibility. As well we will consider the coordinate dependence of the dielectric susceptibility is stipulated for the specific volume v changing as a result of the deformation. So, we obtain $\kappa \propto v^{-1}$ because the dielectric susceptibility is proportional to the media density. The changing of the specific volume as the result of the deformation is determined by the trace of the deformation tensor [13]:

$$\delta v = v u_{ll}, \quad (6)$$

where $u_{ll} = \partial u_l / \partial x_l = \text{div} \mathbf{u}$.

In this case the gradient of the dielectric penetration could be represented in a form

$$\frac{\partial \varepsilon}{\partial x_k} = 4\pi \frac{\partial \kappa}{\partial x_k} \propto \frac{\partial}{\partial x_k} \frac{1}{v} = -\frac{1}{v} \frac{\partial u_{ll}}{\partial x_k} \equiv -\frac{1}{v} \frac{\partial^2 u_l}{\partial x_k \partial x_l} = -\frac{1}{v} \frac{\partial}{\partial x_l} \frac{\partial u_l}{\partial x_k}. \quad (7)$$

Let us rewrite the equation (1) taking into account that in our case $\text{rot} \mathbf{u} = 0$

$$\ddot{u}_i - c_{\parallel}^2 \Delta u_i = \frac{\kappa}{\varepsilon^2 \rho} D_i D_k \Delta u_k, \quad (8)$$

where $c_{\parallel}$ is the longitudinal sound velocity.

The equation (8) is rather complicated yet and we'll make some additional very serious simplifications to get analytical expressions. Let's consider only the radial component of the displacement vector $\mathbf{u}$ and neglect its angular dependence, i.e. $\mathbf{u}(\mathbf{r}) \rightarrow u_r(r)$. In this approximation we'll keep in the induction vector only a dependence on the modulus of r :

$$D_r = \frac{2(\mathbf{d}\mathbf{n})}{r^3} \rightarrow \frac{2d}{r^3}.$$

Only in this approximation we can solve the problem analytically. After all these simplifications we have

$$\ddot{u}_r - \left(c_{\parallel}^2 + \frac{4\kappa d^2}{\varepsilon^2 \rho} \frac{1}{r^6} \right) \Delta_r u_r = 0. \quad (9)$$

It is suitable to search a solution for the radial displacements in a form

$$u_r(r, t) = \frac{\chi(r, t)}{r}. \quad (10)$$

In this case we have the more simple equation for χ :

$$\ddot{\chi} - \left(c_{\parallel}^2 + \frac{4\kappa d^2}{\varepsilon^2 \rho} \frac{1}{r^6} \right) \chi'' = 0, \quad (11)$$

where χ'' is the second derivative on the radial variable r .

For the function $\chi(r, t)$ the one-dimensional Fourier-transformation is valid:

$$\chi(r, t) = \iint_{-\infty}^{\infty} \frac{d\omega dk}{(2\pi)^2} e^{-i(kr - \omega t)} \chi_{\omega, k}, \quad \chi_{\omega, k} = 2 \int_{-\infty}^{\infty} dt e^{-i\omega t} \int_0^{\infty} dr e^{ikr} \chi(r, t). \quad (12)$$

For the Fourier-amplitudes (12) we obtain an integral equation taking into account that the expression for the force in the equation (8) is valid only for $r > R_1$, where R_1 is the radius of the first coordination sphere:

$$(\omega^2 - k^2 c_{\parallel}^2) \chi_{\omega, k} = \frac{4\kappa d^2}{\varepsilon^2 \rho} \int_{-\infty}^{\infty} \frac{dk'}{2\pi} k'^2 \chi_{\omega', k'} \int_{R_1}^{\infty} \frac{dr}{r^6} e^{i(k-k')r}. \quad (13)$$

Let's make the last serious simplification in the equation (13), changing an integral in the right-hand side by a constant before $\chi_{\omega,k}$. Really, values of the wave-vector $k' \approx k$ give the main contribution to the second integral. This permits us to take out the first integral the amplitude $\chi_{\omega',k'}$ at the point k . Values of $k' \sim R_1^{-1}$ give the main contribution to the integral as well. So, for the estimation of the integral in the right-hand side we have $\chi_{\omega,k}/(10\pi R_1^8)$. Finally we obtain a simple dispersion relation:

$$(\omega^2 - k^2 c_{\parallel}^2 - \Omega^2)\chi_{\omega,k} = 0, \quad \Omega = \frac{d\sqrt{2\kappa}}{\varepsilon R_1^4 \sqrt{5\pi\rho}}. \quad (14)$$

3. Electron capture rate

Electric dipole moment creates a scalar potential and an interaction energy with lattice electrons is $\mathcal{U} = e\varphi = e(\mathbf{dr})/(\varepsilon r^3)$. So, taking into account the displacement $\mathbf{u}$ ($\mathbf{r} \rightarrow \mathbf{r} + \mathbf{u}$), we can write an electron-phonon interaction operator

$$\widehat{V}_{e-ph} \approx \frac{e(\mathbf{d}\hat{\mathbf{u}})}{\varepsilon r^3} = \frac{ed}{\varepsilon r^3} \cos\theta \hat{u}, \quad (15)$$

where the operator of radial displacements is equal to [11]

$$\hat{u} = \frac{1}{r} \sum_n \sqrt{\frac{\hbar}{2\rho\omega(k_n)R_\infty}} e^{-ik_n r} (b_n^\dagger + b_n). \quad (16)$$

Here $b_n^\dagger$ and b_n are creation and annihilation operators for radial phonons respectively.

An electron capture rate could be calculated by means of well known Fermi "golden rule"

$$dw_{if} = \frac{2\pi}{\hbar} \left| \langle f | \widehat{V}_{e-ph} | i \rangle \right|^2 \delta(E_f - E_i) d\nu_f \frac{d\mathbf{k}}{(2\pi)^3}, \quad (17)$$

where an initial state $|i\rangle = |\mathbf{k}\rangle|0_{ph}\rangle$ corresponds to a free (in a valence band) electron with the wave-vector $\mathbf{k}$ and the absence of excited radial phonons, and ν_f is the density of final states. The final state is determined by the state of the electron captured in the hybridized state of the cluster [1] and an excitation of a radial phonon with the wave-vector $\mathbf{k}_{ph}$:

$$|f\rangle = (\alpha|2s\rangle + \beta|2p\rangle)|\mathbf{k}_{ph}\rangle, \quad |\alpha|^2 + |\beta|^2 = 1.$$

Eq.(17) takes into account that all electrons with wave-vectors are in the interval from $\mathbf{k}$ to $\mathbf{k} + d\mathbf{k}$ can participate in the process.

Energies of the initial and the final states are equal to $E_i = E_0 + \hbar^2 k^2 / 2m^*$, $E_f = E_- + \hbar\omega(k_{ph})$, $E_0 - E_- = \varepsilon_{ac}$, where ε_{ac} is the acceptor ionization energy and m^* is an effective mass of the electron in the valence band.

We can carry out a partial integration of the expression (17) and obtain a rather short formula

$$dw_{if} = \frac{2m^*}{3\pi\rho\hbar^2} \left(\frac{ed}{\varepsilon} \right)^2 \left| \langle f | \frac{1}{r^4} e^{-ik_{ph}r} | k_0 \mathbf{n} \rangle \right|^2 \frac{k_0}{\omega(k_{ph})} dk_{ph}, \quad (18)$$

where $k_0^2 = 2m^*(\Delta - \omega_{ph})/\hbar$, $\Delta = \varepsilon_{ac}/\hbar$.

For us will be comfortable in the future to introduce dimensionless parameters and variables

$$x = \tilde{Z}r/(2a_0), \quad \tilde{k}_{ph} = 2k_{ph}a_0/\tilde{Z}, \quad \tilde{k}_0 = 2k_0a_0/\tilde{Z} \quad \text{and} \quad \omega_0 = \langle c_{\parallel} \rangle \tilde{Z}/(2a_0). \quad (19)$$

Here $\tilde{Z}$ is the effective nuclear charge for electrons at the appropriate atomic energy level and $\langle c_{\parallel} \rangle$ is the average longitudinal sound velocity. For Boron it is equal to $\tilde{Z} = 2.6$.

In this case we can express a capture cross-section through a dimensionless matrix element:

$$dw_{if} = \frac{2m^*}{3\pi\rho\hbar^2} \left(\frac{ed}{\varepsilon} \right)^2 \left(\frac{\tilde{Z}}{2a_0} \right)^5 \left| \mathcal{A}(\tilde{k}_{ph}, \tilde{k}_0) \right|^2 \frac{k_0}{\omega(k_{ph})} dk_{ph}, \quad (20)$$

where

$$\mathcal{A}(\tilde{k}_{ph}, \tilde{k}_0) = {}_e \langle f \left| \frac{1}{x^4} e^{-i\tilde{k}_{ph}x} \right| \tilde{k}_0 \mathbf{n} \rangle. \quad (21)$$

We can see, that the matrix element (21) has a peculiarity in the point $x = 0$ and the integrals diverge if the low limit is equal to zero. So we must take into account that expression (15) is valid for $r \gg a_0$ also. Thus we need to determine the low limit $r \gg a_0$. It is reasonable to take it equal to the length of the chemical bound in the lattice. In diamond crystal it is equal to $r_0 \approx 1.54 \cdot 10^{-8} \text{cm}$ and the low limit of the integrals (21) is $x_0 = \tilde{Z}r_0/2a_0 \approx 3.78$.

Making rather long calculations and taking into account the dispersion law (14) we obtain the final formula for the capture rate

$$w = G \int_{\tilde{\Omega}} \frac{\left| \tilde{k}_0 \mathcal{A}(\tilde{k}_{ph}, \tilde{k}_0) \right|^2}{\sqrt{(\tilde{\Delta} - \tilde{\omega})(\tilde{\omega}^2 - \tilde{\Omega}^2)}} d\tilde{\omega}, \quad \text{where} \quad G = \frac{(ed)^2}{6\pi\rho m^* \varepsilon^2} \left(\frac{2m^*}{\hbar \langle c_{\parallel} \rangle} \right)^{3/2} \left(\frac{\tilde{Z}}{2a_0} \right)^{13/2}, \quad (22)$$

where $\tilde{\Delta} = \Delta/\omega_0$, $\tilde{\Omega} = \Omega/\omega_0$, $\tilde{\omega} = \omega/\omega_0$.

The following calculations could be carried out numerically.

4. Conclusion

We shall choose hydrogen-like $2s$ and $2p$ wave functions like in Ref.[1] to calculate matrix elements (21). The value of the rate (22) is proportional to the unknown parameter d , but numerical estimates show that $d \lesssim 1\text{D}$ (Debye, $1\text{D} = 10^{-18}\text{CGSE}$). We will regard $m^* = m$ (the free electron mass) and use the following numerical values for diamond parameters [15, 16]: $\rho = 3.51\text{g/cm}^3$, $\varepsilon = 5.75$, $c_{\parallel} = 1.83 \cdot 10^6\text{cm/s}$, $\varepsilon_{ac} = 0.37\text{eV}$, the lattice constant is $R_1 = 3.57 \cdot 10^{-8}\text{cm}$. For these parameter values we calculated the value of the rate (22) in two cases: $d = 1.0\text{D}$ and $d = 0.5\text{D}$.

Numerical results are shown in table 1, where w_s and w_p are the capture rates at $2s$ and $2p$ -states respectively. In spite of serious approximations we obtained a numerical values which give an expected interval for a formation-time of the negatively charged acceptor center as an intermediate state of a radiation defect in crystals.

Negatively charged cluster $(\mu\text{BC}_4)^-$ is the ionized boron acceptor in a diamond lattice, which captures a hole from the valence band of a crystal because of Coulomb interaction and forms a neutral acceptor. This last stage of a radiation defect formation is well known and strongly depends on temperature of a crystal. Thus we can write a formula to determine the total formation rate of the radiation defect induced by negative muon in diamond crystals as a sum of rates of all stages:

$$W = w_{tr} + w_{cl} + w_0 + w_- + w_h. \quad (23)$$

Definitions of all items are obvious ($w_- = w_s + w_p$).

The numerical results show that the lowest stage is connected with the stage of the negatively charged cluster $(\mu\text{BC}_4)^-$ formation. From the table 1 we see that $0.5 \cdot 10^8\text{s}^{-1} < w_- < 2 \cdot 10^8\text{s}^{-1}$. So, we can see that a formation-time of the neutral acceptor center μB is rather large and must

Table 1. Numerical results

d, D	$\Omega, 10^{10}\text{s}^{-1}$	$w_s, 10^8\text{s}^{-1}$	$w_p, 10^7\text{s}^{-1}$
1.0	1.24	2.1	1.26
0.5	0.62	0.55	0.34

be taken into account in the interpretation of experimental results [8, 9]. Namely, a computing of experimental results must be carried out on the base of kinetic equations like in chemistry reactions. This kind of the analysis could give us unknown parameters of the total process. But, this is the other problem.

Acknowledgments

I would like to acknowledge Profs. R. Zaitsev and L. Sukhanov for fruitful discussions.

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