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Electron-Lattice Interaction in Nonmetallic Materials: Configuration Coordinate Diagram and Lattice Relaxation*

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Electron-lattice interactions in nonmetallic materials are reexamined in the many-electron scheme. The difference in the stable atomic configuration between two electronic states is the origin of the electron-lattice interaction. We show the relationship among the adiabatic potentials, one electron (hole) energy and the lattice elastic energy, paying attention to the electron-hole symmetry. Correct configuration coordinate diagrams for deep-level defects in semiconductors are presented which can be used even when the number of carriers changes due to creation and recombination. Radiative and nonradiative carrier capture and recombination processes at deep-level defects are described consistently with particular attention to the charge of a defect, the thermal and the optical depths of a bound carrier, the correlation between successive electron and hole captures, and the energy dissipation to the lattice through the interaction mode.

KEYWORDS: electron-lattice interaction, configuration coordinate diagram, deep level, lattice relaxation, multiphonon recombination

1. Introduction

In condensed matter, a crystalline structure is realized when the electrons and the atoms are in the ground state — the absolute minimum of the total energy. If we optically excite valence electrons in nonmetallic materials, the balance of interatomic forces mediated by electrons is disturbed and the configuration of atoms is then rearranged. This phenomenon, called photoinduced lattice relaxation, is a kind of photostructural change and manifests itself in various ways in nonmetallic solids.^{1–4)} Some examples are the lattice relaxation by a localized excitation of an impurity center,⁵⁾ the photostructural changes of organic and amorphous^{6,7)} semiconductors, and the F-H defect pair creation by a self-trapped exciton in alkali halides.⁸⁾ During the lattice relaxation a part of the electronic energy is transformed into the kinetic energy of the atoms.

It has long been considered that such strong electron-lattice interaction is realized only in ionic materials, but is almost absent in covalent semiconductors. Recent experimental studies have shown that this is not true. If the electronic excitation is spatially localized due to a point defect, impurity, or due to self-trapping as the secondary process, and if the change of the electronic charge distribution is sufficiently large, then the surrounding atoms are affected by the induced force and are displaced significantly, as has been found in some deep-level defects in covalent semiconductors.^{1,3,4)} The electronic excitation thus induces atomic displacements, and sometimes results in metastability of the atomic configurations, photostructural changes, defect reactions, and so on. The strong electron-lattice interaction is now one of the most attractive topics in the physics of nonmetallic materials.⁴⁾

When we discuss various electronic and atomic processes in condensed matter, it is convenient to introduce

the configuration coordinate diagram (CCD), in which the adiabatic potential of the system is presented as a function of the atomic configuration. The CCD was first introduced for localized electron systems, where the adiabatic potential is given by the sum of the electronic energy and the lattice potential energy.⁵⁾ Recently the CCD has also been used for deep-level defects (impurity) in semiconductors, and succeeded in explaining, for example, a large Stokes shift in the optical spectra, the difference between the thermal and the optical depths of a trapped carrier, the metastability and the photostructural change. A deep-level defect in semiconductors can capture and emit electrons and holes. The adiabatic potentials at such defects, however, cannot be given by a sum of carrier energy and the lattice potential energy, because the carrier number is not conserved due to recombination. In 1982 the author presented a consistent way of describing the deep-level defects in terms of CCD.⁹⁾ Unfortunately, the correct CCD has scarcely been used in the literature. An incorrect CCD leads to misunderstanding of the phenomenon and impedes developments in semiconductor physics.

The purpose of the present review is to show the true meanings of the electron-lattice interaction and the configuration coordinate diagram in nonmetallic materials. In §2 the electron-lattice interaction in condensed matter is reconsidered in the many-electron scheme, which helps us to understand the true meanings of the CCD. In §3 we discuss the lattice relaxation process after an electronic transition and the energy dissipation into the atomic energy in terms of the interaction mode. Section 4 is devoted to the presentation of the correct configuration coordinate diagrams for deep-level defects which can be consistently used even when the number of carriers changes. The dynamics of non-radiative multiphonon recombinations is discussed with particular attention to the charge of a defect, the thermal and the optical depths of a bound carrier and the correlation between successive electron and hole captures.

*This is a revised, updated and translated version of the original paper which appeared in *Oyo Buturi* **57** (1988) 1877 [in Japanese].

2. Electron-Lattice Interaction

When we discuss electronic and atomic properties of condensed matter we usually start with one of the following three schemes depending on the typical energy of the phenomenon.

- (A) all electrons + all nuclei,
- (B) all valence electrons + all ions,
- (C) several electrons and holes + lattice.

Scheme (C), which is essentially the one-electron scheme, is popular in semiconductor physics. However, we start here with a more basic scheme (B), which we call the many-electron scheme in this paper, to clarify the electron-lattice interaction used in scheme (C), and to find the correct CCD that can consistently describe the processes with carrier number change.

In condensed matter valence electrons ($\sim 10^{23}$) and ions ($\sim 10^{23}$) interact with each other. Let us consider a system which consists of n electrons ($i=1, 2, \dots, n$) and N ions ($j=1, 2, \dots, N$). The latter include impurity atoms if any. The Hamiltonian of the system is formally written as

$$H = H_e(r_1, r_2, \dots) + V_{ei}(r_1, r_2, \dots, R_1, R_2, \dots) + H_I(R_1, R_2, \dots), \quad (2.1)$$

where

$$H_e(r_1, r_2, \dots) = \sum_i \frac{p_i^2}{2m} + V_e(r_1, r_2, \dots), \quad (2.1a)$$

$$H_I(R_1, R_2, \dots) = \sum_j \frac{P_j^2}{2M_j} + V_I(R_1, R_2, \dots). \quad (2.1b)$$

Here r_i and p_i are, respectively, the position and the momentum of the i -th electron with mass m . R_j and P_j are those of the j -th ion with mass M_j . The set of these variables will be abbreviated to $\{r\} \equiv (r_1, r_2, \dots, r_n)$, $\{R\} \equiv (R_1, R_2, \dots, R_N)$ and so on. The terms V_e , V_{ei} and V_I denote, respectively, the interactions of electron-electron, electron-ion and ion-ion. We will not go into the details of their explicit forms. Hereafter we call ions "atoms", which will not cause any confusion.

Because M_j is much larger than m , the adiabatic approximation can be applied to separate the electronic motion and the atomic motion. First, we fix the atomic configuration $\{R\}$ and solve the Schrödinger equation of the electrons formally as

$$[H_e(\{r\}) + V_{ei}(\{r\}, \{R\})]\Psi_{l,\{R\}}(\{r\}) = E_l(\{R\})\Psi_{l,\{R\}}(\{r\}). \quad (2.2)$$

Here $\Psi_{l,\{R\}}(\{r\})$ is the l -th eigenstate with the energy $E_l(\{R\})$ for the fixed atomic configuration $\{R\}$. The adiabatic potential $U_l(\{R\})$ for the l -th electronic state is given by

$$U_l(\{R\}) = E_l(\{R\}) + V_I(\{R\}), \quad (2.3)$$

which is schematically shown in Fig. 1. The adiabatic potentials are numbered by l in the order of increasing energy. It should be noted that within the same (l -th) branch of the adiabatic potential the electronic wave function $\Psi_{l,\{R\}}(\{r\})$ changes continuously with the

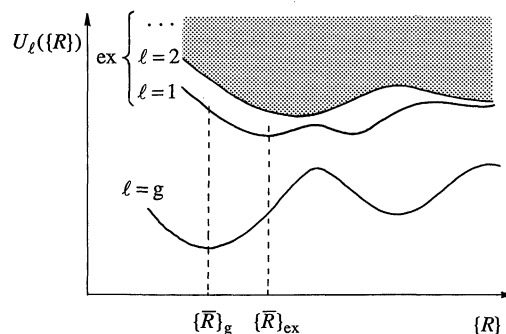


Fig. 1. A schematic illustration of adiabatic potentials for nonmetallic condensed matter. Note that the abscissa $\{R\}$ is considered to be $3N$ dimensional.

atomic configuration $\{R\}$ changes.

Let us focus on the minimum points of the adiabatic potentials. They are different for different electronic states (l) because the stable configurations are determined through the interaction between electrons and atoms. Suppose that electrons are in the ground state and the atomic configuration is the minimum $\{\bar{R}\}_g$ of the ground state. If we optically excite the electrons from the ground state to an excited state, the configuration $\{\bar{R}\}_g$ does not change during the transition (Franck-Condon principle). In the excited state, however, the configuration $\{\bar{R}\}_g$ becomes unstable and the atoms will move to a new minimum position $\{\bar{R}\}_{ex}$ where $U_{ex}(\{\bar{R}\})$ takes a minimum value. This difference in the equilibrium configuration between two electronic states is the origin of the electron-lattice interaction in condensed matter. Its strength can be estimated by the following quantities:

- (a) the atomic displacement

$$\{\bar{R}\}_{ex} - \{\bar{R}\}_g, \quad (2.4a)$$

- (b) the lattice relaxation energy

$$U_{ex}(\{\bar{R}\}_g) - U_{ex}(\{\bar{R}\}_{ex}) \quad \text{or} \quad U_g(\{\bar{R}\}_{ex}) - U_g(\{\bar{R}\}_g), \quad (2.4b)$$

- (c) the derivative of the adiabatic potential, i.e., the generalized force

$$-\left(\frac{\partial U_{ex}}{\partial R_j}\right)_{\{\bar{R}\}_g} \quad \text{or} \quad -\left(\frac{\partial U_g}{\partial R_j}\right)_{\{\bar{R}\}_{ex}}. \quad (2.4c)$$

In some cases these three quantities are related to each other in a simple way as will be shown in §3. In general, however, the configuration $\{\bar{R}\}_{ex}$ and the wave function $\Psi_{ex,\{\bar{R}\}_{ex}}(\{r\})$ of the relaxed excited state can be predicted only with extremely complicated *ab initio* calculation. The generalized force depends on the excited state (l). In the next section we will first define the strength of the electron-lattice interaction in a way which does not depend on l as is usually done, and then apply it to the individual excited state.

2.1 Perfect crystal

2.1.1 Ground state

For a macroscopic and electrically neutral system, the atomic configuration $\{\bar{R}\}_g$ of the ground state has a

translational symmetry and forms a crystal structure. Because of the kinetic energy, atoms can vibrate around equilibrium positions, \bar{R}_j . As long as the displacements $\Delta R_j \equiv R_j - \bar{R}_j$ remain small enough, one can use the harmonic approximation for $U_g(\{R\})$. The quadratic form can be diagonalized by transforming $\{\Delta R_j\}$ into the normal modes $\{Q_{k,\sigma}\}$ of the lattice vibrations, as follows.

$$\Delta R_j \propto \sum_{k,\sigma} Q_{k,\sigma} \exp(ik \cdot \bar{R}_j), \quad (2.5)$$

$$U_g(\{\Delta R_j\}) = U_g(\{Q_{k,\sigma}\}) = \text{const.} (=0) + \frac{1}{2} \sum_{k,\sigma} \omega_{k,\sigma}^2 Q_{k,\sigma}^2, \quad (2.6)$$

$$\langle \Psi_{g,\{R\}} | H | \Psi_{g,\{R\}} \rangle = \frac{1}{2} \sum_{k,\sigma} (P_{k,\sigma}^2 + \omega_{k,\sigma}^2 Q_{k,\sigma}^2) \equiv H_L. \quad (2.7)$$

Here, k represents the wave vector, σ the branch index and ω_k the angular frequency. The normal modes are classified into the acoustic modes ($\sigma = \text{ac}$) and the optical modes ($\sigma = \text{op}$). Thus, in the ground state, the interaction between n valence electrons and N ions results in the lattice vibrations H_L . There is no electron-lattice interaction in the ground state which is our reference state; in fact, the quantities (2.4.a)–(2.4.c) vanish if the suffix (ex) is replaced by (g).

2.1.2 Polaron

Before we discuss the excited states of a perfect crystal, it is informative to look at a polaron which is an electron (or a hole) in the conduction (valence) band accompanied by lattice distortion it induces.¹⁰⁾ This is a typical and familiar example of the electron-lattice interaction in condensed matter. However, it is not a problem of the excited states of n electrons but a problem of the ground state of $n+1$ ($n-1$) electrons. If an electron is added to (removed from) a crystal, the stable atomic configuration $\{\bar{R}\}_g^{n+1}$ ($\{\bar{R}\}_g^{n-1}$) of the ground state of this $n+1$ ($n-1$) electron system differs from $\{\bar{R}\}_g^n$ of n electrons. This difference is the origin of the electron-lattice interaction in a polaron system. Although our attention is directed to the $n+1$ electron system ($\Psi_{g,\{\bar{R}\}}^{n+1}(\{r\})$ and $\{\bar{R}\}_g^{n+1}$) we implicitly refer to the configuration $\{\bar{R}\}_g^n$ of the n electron system, in which the lattice vibrations are defined. Let us denote r_e as the position of an extra electron and approximate the electronic states as

$$|\Psi_{l,\{R\}}^{n+1}\rangle \cong |\phi_{l,\{R\}}(r_e)\rangle |\Psi_{g,\{R\}}^n\rangle. \quad (2.8)$$

Instead of the one-electron eigenstate $\phi_{l,\{R\}}(r_e)$, we usually employ a localized Wannier state $\phi_{\bar{R}_j}(r_e) = a(r_e - \bar{R}_j)$, which is obtained as a linear combination of the Bloch states of the conduction band. The effective Hamiltonian of a polaron in this subspace is given by

$$H_{eL} = h_e + V_{eL} + H_L, \quad h_e = \frac{p_e^2}{2m_e^*}, \quad H_L = \frac{1}{2} \sum_{k,\sigma} (P_{k,\sigma}^2 + \omega_{k,\sigma}^2 Q_{k,\sigma}^2). \quad (2.9)$$

Here m_e^* is the effective mass of a conduction electron. The form of the electron-lattice interaction V_{eL} with

respect to the normal mode $Q_{k,\sigma}$ can be obtained by the method of eq. (2.4.c). Replacing the discrete variable $l = \bar{R}_j$ by the continuous variable r_e , we obtain the deformation-potential-type interaction for the acoustic modes $Q_{k,\text{ac}}$, and the Fröhlich-type interaction for the optical modes $Q_{k,\text{op}}$ in ionic materials.¹¹⁾

$$V_{eL} = - \sum_{k,\sigma} A_{k,\sigma}^e Q_{k,\sigma} \exp(ik \cdot r_e),$$

$$A_{k,\text{ac}}^e = \left(\frac{2}{NM} \right)^{1/2} E_d^e k,$$

$$A_{k,\text{op}}^e = \left[\frac{2\pi\omega_{\text{op}}^2 e^2}{V} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \right]^{1/2} k^{-1}. \quad (2.10)$$

Here E_d^e is the deformation potential of the conduction band, ω_{op} the optical phonon frequency, ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants.

What is the minimum point $\{\bar{R}\}_g^{n+1}$ of the atomic configuration for a polaron? The polaron problem has been intensively studied for many years.¹⁰⁾ It has been shown that polarons are classified into two types: large (radius) polarons accompanied by few phonons and small (radius) polarons with large lattice distortion (self-trapped electrons).^{1,2,8,10,12)} The type is qualitatively determined by three parameters: the electron kinetic energy B , the lattice relaxation energy for the optical modes, $E_{\text{LR}}^{\text{op}}$, and that for the acoustic modes, $E_{\text{LR}}^{\text{ac}}$, for an electron completely localized at a lattice site. If $E_{\text{LR}}^{\text{op}} + E_{\text{LR}}^{\text{ac}} \lesssim B$, it becomes a large polaron, while for $E_{\text{LR}}^{\text{op}} + E_{\text{LR}}^{\text{ac}} \gtrsim B$, it becomes a small polaron. The transition between large polaron and small polaron is shown to depend strongly on the force range related with the k -dependence of the interaction coefficients $A_{k,\sigma}^e$ (eq. (2.10)) and on the dimensionality of the system.^{12–14)}

2.1.3 Excited state

Let us return to the n electron system. The first electronic excited state of nonmetallic solids is a pair of an electron in the conduction band and a hole in the valence band. Sometimes they are bound to form an exciton. The sudden appearance of an electron-hole pair causes the imbalance of the interatomic force, and displaces atoms to the new equilibrium position $\{\bar{R}\}_{\text{ex}}$. The difference between the minimum positions $\{\bar{R}\}_{\text{ex}} - \{\bar{R}\}_g$ can be attributed to the appearance of an electron-hole pair. If we approximate this one-pair excited state as

$$|\Psi_{\text{ex},\{R\}}^n\rangle \cong |\phi(r_e, r_h)\rangle |\Psi_{g,\{R\}}^n\rangle, \quad (2.11)$$

where r_e and r_h are, respectively, the position of an electron in the conduction band and a hole in the valence band, the effective Hamiltonian in the subspace of one-pair excitation is formed as

$$H_{\text{ehL}} = h_e + h_h + V_{\text{eh}} + V_{eL} + V_{hL} + H_L, \quad (2.12)$$

$$h_e = \frac{p_e^2}{2m_e^*}, \quad h_h = \frac{p_h^2}{2m_h^*},$$

$$V_{\text{eh}} = - \frac{e^2}{4\pi\epsilon_\infty |r_e - r_h|}, \quad (2.12a)$$

$$H_L = \frac{1}{2} \sum_{k,\sigma} (P_{k,\sigma}^2 + \omega_{k,\sigma}^2 Q_{k,\sigma}^2), \quad (2.12b)$$

$$\begin{aligned}
V_{eL} &= - \sum_{k,\sigma} A_{k,\sigma}^c Q_{k,\sigma} \exp(ik \cdot r_e), \\
V_{hL} &= - \sum_{k,\sigma} A_{k,\sigma}^v Q_{k,\sigma} \exp(ik \cdot r_h). \\
(A_{k,op}^c &= -A_{k,op}^v)
\end{aligned} \quad (2.12c)$$

This is nothing but scheme (C) shown in §2.1, where the system is composed of an electron, a hole and the lattice vibrations (phonons). The interaction of all $n-1$ electrons in the valence band is incorporated into the lattice potential energy $((1/2) \sum_{k,\sigma} \omega_{k,\sigma}^2 Q_{k,\sigma}^2)$.

2.2 Localized centers

If the translational symmetry of a crystal is broken by a defect (impurity, vacancy, \dots), electronic states can be spatially localized around the defect.

2.2.1 Trapping of a conduction electron

Let us discuss trapping and detrapping processes of a conduction electron by a point-defect in semiconductors. This is an $n+1$ electron problem. An extra electron occupies a localized state at the defect or a free state in the conduction band. If trapping and detrapping of an electron have little effect on the rest of the n electrons in the valence band, we can introduce the effective Hamiltonian for an extra electron (r_e) and the lattice;

$$H_{eL} = h_e + V_{eL} + H_L. \quad (2.13)$$

The Schrödinger equation for one electron state $\phi_{l,\{R\}}(r_e)$ at the configuration $\{R\}$ is given by

$$\begin{aligned}
[h_e(r_e, p_e) + V_{eL}(r_e, \{R\})] \phi_{l,\{R\}}(r_e) &= \varepsilon_l(\{R\}) \phi_{l,\{R\}}(r_e), \\
h_e(r_e, p_e) &= \frac{p_e^2}{2\tilde{m}_e} + V_{\text{def}}(r_e),
\end{aligned} \quad (2.14)$$

where $V_{\text{def}}(r_e)$ is a defect potential. Unless an electron is very deeply localized, \tilde{m}_e and $V_{eL}(r_e, \{R\})$ can be approximated, respectively, by m_e^* and eq. (2.10) of a polaron in the relevant perfect crystal. The number of localized states depends on the potential $V_{\text{def}}(r_e)$ and the configuration $\{R\}$. The dependence of $\varepsilon_l(\{R\})$ on

$\{R\}$ is strong for localized states while is infinitesimally small for extended states (Fig. 2(a)). The adiabatic potential is given by

$$\tilde{U}_l^{n+1}(\{R\}) = \varepsilon_l(\{R\}) + \tilde{U}_g^n(\{R\}). \quad (2.15)$$

Here, $\tilde{U}_g^n(\{R\})$ with a tilde is the adiabatic potential for the ground state of the n electrons with a defect. The presence of a defect (impurity, vacancy, \dots) displaces surrounding host atoms. The displacement from the crystal point $\{\bar{R}\}_{\text{def},g}^n - \{\bar{R}\}_g^n$ should be treated as static distortion. Without extra electrons, atoms vibrate around the minimum $\{\bar{R}\}_{\text{def},g}^n$, and $\tilde{U}_g^n(\{R\})$ in the harmonic approximation can be written as a quadratic form in the displacements $\Delta R_j \equiv R_j - (\bar{R}_j)_{\text{def},g}^n$, which can be diagonalized with the normal modes $(\{\tilde{\omega}_k\}, \{\tilde{Q}_k\})$.

$$\tilde{U}_g^n(\{R\}) = \text{const.} + \frac{1}{2} \sum_{k,\sigma} \tilde{\omega}_{k,\sigma}^2 \tilde{Q}_{k,\sigma}^2. \quad (2.16)$$

Some of these normalized modes may be localized modes at the defect.

Figure 2(b) shows an example of the adiabatic potentials. As a result of the electron-lattice interaction the energy depth of a localized electron depends on $\{\Delta R_j\}$. The optical depth (ionization energy) E_e^{op} is larger than the thermal depth E_e^{th} . If the lattice distorts such that the depth becomes zero ($\{\Delta R_j\} = \{\Delta R_j\}_c$), a nonradiative electron transition is possible.¹⁵⁾ This process will be discussed thoroughly in §4.

2.2.2 Trapping of a valence hole

The trapping process of a valence hole by a point-defect is an $n-1$ electron problem. If a defect potential is repulsive for electrons, localized state(s) splits off from the valence band (Fig. 3(a)). In the ground state a localized state is empty, while in the excited state it is occupied by an electron. The adiabatic potential for the l th state is given by

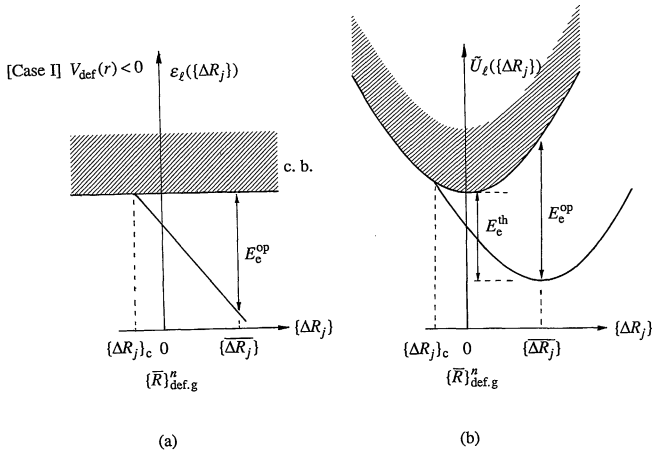


Fig. 2. (a) One-electron energy $\varepsilon_l(\{\Delta R_j\})$ and (b) adiabatic potentials $\tilde{U}_l(\{\Delta R_j\})$ as a function of the atomic coordinates $\{\Delta R_j\}$ for a neutral point defect which attracts a conduction electron ($V_{\text{def}}(r) < 0$). The hatching represents a continuous spectrum of a free electron.

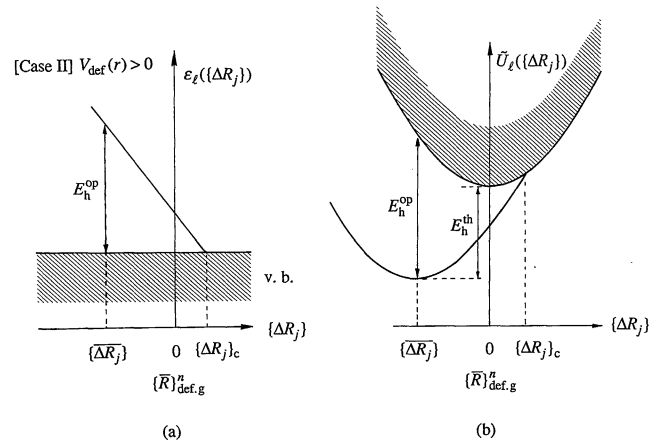


Fig. 3. (a) One-electron energy $\varepsilon_l(\{\Delta R_j\})$ and (b) adiabatic potentials $\tilde{U}_l(\{\Delta R_j\})$ as a function of the atomic coordinates $\{\Delta R_j\}$ for a neutral point defect which attracts a valence hole ($V_{\text{def}}(r) > 0$). The hatching represents a continuous spectrum of a free hole.

$$\begin{aligned}\tilde{U}_l^{n-1}(\{R\}) &= \tilde{E}_l^{n-1}(\{R\}) + \tilde{V}_l(\{R\}) \\ &= \tilde{E}_g^n(\{R\}) - \varepsilon_l(\{R\}) + \tilde{V}_l(\{R\}) \\ &= -\varepsilon_l(\{R\}) + \tilde{U}_g^n(\{R\}),\end{aligned}\quad (2.17)$$

where $\varepsilon_l(\{R\})$ is the one-electron energy at the configuration $\{R\}$ (Fig. 3(a)). If $\tilde{U}_g^n(\{R\})$ is considered to be the potential energy of the lattice vibrations, $-\varepsilon_l(\{R\})$ can be regarded as a hole energy. In this case we can introduce the effective Hamiltonian for a hole and the lattice.

$$H_{\text{hL}} = h_{\text{h}} + V_{\text{hL}} + H_{\text{L}}, \quad (2.18)$$

A similar argument can be developed for a valence hole (r_{h}) for its trapping and detrapping if we replace the suffix (e) by (h) in eq. (2.14) in the previous section.

2.2.3 Several localized electrons

If we discuss electronic transitions of several localized electrons at a defect, there are three methods to discuss the electron-lattice interaction.

The first one is to introduce an effective Hamiltonian which consists of several localized electrons (the number $n' \ll n$) and the lattice vibrations, into which the rest of n electrons are incorporated. The Hamiltonian can be written as

$$H_{\text{eff}} = H_{\text{e}}(\{r\}') + V_{\text{eL}}(\{r\}', \{R\}) + H_{\text{L}}(\{R\}), \quad (2.19)$$

$$H_{\text{e}}(\{r\}') = \sum_{i=1}^{n'} \frac{p_i^2}{2\tilde{m}_{\text{e}}} + V_{\text{def}}(\{r\}') + V_{\text{e}}(\{r\}'), \quad (2.19a)$$

$$V_{\text{eL}}(\{r\}', \{R\}) = - \sum_{k,\sigma} \sum_{i=1}^{n'} \tilde{A}_{k,\sigma} \tilde{Q}_{k,\sigma} \exp(ik \cdot r_i), \quad (2.19b)$$

$$H_{\text{L}}(\{R\}) = \frac{1}{2} \sum_{k,\sigma} (\tilde{P}_{k,\sigma}^2 + \tilde{\omega}_{k,\sigma}^2 \tilde{Q}_{k,\sigma}^2). \quad (2.19c)$$

Here, $V_{\text{def}}(\{r\}')$ denotes the defect potential and $V_{\text{e}}(\{r\}')$ the electron-electron interaction. If all the localized states are related to the conduction band, that is, they can be expressed by a linear combination of the Wannier states of the conduction band, \tilde{m}_{e} can be replaced by the electron effective mass m_{e}^* and the form of the electron-lattice interaction of a polaron (eq. (2.10)) can be employed.¹⁶⁾

The second way is to formally expand the adiabatic potentials of the *excited* states with respect to the lattice distortion $\{\Delta R_j\}$ or the normal modes $\{\tilde{Q}_{k,\sigma}\}$ which are defined in the ground state.

$$\begin{aligned}U_l(\{\Delta R_j\}) &= U_l(\{\Delta R_j=0\}) + \sum_j \left(\frac{\partial U_l}{\partial \Delta R_j} \right)_{\{\tilde{R}\}_g} \Delta R_j + \cdots \\ &= U_l(\{0\}) + \sum_{k,\sigma} a_{k,\sigma}^l \tilde{Q}_{k,\sigma} + \cdots, \\ &\quad \text{for } l = \text{ex.}\end{aligned}\quad (2.20)$$

The second term expresses the electron-lattice interaction. The coefficient $a_{k,\sigma}^l$ and $U_l(\{0\})$ are regarded as parameters, with which one can calculate the l -th adiabatic potential and fit it to the experimental data, paying attention to the point symmetry of the system. This is usually done in the Jahn-Teller system.⁵⁾

The third way is to perform an *ab initio* calculation, which directly gives us the adiabatic potentials.

3. Lattice Relaxation

In this section we discuss the lattice relaxation process after an electronic transition at defects. We consider a simple case where the adiabatic potentials of the ground state and an excited state have the same curvature but have different minima

$$U_{\text{g}}(\{Q_k\}) = \varepsilon_{\text{g}} + \frac{1}{2} \sum_k \omega_k^2 Q_k^2, \quad (3.1a)$$

$$U_{\text{ex}}(\{Q_k\}) = \varepsilon_{\text{ex}} - \sum_k a_k Q_k + \frac{1}{2} \sum_k \omega_k^2 Q_k^2, \quad (3.1b)$$

where Q_k is the lattice coordinate of the normal mode with a frequency ω_k defined in the ground state (we will omit the tilde hereafter). The suffix k includes wave vector k , the branch index σ and also localized modes (if any). The minima of two adiabatic potentials are separated by $\{\bar{Q}_k = a_k/\omega_k^2\}$ (eq. (2.4.a)). The lattice relaxation energies (eq. (2.4.b)) for the excited and the ground states are both given by

$$E_{\text{LR}} = \sum_k a_k^2 / 2\omega_k^2, \quad (3.2)$$

and the generalized forces (eq. (2.4.c)) are a_k and $-a_k$.

Let us introduce an orthogonal transformation from $\{\omega_k Q_k\}$ to $\{Q_l\}$ in which one of the modes is chosen to be

$$Q_1 = \frac{1}{\bar{Q}_1} \sum_k a_k Q_k. \quad (3.3)$$

The adiabatic potentials are then expressed as

$$U_{\text{g}}(Q_l) = \varepsilon_{\text{g}} + \frac{1}{2} \sum_l Q_l^2, \quad (3.4a)$$

$$U_{\text{ex}}(Q_l) = \varepsilon_{\text{ex}} - \bar{Q}_1 Q_1 + \frac{1}{2} \sum_l Q_l^2. \quad (3.4b)$$

The electron-lattice interaction appears only through the Q_1 mode, which is called the interaction mode.^{11,17)} The distance between two minima of the adiabatic potentials is \bar{Q}_1 , the lattice relaxation energy is $\bar{Q}_1^2/2$ and the generalized forces are \bar{Q}_1 and $-\bar{Q}_1$. Since the other Q_l modes do not affect the electronic energy, it is sufficient to express the adiabatic potentials only in the Q_1 direction (Fig. 4). The interaction mode is defined

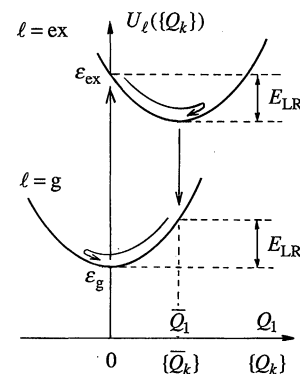


Fig. 4. A simple example of adiabatic potentials for the ground and excited states.

between two electronic states (configurations) and is not a normal mode. It depends on the difference in the electronic charge distributions between two states. At a point defect with cubic symmetry, for example, it looks like a breathing mode for two totally symmetric states.

Let us suppose that electrons are in the ground state and atoms are at rest ($\{Q_k=0\}$, $\{Q_l=0\}$) and at $t=0$ electrons are excited optically. Just after the excitation the lattice starts to vibrate around the new equilibrium \bar{Q}_k starting from $Q_k=0$ (Franck-Condon principle).

$$Q_k(t) = \bar{Q}_k(1 - \cos \omega_k t). \quad (3.5)$$

The trajectory $\{Q_k(t)\}$ is a Lissajous figure in $3N$ dimensional $\{Q_k\}$ space. While in $\{Q_l\}$ space,

$$Q_l(t) = \frac{1}{Q_1} \sum_k a_k \bar{Q}_k (1 - \cos \omega_k t). \quad (3.6)$$

If there is dispersion in the phonon frequencies $\{\omega_k\}$, the interaction mode shows a damping oscillation because of the dephasing among $\cos \omega_k t$, provided that all amplitudes \bar{Q}_k are on the order of $1/3N$. The oscillation is damped in a period $\tau \sim 2\pi/\bar{\omega}_k$, where $\bar{\omega}_k$ is the average frequency. During the lattice relaxation, a part of the electronic excitation energy ($\varepsilon_{\text{ex}} - \varepsilon_g$) has changed into the atomic energy, namely, the energy

$$E_{\text{LR}} = \frac{1}{2} \bar{Q}_1^2 = \frac{1}{2} \sum_k \frac{a_k^2}{\omega_k^2}, \quad (3.7)$$

is dissipated to the extended lattice vibrations (phonons) (whence the name "lattice relaxation energy" follows), and the same amount of elastic energy $U_L (=E_{\text{LR}})$ is stored as a local strain around the defect if referred to $\{\bar{R}\}_g$ of the ground state. It should be noted that each normal mode Q_k just vibrates within the harmonic approximation, as if no dissipation occurs. The lattice relaxation energy divided by the average phonon energy $\hbar\bar{\omega}_k$ is called Huan-Rhys factor $S = E_{\text{LR}}/\hbar\bar{\omega}_k$,¹⁸⁾ which represents the average number of phonons created during the relaxation.¹⁹⁾

If there is a local mode Q_{loc} , and $a_{\text{loc}}\bar{Q}_{\text{loc}}$ is on the order of 1, the oscillation is continued after $t \gtrsim \tau$

$$Q_1(t) \approx \frac{1}{Q_1} a_{\text{loc}} \bar{Q}_{\text{loc}} (1 - \cos \omega_{\text{loc}} t). \quad (3.8)$$

During a period $0 < t \lesssim \tau$, a part of the lattice relaxation energy

$$E'_{\text{LR}} = \frac{1}{2} \sum_{k \neq \text{loc}} \frac{a_k^2}{\omega_k^2}, \quad (3.9)$$

is dissipated. After that, the remaining energy $E_{\text{LR}} - E'_{\text{LR}}$ is gradually dissipated due to the anharmonicity in $U_{\text{ex}}(\{Q_k\})$, which is neglected in eq. (3.1b).

If an optical emission takes place at $t = \tau_{\text{rad}}$ sufficient-ly after the lattice relaxation has been completed ($\tau_{\text{rad}} \gg \tau$), the emitted photon has an energy $\varepsilon_{\text{ex}} - \varepsilon_g - (E_{\text{LR}} + U_L)$. Again the lattice shows a damping oscillation

$$Q_1(t) = \frac{1}{Q_1} \sum_k a_k \bar{Q}_k \cos \omega_k (t - \tau_{\text{rad}}). \quad (3.10)$$

The stored lattice strain energy $U_L (=E_{\text{LR}})$ is dissipated into the lattice vibrations over the crystal.

4. Configuration Coordinate Diagram for Deep-Level Defects

Recently a variety of deep-level defects in covalent semiconductors have been found to show large lattice relaxation. Depending on the electronic occupation of localized states, the lattice distorts and the energy level of a localized state moves up and down in the band gap. If the energy shift is sufficiently large, nonradiative recombination is possible by successive capture of an electron and a hole. To discuss various electronic and atomic processes at deep-level defects, it is convenient to introduce the configuration coordinate diagram (CCD). In the literature, however, the correct diagram has seldom been used. In this section we will explain the meaning of the CCD for deep-level defects and show how to calculate and present the correct diagram.

We are familiar with the one-electron energy scheme in semiconductor physics. In a perfect crystal one electron state $\phi_{k,s}(r)$ and its energy $\varepsilon_{k,s}$ are defined with a wave vector k and a band index s . In Fig. 5 the energy of a conduction electron increases upwards and that of a valence hole increases downwards. The abscissa is sometimes supposed to be spatial coordinates. We can put several electrons and holes at a time in this figure and add some localized electrons and holes at defects. Electronic processes in semiconductors can be described with this scheme, except for the electron-lattice interaction.

When the electron-lattice interaction is strong, electronic states $\Psi(\{r\})$ depend on the atomic configuration $\{R\}$. When an electron or a hole is localized at a defect, it couples with several lattice distortions $\{\Delta R_j\}'$ around the defect. One-electron state $\phi_{l,\{\Delta R_j\}'}(r)$ and its energy $\varepsilon_l(\{\Delta R_j\}')$ can be calculated in principle with a suitable method. There are some localized bound states in addition to continuous free states of the conduction and the valence bands (Fig. 6). The energy of localized states depend strongly on $\{\Delta R_j\}'$, while those of the other extended states do not.¹⁹⁾

One is likely to calculate adiabatic potentials simply by adding the lattice elastic energy to this one-electron energy, similarly to eq. (2.15),

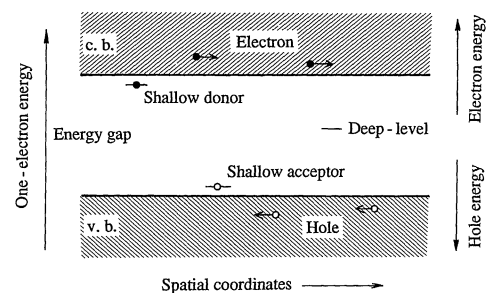


Fig. 5. One-electron energy scheme for a nonmetallic material. We can put several electrons and holes in it at a time.

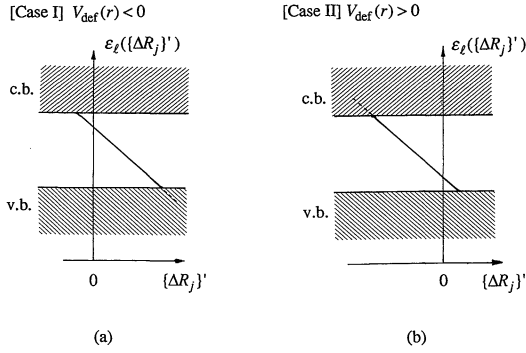


Fig. 6. An example of one-electron energy $\varepsilon_l(\{\Delta R_j\}')$ for a point defect ((a) $V_{\text{def}}(r) < 0$ and (b) $V_{\text{def}}(r) > 0$) as a function of local distortions $\{\Delta R_j\}'$.

$$U_l(\{\Delta R_j\}) = \varepsilon_l(\{\Delta R_j\}') + U_g(\{\Delta R_j\}) \\ = \varepsilon_l(\{\Delta R_j\}') + \frac{1}{2} \sum_k \omega_k^2 Q_k^2, \quad (4.1)$$

and put an electron and a hole, with the understanding that $-\varepsilon_l(\{\Delta R_j\}')$ in the valence band represents the energy of a hole. This type of adiabatic potential (Fig. 7) can be found in much of the literature, including a pioneering paper by Henry and Lang.¹⁵⁾ If we confine ourselves to capture and emission of a conduction electron and neglect the valence band (hence a hole), this figure works in part, as has been seen in §2.2.1 (Fig. 2). Via deep levels, however, capture and emission are possible for both an electron in the conduction band and a hole in the valence band. Equation (4.1) and Fig. 7 cause serious inconsistencies if we put an electron and a hole at the same time. This is seen as follows.

In Fig. 7, where should we put a hole? Is the direction of a hole energy in the valence band opposite to that of an electron? Since the energy refers to the electron, the electron-hole symmetry is broken. In which direction does the lattice relax if a hole is captured? Can we put several electrons and holes at one time in Fig. 7 as have done in Fig. 5?

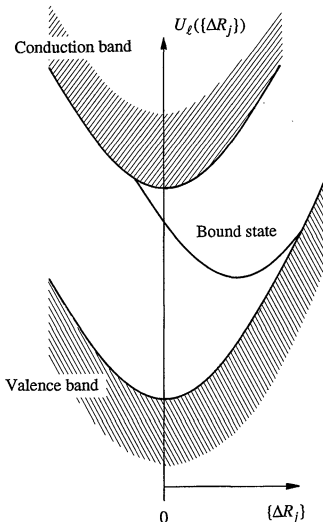


Fig. 7. An incorrect CCD for a deep-level defect in semiconductors.

Then is it valid to calculate the adiabatic potentials as a sum of the energy of an electron in the conduction band, that of a hole in the valence band and the lattice elastic energy?

$$U_{ll}(\{\Delta R_j\}) = \varepsilon_e(\{\Delta R_j\}') + \varepsilon_h(\{\Delta R_j\}') + \frac{1}{2} \sum_k \omega_k^2 Q_k^2, \quad (4.2)$$

where $\varepsilon_e(\{\Delta R_j\}') = \varepsilon_l(\{\Delta R_j\}')$ and $\varepsilon_h(\{\Delta R_j\}') = -\varepsilon_l(\{\Delta R_j\}')$. However, this also does not work, for the following reason. The number of electrons and holes is not conserved if electron-hole recombination occurs at a deep-level defect, and then it slips out of the scheme. In addition, it is unclear as to whether we should relate a localized state in the band gap to an electron or hole.

4.1 Correct diagram

We should return to the starting point of the electron-lattice interaction discussed in §2. Consider a neutral defect which attracts conduction electrons ($V_{\text{def}}(r) < 0$: case I), or a neutral defect which attracts valence holes ($V_{\text{def}}(r) > 0$: case II). At least three electronic states for each case must be considered.^{9,21)}

[case I] ($V_{\text{def}}(r) < 0$)

(a) The ground state (g.s.): All n electrons occupy the valence band. There are no electrons or holes. The defect is neutral.

(b) One free electron + one free hole state (f.e. + f.h.): one electron occupies a free state in the conduction band and $n-1$ electrons occupy the valence band; i.e., one free hole is in the valence band. The defect is neutral. This has a *double-continuum spectrum* due to the free motions of an electron and a hole. The lowest energy is E_g larger than that of (g.s.) where E_g is the band gap energy.

(c) One trapped electron + one free hole state (t.e. + f.h.): The defect is occupied by an electron and charged $-e$. $n-1$ electrons occupy the valence band; i.e., one free hole is in the valence band. This has a *single-continuum spectrum* due to the free motion of a hole.

[case II] ($V_{\text{def}}(r) > 0$)

(a) The ground state (g.s.): All n electrons occupy the valence band including a localized state in the gap. There are no electrons or holes. The defect is *neutral*.

(b) One free electron + one free hole state (f.e. + f.h.): one electron occupies a free state in the conduction band and $n-2$ electrons occupy $n-2$ free states in the valence band and a localized state in the gap; i.e., one free hole is in the valence band. The defect is *neutral*. This has a *double-continuum spectrum* due to the free motions of an electron and a hole. The lowest energy is E_g larger than that of (g.s.).

(c') One free electron + one trapped hole state (f.e. + t.h.): an electron occupies a free state in the conduction band and $n-1$ electrons occupy free states of the valence band. A localized state which comes from the valence band is empty; i.e., the defect is occupied by a hole and charged $+e$. This has a *single-continuum*

spectrum due to the free motion of an electron.

As has been discussed in §2, the adiabatic potential is the energy of all electrons and atoms except for the kinetic energy of atoms.

$$U_l(\{R\}) = E_l(\{R\}) + V_l(\{R\}), \quad (4.3)$$

where $E_l(\{R\})$ is the total energy of all electrons and $V_l(\{R\})$ is the potential energy of all atoms for a configuration $\{R\}$. Fortunately, complicated many-body calculations are not necessary for the present problem. In the ground state where there is neither electron nor hole, this sum is nothing but the lattice elastic energy. With a suitable choice of the origins of the coordinates and the energy, it is given by²²⁾

$$U_{g.s.}(\{\Delta R_j\}) = U_{g.s.}(\{Q_k\}) = \frac{1}{2} \sum_k \omega_k^2 Q_k^2. \quad (4.4)$$

Then for an excited state where one-electron state $\phi_{occ}(r_e)$ with one-electron energy $\varepsilon_{occ}(\{\Delta R_j\}')$ is occupied and $\phi_{unocc}(r_h)$ with $\varepsilon_{unocc}(\{\Delta R_j\}')$ is empty with respect to the ground state, the adiabatic potential is given by²²⁾

$$U_{ex}(\{Q_k\}) = \varepsilon_{occ}(\{\Delta R_j\}') - \varepsilon_{unocc}(\{\Delta R_j\}') + U_{g.s.}(\{Q_k\}),$$

for $ex = (f.e. + f.h.), (t.e. + f.h.), (f.e. + t.h.)$. (4.5)

Here we neglect the Coulomb interaction between an electron and a hole for simplicity.

Usually the $\{\Delta R_j\}'$ dependence of $\varepsilon_l(\{\Delta R_j\}')$ for a free state can be neglected; then the adiabatic potential for $(f.e. + f.h.)$ is a parabola which is shifted $U_{g.s.}(\{Q_k\})$ by the amount of $\Delta E_e + \Delta E_h + E_g$. Here, $\Delta E_e (> 0)$ and $\Delta E_h (> 0)$ are the kinetic energies of a free electron and a free hole.

When a localized state is occupied by an electron in case I or by a hole in case II, it couples with the lattice distortion $\{\Delta R_j\}'$ around the defect. The other distortions far from the defect can be neglected unless self-trapping of a carrier at a host site is considered. The interaction mode Q_1 can be introduced from $\{\Delta R_j\}'$ with a suitable transformation, in terms of which the adiabatic potentials are expressed as

$$U_{g.s.}(Q_1) = \frac{1}{2} Q_1^2, \quad (4.6a)$$

$$U_{f.e. + f.h.}(Q_1) = \Delta E_e + \Delta E_h + E_g + \frac{1}{2} Q_1^2, \quad (4.6b)$$

$$U_{t.e. + f.h.}(Q_1) = \varepsilon_{occ}(Q_1) + \Delta E_h + \frac{1}{2} Q_1^2, \text{ [case I]} \quad (4.6c)$$

$$U_{f.e. + t.h.}(Q_1) = E_g + \Delta E_e - \varepsilon_{unocc}(Q_1) + \frac{1}{2} Q_1^2, \text{ [case II]}. \quad (4.6c')$$

In eqs. (4.6.c) and (4.6.c') one-electron energy $\varepsilon_l(Q_1)$ is measured from the top of the valence band.

Figures 8(a) and 8(b) show typical examples of the adiabatic potentials for a neutral defect. At a first glance, the diagram (Fig. 8(a)) seems to be almost the same as that of Fig. 7, except for the continuum spectrum of a free hole. However, any point in the correct diagram represents a *total electronic state* for a fixed

configuration $\{R\}$, as is shown in the inserts in Fig. 8. It does not merely represent a one-electron state (an electron or a hole) as in Fig. 5. The following must be emphasized:

(1) The energy always increases upwards. The direction of an excitation is upwards and that of relaxation is downwards. In case I, for example, a point with energy ΔE_h larger than the minimum of the adiabatic potential for $(t.e. + f.h.)$ state represents a state where an electron is bound to a defect with a binding energy E_e^{op} and a free hole moves with a kinetic energy ΔE_h .

(2) Any optical electronic transition occurs vertically from the minimum of the adiabatic potential of the initial state, except for hot luminescence. In case I, a transition from $(t.e. + f.h.)$ to $(f.e. + f.h.)$ corresponds to an electron emission with the optical ionization energy (optical depth) E_e^{op} . That from $(g.s.)$ to $(t.e. + f.h.)$ corresponds to a hole emission with the optical ionization energy (optical depth) E_h^{op} as if a hole is trapped by the defect in $(g.s.)$. After an optical transition the lattice relaxation energy E_{LR} is dissipated into the lattice: $E_e^{op} + E_h^{op} = E_g + 2E_{LR}$.

(3) A nonradiative transition can occur if the lattice distorts so as to reach a crossing point of the adiabatic potentials. A nonradiative capture of an electron (hole) starts from free electron (hole) states with a continuum energy spectrum to a localized state. We can discuss successive captures of an electron and a hole and their correlation in one scheme.

(4) The lattice relaxation occurs after an electron capture and also after a hole capture. In case I, after an electron (hole) capture the coordinate $Q_1(t)$ vibrates around $\bar{Q}_1(Q_1=0)$ with damping, and an energy equal to the thermal depth $E_e^{th}(E_h^{th})$ is dissipated into phonons over the crystal (multiphonon process: the average phonon number is $E_e^{th}/\hbar\bar{\omega}_k$ ($E_h^{th}/\hbar\bar{\omega}_k$): $E_e^{th} + E_h^{th} = E_g$).

(5) If we confine ourselves to capture and emission processes of a single carrier, we extract a part of the diagram (surrounded by a dotted line in Fig. 8). This part is the same as Fig. 2(b) or 3(b). For an electron capture and emission, a hole remains in a free state, so we can disregard a hole. In Fig. 8(a), delete "f.h.", the single hatching which represents its continuum spectrum, and $(g.s.)$. This gives us Fig. 2(b).

So far we have neglected the Coulomb interaction between electron and hole. If it is taken into account, we must add two states:

(f.ex.): free exciton states with a single-continuum spectrum; the lowest adiabatic potential is located $E_B = m_e^* m_h^* e^4 / 2\varepsilon_0^2 \hbar^2 (m_e^* + m_h^*)$ below that of $(f.e. + f.h.)$, where E_B is the exciton binding energy.

(t.ex.): a trapped exciton state; the adiabatic potential is located $\sim E_B$ below that of $(t.e. + f.h.)$ or $(f.e. + t.h.)$.

The transition from $(t.e. + f.h.)$ or $(f.e. + t.h.)$ to $(g.s.)$ is a capture by a charged defect.

4.2 CCD for a charged defect

Usually a deep-level defect shows many charged states. The CCD at a charged defect can be obtained in a similar way. For example at the EL2 center in GaAs,

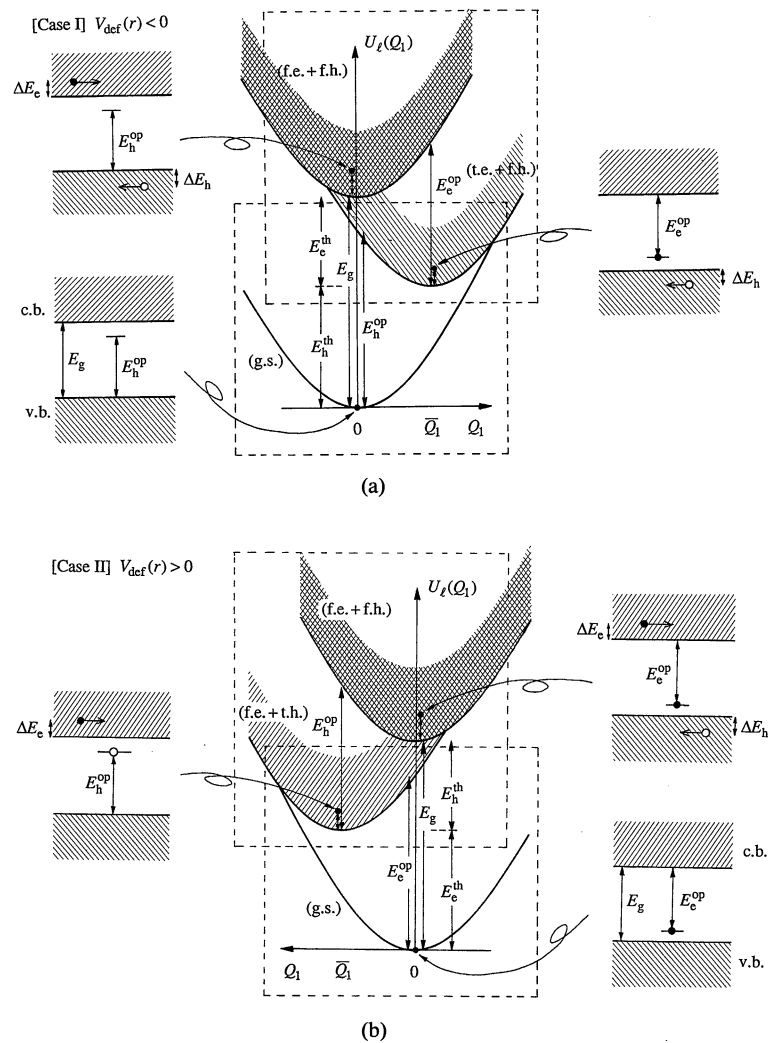


Fig. 8. An example of the correct diagram for a point defect ((a) $V_{def}(r) < 0$ and (b) $V_{def}(r) > 0$). The single hatching represents a continuous spectrum of a free electron or a free hole. The inserts shows, respectively, the electronic configurations of (g.s.), (f.e. + f.h.) and (t.e. + f.h.) or (f.e. + t.h.). Note that the energy scale is reduced, and the directions of the hatchings are coordinated.

the replacement of three electronic states in Fig. 8(a)

$$(f.e. + f.h.) \rightarrow EL2^+ + f.e. + f.h.$$

$$(t.e. + f.h.) \rightarrow EL2^0 + f.h.$$

$$(g.s.) \rightarrow EL2^+$$

gives a qualitatively correct CCD for $EL2$.²³⁾ The quantitative energy positions between three states are obtained by experimental measurements of two quantities among four: the optical ionization energy (optical depth) E_e^{op} , E_h^{op} and the thermal depth E_e^{th} , E_h^{th} for an electron and a hole. The interaction mode Q_1 is defined between the minima of $EL2^+$ and $EL2^0$ configurations and the origin $Q_1 = 0$ refers to $EL2^+$. The absolute value of \bar{Q}_1 cannot be obtained by energy spectroscopies except for ENDOR; hence, it usually remains a conceptual quantity. When the absolute atomic displacements at and around the defect with respect to the crystalline positions are large, the forms of the electron lattice interaction and the elastic energy of the perfect crystal cannot be used; the first-principle calculations are necessary, as in the predicted metastable

configuration of $EL2$ in GaAs.²⁴⁻²⁶⁾

4.3 CCD with many carriers and CCD for multiple charged defects

In real semiconductors the number of carriers is not limited to one. When there are n_e electrons in the conduction band and n_h holes in the valence band, the adiabatic potentials for the defect in Fig. 8 can be obtained by piling up those of (g.s.) and (t.e. + f.h.) or (f.e. + t.h.) with a sequence of the band gap energy E_g (Fig. 9). The interaction mode Q_1 is determined only by the charge distribution at the defect and is not affected by the number of free carriers. It is readily seen that if electrons (holes) are the majority carrier, the defect usually binds an electron (a hole) and the lattice configuration is $Q_1 = \bar{Q}_1$ ($Q_1 = 0$). Once a minority carrier is captured, the transient lattice vibration influences a successive opposite carrier capture process and reduces the activation energy. Hence, the minority carrier capture is usually a thermal activated process, while the majority capture is accelerated.^{9,27,28)}

If a defect shows three types of charged states, for

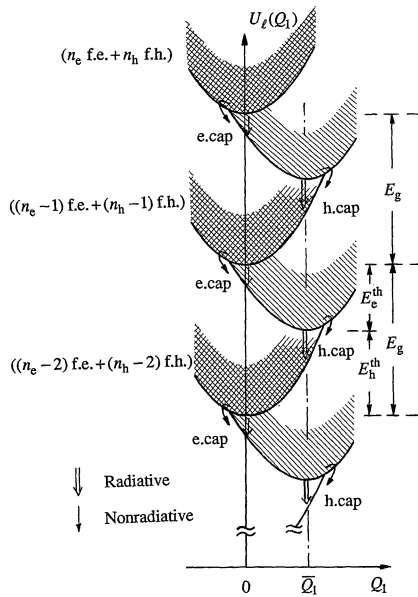
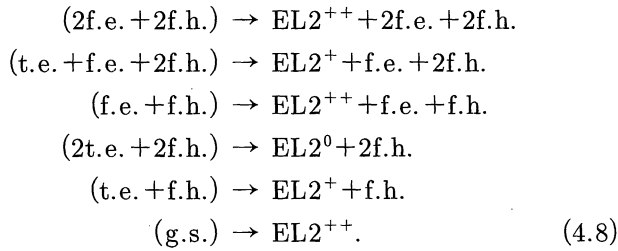


Fig. 9. An example of the correct diagram for a point defect ($V_{\text{def}}(r) < 0$) with many carriers.

example $\text{EL}2^0$, $\text{EL}2^+$ and $\text{EL}2^{++}$ in GaAs, at least six electronic states must be considered: for example,



The adiabatic potentials should be presented in two configurational coordinate space $Q_{+,0}$ and $Q_{++,+}$. Here the interaction mode $Q_{+,0}$ ($Q_{++,+}$) is defined in the direction between two minima of $\text{EL}2^+$ and $\text{EL}2^0$ ($\text{EL}2^{++}$ and $\text{EL}2^+$).

5. Conclusions

We have discussed the electron-lattice interactions in nonmetallic materials in the many-electron scheme. In semiconductor physics various electronic processes have been discussed within the one-electron scheme. If one is concerned with deep levels and strong lattice relaxation, however, one cannot describe the entire process self-consistently without the many-electron scheme.

Recently a variety of strong electron-lattice interaction phenomena have been found in covalent semiconductors, in which such phenomena were once considered to be absent. The reason for this can be explained as follows. The effective mass m^* of a carrier in covalent semiconductors is small and the strength of the electron-lattice interaction with the optical modes is weak ($E_{\text{LR}}^{\text{op}} \sim 0$). Hence, carrier self-trapping does not occur because the carrier kinetic energy $B(\propto 1/m^*)$ is larger than $E_{\text{LR}}^{\text{op}} + E_{\text{LR}}^{\text{ac}}$ (see §2.1.2). At a donor (acceptor) impurity, because of the large dielectric constant ϵ_∞ the long-range Coulomb potential is not strong

enough to localize a carrier completely even if it cooperates with the electron-lattice interaction. Then donor (acceptor) impurity states are shallow without noticeable lattice relaxation, although the latent lattice relaxation energy $E_{\text{LR}}^{\text{ac}}$ is on the order of 1 eV. Only when the cooperation of the defect potential and the electron-lattice interaction wins the carrier kinetic energy B and localizes a carrier sufficiently does the latent lattice relaxation energy $E_{\text{LR}}^{\text{ac}}$ manifest itself. This mechanism is called extrinsic self-trapping.^{1,2,13)} Thus large lattice relaxation is realized only at deep states, while it is absent in shallow states.

Randomness also helps to localize a carrier and induce a large lattice relaxation. The problem in amorphous systems is that we do not know the electronic quasi-ground and excited states, and the corresponding atomic configurations. This may be the main reason why amorphous semiconductor physics faces a deadlock.^{6,7)} In particular, very little is known on the mechanism of photostructural changes and carrier self-trapping, and the character of impurity and defect states. In §4 we have assumed that atomic distortions induce only one type of localized state in the gap which comes from either the conduction band or the valence band, because the character of localized states is usually determined by the sign of the defect potential $V_{\text{def}}(r)$. In covalent amorphous semiconductors, however, both types of localized states may appear at the same time if a bond length is enlarged, because the valence (conduction) band is constructed of (anti-)bonding orbitals. Then it is possible that the CCD is qualitatively different from those in Fig. 8.²⁹⁾

We have shown in the present paper that the electron-lattice interaction in condensed matter is a response to the electronic excitation. It is not restricted to phenomena in the vicinity of perfect crystals, such as the polaron problem, but is one aspect of strong and complicated interactions between many electrons and ions. Thus it will play an important role in future semiconductor technology in two respects. First, the electronic excitation can induce large atomic displacements and thus is a promising technique for realizing new structures and new materials which cannot be attained by the thermal process from the electronic ground state. Secondly, suppose we succeed in fabricating nanometer-scale semiconductor devices, where carriers are confined to a small region. The coupling between electrons and atoms there may differ from that in perfect crystals. Then the electron-lattice interaction might manifest itself so strongly that electronic states and atomic configurations are entangled with each other and cannot be discussed separately. We hope that the present article will help to unify two areas (atomic structure and electronic state) of condensed-matter physics and create a new stage of materials science.⁴⁾

Acknowledgment

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- 19) The Huang-Rhys factor S is often used as a measure of the electron-phonon coupling. In the strong coupling limit ($S \gg 1$), the motion of the lattice during electronic transitions can be treated classically, as has been done in §3. While in the weak limit ($S \lesssim 1$), it should be treated quantum mechanically. See refs. 2 and 5.
- 20) The energy dependence of an extended state on the local distortion is on the order of $1/N$, then can be neglected if we refer to *one-particle energy*. When there is no localized state, however, that of the *total energy* of n extended valence electrons is on the order of 1. This should be noted in calculating the adiabatic potentials and the lattice elastic energy. See refs. 9 and 22.
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- 22) When the lattice distortion is so large that a localized state which comes from the conduction (valence) band mixes with the valence (conduction) band, the one-particle scheme (eqs. (4.4) and (4.5)) no longer holds. The charge distribution of a carrier is not given by $|\phi_{\text{occ}}(r_e)|^2$ or $|\phi_{\text{unocc}}(r_h)|^2$, and the adiabatic potential for (g.s.) and hence the lattice elastic energy is no longer given by eq. (4.4); see §3.1 of ref. 9.
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