

Electronic supporting information: A quantum model of charge capture and release onto/from deep traps

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1 Phonon statistics

Consider a sample that has a temperature below the Debye limit. This condition allows to neglect acoustic phonons which are not able to induce significant variations of inter-ion distances, and work only with optical phonons, which are in fact mutual oscillations of two sub-lattices including different atomic species. Now consider the energy of a specific optical mode active in a crystal. Here we do not consider phonon-phonon interactions, and ignore also a presence of impurities/defects:

$$E_{\text{tot}} = \frac{V_s}{(2\pi)^3} \int_{\text{BZ}} d^3k E(k) D(k) \quad (1s)$$

where V_s is the volume of the sample, $E(k)$ is the phonon dispersion relation, $D(k)$ is the average phonon occupation number. Applying simplifying assumptions that optical phonons are dispersion-less particles with the energy $\hbar\omega_0$, and adopting thermodynamic expression for equilibrium average number of bosons per atomic site at the low temperature limit ($\hbar\omega_0 > k_B T$) one can get:

$$E_{\text{tot}} = \frac{V_s}{(2\pi)^3} \frac{N' \hbar\omega_0}{e^{\frac{\hbar\omega_0}{k_B T}} - 1} \int_{\text{BZ}} d^3k \approx N' \hbar\omega_0 e^{-\frac{\hbar\omega_0}{k_B T}} V_s N_{\text{uc}} \quad (2s)$$

where N_{uc} is the unit cells concentration, and N' is the number of ions in the unit cell. This means, that on average there is an exponentially decaying probability to excite the trapped electron out of impurity site by given thermal energy $k_B T$:

$$\bar{E}_{\text{impurity}} = \hbar\omega_0 e^{-\frac{\hbar\omega_0}{k_B T}} \quad (3s)$$

On the other hand the very same results can be obtained using phonon occupation number (n) introduced in the following form:

$$\rho(n) = (1 - e^{-\frac{\hbar\omega_0}{k_B T}}) e^{-\frac{n\hbar\omega_0}{k_B T}}, \text{ noting that } \sum_{n=0}^{\infty} \rho(n) = 1 \text{ and } \sum_{n=0}^{\infty} n\hbar\omega_0 \rho(n) = \hbar\omega_0 e^{-\frac{\hbar\omega_0}{k_B T}} \quad (4s)$$

Also, we emphasize the following feature of the probability density function: to accumulate any additional energy higher than the minimum energy of E_{min} it is needed to host at least:

$$n_{\text{min}} = \frac{E_{\text{min}}}{\hbar\omega_0} - \frac{1}{2} \quad (5s)$$

phonons on an impurity site. One can check that the probability to achieve this condition is:

$$P(E \geq E_{\text{min}}) = \sum_{n=n_{\text{min}}}^{\infty} \rho(n) = \text{const} \quad (6s)$$

The probability to accumulate more than the minimum required number of phonons is constant for any given phonon energy $\hbar\omega_0$.

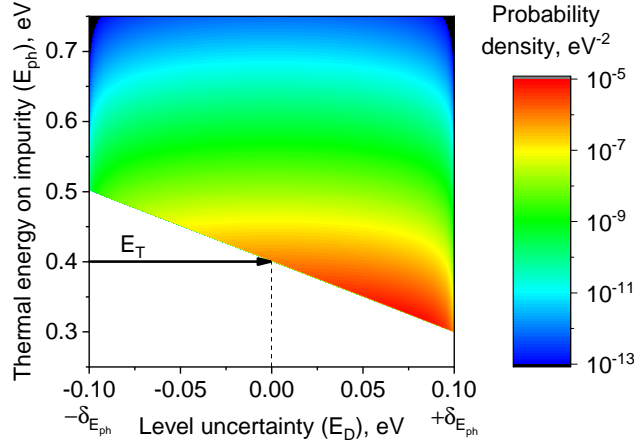


Figure S1 The probability density for an electron occupying the localized level to become aligned with the CB states by interaction with phonons.

2 Broadening for phonon occupation number

For feasible numerical integration and demonstration of the general principle, we adopt a cut parabola as shape function for broadening of the localized level:

$$\rho(E_D) = \frac{3}{4\delta_{E_{ph}}^3} (\delta_{E_{ph}}^2 - E_D^2) \quad (7s)$$

Combination of the probability distribution of phonon occupation of the given localized level with the uncertainty broadening of this level allows to quantitatively assess the thermal probability for activation of the trapped electron into the CB with varying number of phonons. The trap-site becomes levelled with the CB with probability $P(E_{ph})$, see Fig. S1.

3 Release rate integration

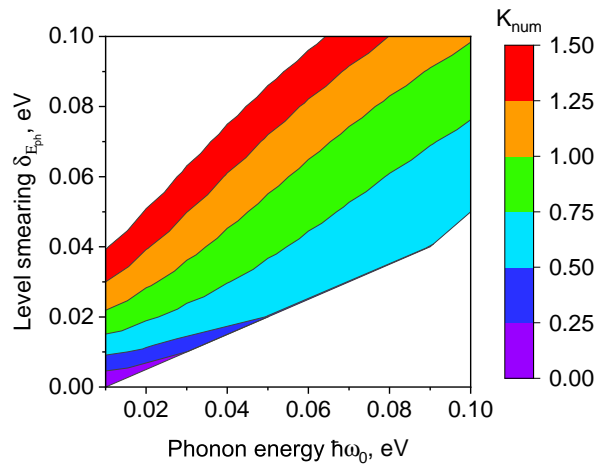


Figure S2 The dependence of numerical coefficient on phonon energy and level broadening for approximation of thermal release rate.

In this paragraph we perform the integration of eq. (15) numerically, see eq. (8s). The integration in the formula (8s) is excellently approximated by the following expression:

$$K_{\text{num}} e^{-\frac{E_T - \frac{\delta_{E_{ph}}}{2}}{k_B T}} \frac{1}{4\delta_{E_{ph}}} \int_0^{\infty} e^{-\frac{E_{CB}^{\text{kin}}}{k_B T}} \sqrt{E_{CB}^{\text{kin}}} dE_{CB}^{\text{kin}}.$$

The K_{num} coefficient has no physical meaning being unavoidable contribution resulting from several contributions:

$$\int_{E_{CB}^{kin} \geq 0} \sqrt{E_{CB}^{kin}} \times dP(n, E_T) = \left\{ \int_{E_T + \delta_{E_{ph}}}^{\infty} dE_{ph} \int_{-\delta_{E_{ph}}}^{+\delta_{E_{ph}}} dE_T + \int_{E_T - \delta_{E_{ph}}}^{E_T + \delta_{E_{ph}}} dE_{ph} \int_{E_T - E_{ph}}^{+\delta_{E_{ph}}} dE_T \right\} \times \left((1 - e^{-\frac{\hbar\omega_0}{k_B T}}) e^{-\frac{E_{ph}}{k_B T}} \frac{1}{\hbar\omega_0} \right) \left\{ \frac{3}{4\delta_{E_{ph}}^3} (\delta_{E_{ph}}^2 - E_T^2) \right\} \sqrt{E_{ph} - E_T + E_D} \quad (8s)$$

$$\gamma_{ion} = \int W_{res.rel.} dP = \frac{2\pi}{\hbar} V_{sc} |M_{model}|^2 \frac{8\pi}{2} \left\{ \frac{2m^*}{\hbar^2} \right\}^{\frac{3}{2}} K_{num} e^{-\frac{E_T - \frac{\delta_{E_{ph}}}{2}}{k_B T}} \frac{1}{4\delta_{E_{ph}}} \sqrt{\pi} (k_B T)^{\frac{3}{2}} = \frac{2\pi}{\hbar} V_{sc} |\mathcal{M}_{model}|^2 \frac{1}{\delta_{E_{ph}}} K_{num} N_c e^{-\frac{E_T - \frac{\delta_{E_{ph}}}{2}}{k_B T}} \quad (9s)$$

approximation of the broadening function, substitution of summation by integration over the phonon occupation numbers, and interpolation of the numerical integration of eq. (15). The value of K_{num} depends on the localized level broadening $\delta_{E_{ph}}$ and phonon mode energy $\hbar\omega_0$, see Fig. S2. Typical K_{num} value for $\delta_{E_{ph}} \approx \hbar\omega_0$ (green domain) is close to unity.

The natural value of broadening $\delta_{E_{ph}}$ that can be adopted is $\delta_{E_{ph}} \approx \hbar\omega_0$. If it is larger than the phonon energy, then the phonon occupation number loses its meaning and must be shifted and renormalized. Otherwise, if it is significantly smaller than $\hbar\omega_0$ then the probability of thermal excitation cannot be considered as a continuous function (see eqs. (6) and (7)).

Now, after performing numerical integration and estimating the K_{num} value, we can rewrite the resonant release rate approximation in the final form, see eq. (9s). Here we have arrived at eqs. (15) and (16) of the main body of the manuscript.

4 Effective mass limit

Let us consider the fundamental correlation of the presented quantum model with the standard effective mass theory¹. Below we connect them in a formal way.

On the one hand, in the description of the CB-electron as a wave-packet its group velocity is introduced as:

$$v_{gr} = \frac{1}{\hbar} \frac{\partial E}{\partial k}. \quad (10s)$$

Assuming parabolic dispersion of a conduction band minimum the group velocity is rewritten via effective mass as:

$$v_{gr} = \frac{1}{\hbar} \frac{\hbar^2 k}{m^*} = \frac{p}{m^*} \quad (11s)$$

where m^* is the effective mass.

On the other hand, we can write out our capture coefficient in a more transparent way. In subsection ‘‘Coulomb attractive center’’ we have obtained the capture coefficient in the form of eq. (30):

$$A_{res} = 16\sqrt{2}\pi^{\frac{3}{2}} \kappa^2 e^{-\kappa^2} \times \frac{1}{\frac{\delta_{E_{ph}}}{Ry^*}} \times \frac{Ry^*}{\hbar} a_* \times \pi a_*^2 \quad (12s)$$

the first two terms are dimensionless coefficients describing the overlap of wavefunctions and the uncertainty broadening of states, the $\frac{Ry^*}{\hbar} a_*$ term has the units of velocity [cm s^{-1}], and πa_*^2 has the units of geometric cross-section [cm^2]. Decomposing Ry^* as doubled kinetic energy $Ry^* = \frac{p_*^2}{2m_e}$, $\hbar = p_* a_*$ where p_* is the electron momentum on impurity orbital, m_e is the electron mass, we obtain:

$$A_{res} = D_1 \frac{1}{D_2} \frac{p_*}{m_e} \pi a_*^2 \quad (13s)$$

the first two terms (D_1, D_2) are repeated dimensionless coefficients, the p_*/m_e term has the units of velocity [cm s^{-1}], and πa_*^2 has the units of geometric cross-sections [cm^2]. By substituting the electron mass m_e by a coefficient m_{eff} that contains all the dimensionless terms we write A_{res} in a short form that is very similar to eq. (11s):

$$A_{\text{res}} = \frac{P^*}{m_{\text{eff}}} \pi a_*^2 = v_{\text{eff}} \pi a_*^2 \quad (14s)$$

the introduced v_{eff} coefficient in our model is still the description of the CB-electron behavior, and has the same form as the eq. (11s) for group velocity in the effective mass model.

The direct correlation of the effective mass approach with our proposed model allows us to strengthen some of our discussion points. In discussion of our model we showed that the frequency factor depends on the overlap of defect- and CB-states. We suppose that it should lead to lower (higher) frequency factors in ionic (covalent) compounds due to close (loose) packing of charge density.

Similar conclusion has been drawn for the dependence of the effective mass on the covalency/ionicity of the host². In the Ref. 2 the covalency of the host was connected to structural polarizability ($\frac{\epsilon_{\text{ion}}}{\epsilon_{\text{electron}}} \approx \frac{\epsilon_s}{\epsilon_\infty} - 1$) of a material and bandgap-pressure coefficient ($\frac{dE_g}{dp}$). Both parameters showed full proportionality to the effective mass of the compound. The effective mass systematically depends on the covalency of the material², moreover compounds with higher covalency have lower effective mass. From eq. (14s) we see that indeed lower effective mass leads to higher capture coefficient and frequency factor.

Please note that the effective mass model is defined for the regular lattice, thus describing interaction of CB-electrons and defect with it should be handled with caution. Local distortion of the effective mass next to irregular sites is to be expected.

Notes and references

- 1 A. Halperin and A. A. Braner, *Phys. Rev.*, 1960, **117**, 408–415.
- 2 Y. Rakita, T. Kirchartz, G. Hodes and D. Cahen, *Type and Degree of Covalence: Empirical Derivation and Implications*, 2019, arXiv preprint: ARXIV.1907.03971.