

Electronically-enhanced Atomic Processes in Condensed Matter

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Abstract

An overview is presented on various electronic-atomic processes in nonmetallic materials. The off-center instability of a self-trapped exciton in alkali halides and a substitutional impurity in covalent semiconductors are discussed in connection with (pseudo) Jahn-Teller effect. Mesatable configurations of (sp^3) tetrahedral systems are examined with T_d T - U - S model including the effect of electron-lattice interaction and electron-electron interaction. Strategy to fabricate new structures is proposed upon multiple excitation mechanism.

Keywords: electronic excitation, structural change, Jahn-Teller effect, sp^3 -, sp^2 - hybridization

Introduction

In condensed matter, a crystal structure is realized when electrons and atoms are in the lowest ground state. In the given structure, characterized by a translational space group, each atom cooperatively vibrates around each equilibrium position. The atomic elementary excitations are called phonons. The electronic elementary excitations in crystals are all delocalized as a result of the Bloch's theorem. In nonmetallic materials it is a pair of a conduction electron and a valence hole, sometimes they form into an exciton. These elementary excitations are the main actors and actresses on the "stage" of the crystal structures. In order to discuss the physics of elementary excitations and their interaction, we usually introduce the excitation (creation) operator a_k^* which operates on the vacuum $|0\rangle$, as

$$a_k^* |0\rangle, \quad (1)$$

which indicates the ground state electronic and atomic structure.

excitations as a result of their mutual interaction have been main interests in the solid state physics, especially in semiconductor physics. This is schematically shown in the left part of Fig. 1.

Recently, however, there have been found various phenomena (Fig. 2) which break out this "solid state physics" [1, 2]. When we excite valence electrons in solids, it sometimes induces a local structural change: several atoms show large displacement. For example, a localized electronic excitation induces large lattice distortion at a point defect, desorption of an atom from a surface, defect reaction, bond switching, and so on. All these phenomena cannot be treated as a small perturbation. We would rather say that the vacuum $|0\rangle$ itself is destroyed, or locally changes into a new vacuum $|0'\rangle$. Then several fundamental questions on the structure arise: why the original vacuum $|0\rangle$ has such configuration? Do another vacuum(s) $|0'\rangle$ really exist? How can they be stabilized? What kind of elementary excitations are

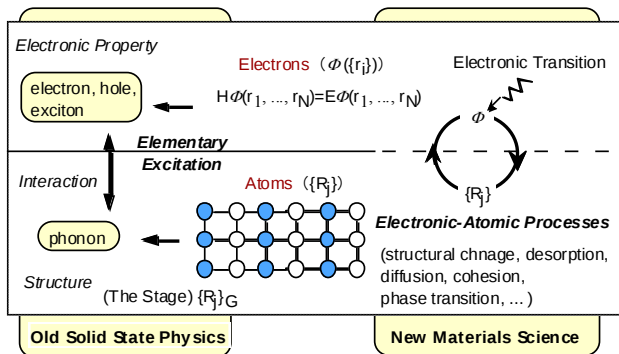


Fig. 1 The physics of the elementary excitations in solids and the new stage of materials science by electronic excitation.

The energy spectrums of these excitations and composed

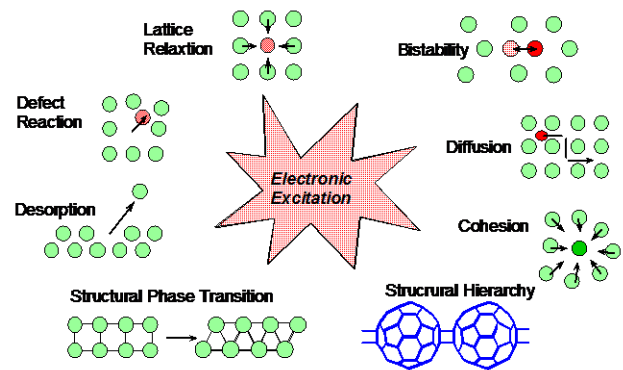


Fig. 2 Various electronically-enhanced atomic processes in non-metallic solids.

there in the new vacuum $|0\rangle$? The purpose of my talk is to give an overview on various electronic-atomic processes in nonmetallic materials.

Localization

Since electronically excitations in perfect crystals are all delocalized, their localization process is necessary to induce a local structural change. This is realized by

- absence of translational symmetry such as impurity, vacancy, dislocation, surface, ...
- self-localization of an electron (hole, exciton) as a result of the strong electron-lattice interaction.

In three and two dimensional system, self-localization only occurs when the electron-lattice coupling exceeds a critical strength. In one-dimensional systems all the electronic excitations are predicted to be always self-localized (self-trapping) without potential barrier.

The energy of an elementary electronic excitation in semiconductors is around 1eV. Then this seems not enough to break a bond because the bonding energy per atom is usually around several eV. Thus structural change takes place by either

- bond switching where the potential barrier needs lower energy.
- multiple electronic excitation.

Off-center Instability

Self-trapping of an exciton in alkali halides has been intensively studied in connection with the F-H defect pair formation [2]. It is recently found that self-trapped excitons in alkali halides have an off-center configuration (type III (II)) as well as an on-center configuration (type I) [3], as shown in Fig. 3(b). Their stabilities depend on the material. In the type I configuration, a hole is self-trapped by attracting two halogen ions to form a V_k center by which an electron is loosely bound. The effective charge of the V_k center seen by an electron away from it would be $+e$, because the charges of anions and cations are canceled. On the other hand, if an electron comes close to the V_k center, it feels the bare charge of two anions: the effective charge would be $(1-1-1)e = -e$. Thus the effective potential between an electron and a V_k center will be attractive at large distance and repulsive for short distance. Then an electron can be strongly localized pushing away the V_k center to the [110] direction to create a pair of an F center (anion vacancy) and an H center (interstitial anion pair): the type III (II) configuration.

In covalent semiconductors, when IV or VI elements are doped into III-V compound semiconductors, there appears a deep donor level in addition to a normal shallow donor level. This deep level, called DX-level can be interchanged by a photoexcitation or a carrier trapping, and is considered as the origin of the persistent photoconductivity. The shallow-deep transition is caused

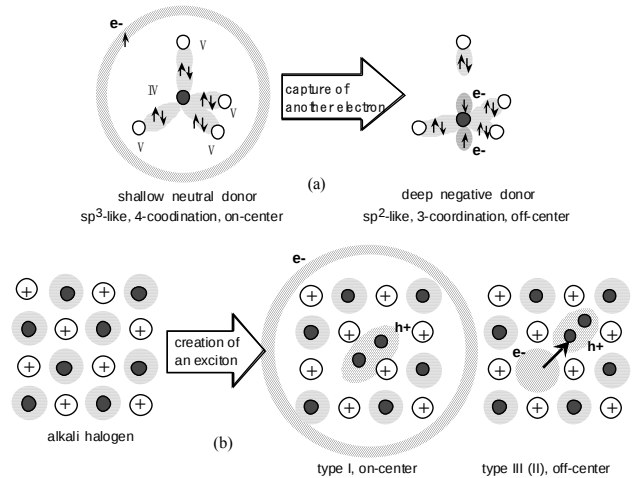


Fig. 3 (a) The off-center instability of a substitutional donor (IV) in III-V semiconductors and (b) the self-trapping of an exciton in alkali halides.

by the on-off instability of a substitutional donor atom itself [4, 5]. The similar off-center instability are found in many impurity, such as EL2 in GaAs and N in Si [6, 7]. When a III element is replaced by a IV element such as Si, it behaves as a single donor (Fig. 3(a)). The local chemical bonding of Si needs three valence electrons (T_d , sp^3). The rest one electron feels $+e$ positive charge of the Si impurity when it is far away from. The Si atom can attract one more electron, and if it displaces from the center (C_{3v} , sp^2), two electrons will occupy a created dangling bond. The Anderson's negative U is realized. Finally four electrons which have to occupy in a Si-As bond repel each other to create a pair of dangling bonds. In this case, the As becomes neutral and satisfies the local valency, while the Si is singly charged $-e$.

Structural Change of a Tetrahedral Point Defect

In case of strong electron localization we must also take account of the electron-electron interaction. Even if we start with a single electron in the conduction band, as it becomes strongly localized around a particular bond, it interacts with another valence electrons which have been regarded to be combined with ions to form the lattice medium in the first place. Then we have to extend the concept of the electron-lattice interaction, which can be consistently treated with the many-electron scheme (see a review article [8]).

Most of covalent semiconductors have either the diamond, zincblende or wurtzite structures, which are constructed by the four-fold coordination network with sp^3 hybridization of valence electrons. There the tetrahedral symmetry (T_d) is the most frequent and important point symmetry. Several point defects have been found to show symmetry breaking structural changes from T_d to

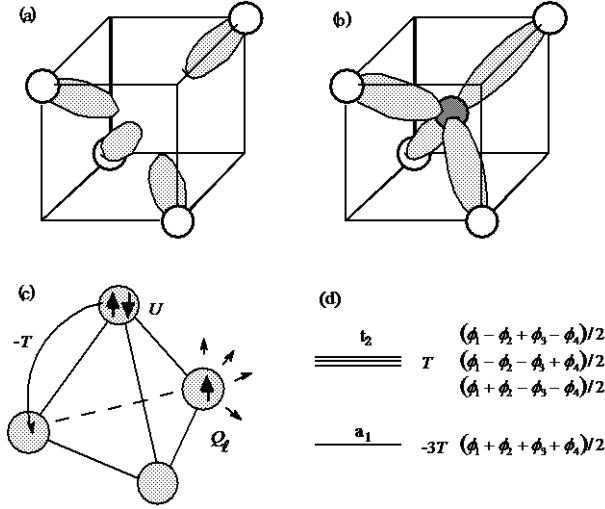


Fig. 4 (a) a vacancy and (b) a substitutional impurity in semiconductors. (c) the four-site T_d T - U - S model. Hatching in (c) represents (a) sp^3 dangling bond and (b) bonding or antibonding orbitals. (d) One-electron scheme for $U=S=0$, where ϕ_ℓ is one-electron orbital at the ℓ -th site.

D_{2d} , C_{2v} or C_{3v} when the electronic occupation is changed. The stable structure is governed by the electron-electron interaction and the electron-lattice interaction. The simplest model to discuss the cooperation and competition between them would be the T - U - S model, which consists of several interacting electrons coupled with a deformable lattice. Recently El-Maghraby and Shinozuka [9] have done a comprehensive study on a tetrahedral (T_d) four-site system to discuss the competition between these interactions and the metamorphosis of the stable structures.

Figure 4 schematically shows (a) a vacancy and (b) a substitutional impurity in the diamond (zincblende) lattice. As a first step of approximation we cut them out of the crystal and form them into the T_d T - U - S model shown in Fig. 4(c). It is characterized by the electronic transfer energy, $-T$, describing the quantum hopping of an electron from site to site, the on-site Coulomb repulsion energy, U , between two electrons, the lattice relaxation energy, S , due to the short range interaction of an electron with the lattice mode, Q_ℓ , at the site ℓ ($\ell=1\sim 4$) and the number n ($=0\sim 8$) of the occupied electrons. The site ℓ represents either atomic or molecular orbital: four dangling bonds for a vacancy and four bonding (or antibonding) orbitals for a substitutional impurity.

In the rigid lattice ($Q_\ell=0$), if the electron-electron interaction is neglected ($U=0$), one electron eigenstates are one a_1 state with an eigenenergy $-3T$ and three t_2 states with T . Then the system does not have the electron-hole symmetry. If we allow the lattice to deform ($Q_\ell \neq 0$) and

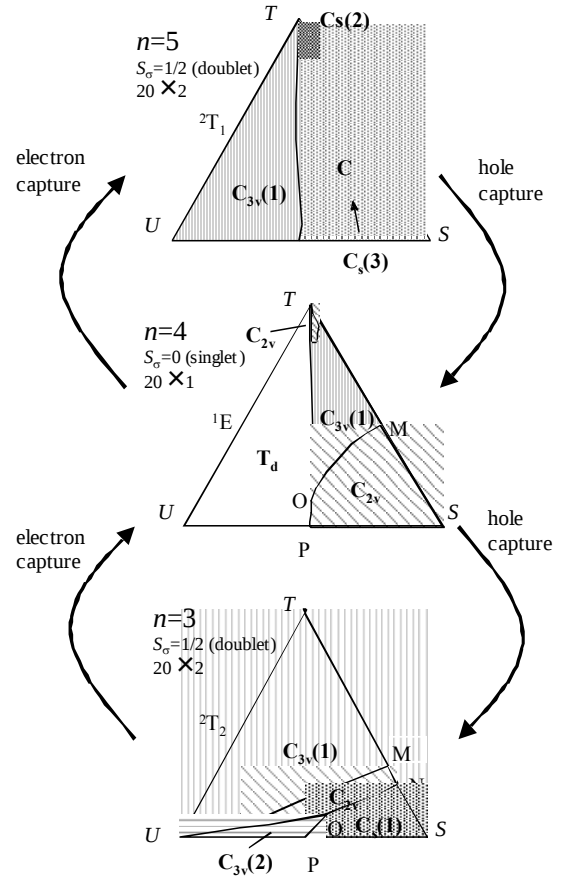


Fig. 5 Phase diagrams of T_d T - U - S model.

if the electron-electron interaction is switched on ($U \neq 0$), however, eigenstates of n electrons become complicated and structural changes may take place lowering the symmetry.

Calculated possible stable structures characterized by point symmetries are T_d , C_{3v} , C_{2v} , C_s , C . The obtained stable configurations for the electronic ground state of each subspace (n, S_σ) are summarized in the phase diagrams [9]. Fig. 5 shows the diagrams for the $n=3, 4, 5$. Along the T - U side of each phase diagram, the character of the lowest electronic state for the rigid lattice ($Q_\ell=0$) is indicated. We can see that if it is triply degenerate (T_1 and T_2) the stable structure is always C_{3v} for $S \neq 0$, as has been predicted with the Jahn-Teller effect [10, 11]. For excited states the T_d configuration is more unstable because they contain large amplitude of the charge transfer electronic states. Thus 4-site T_d “defect molecule” shows various stable structures depending on the electron number, n , total spin, S_σ and the strengths of the electron-lattice interaction, S/T , and the electron-electron interaction, U/T . When the electron occupation is changed by an electron (hole) capture or a photoexcitation, a structural change takes place. The corresponding lattice distortion for a substitutional impurity is illustrated in Fig. 6.

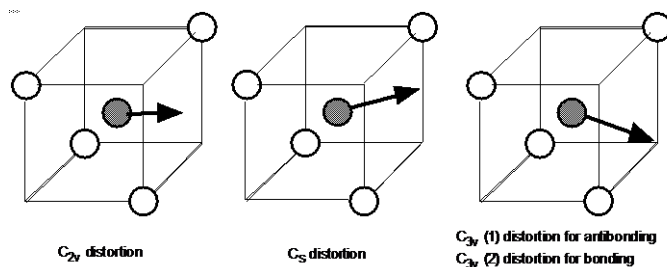


Fig. 6 Several types of the displacement of an impurity at T_d site.

Towards New Materials Science

Recently many nonequilibrium processes have been proposed to fabricate new materials and nanostructures. Among them electronic excitation is one of the most promising methods because of its high efficiency and selectivity in time, energy and space. Following four important points should be investigated over the total process of electronically induced structural change (Fig.7):

- 1) **[from]** the ground state structure G :
dimensionality, surface, interface, impurity, dislocation,
- 2) **[how]** electronic excitation E :
valence excitation, core excitation, charged state change by carrier trapping or detrapping,
- 3) **[via]** relaxation path:
dynamics of the system, change in the character of excited electronic state.
- 4) **[to]** obtained metastable structure M :
atomic structure, electronic structure, elementary excitation,

Finally, I would like to comment on multiple excitation mechanism, which is a key concept of many proposed mechanisms, for example:

- a) two hole localization (self-trapping) mechanism for desorption of atom from surface [12]
- b) Auger mechanism after core excitation: there are two localized holes in the intermediate state [13].
- c) Anderson's negative U mechanism in structural change of defects [14].
- d) multiple and coherent carrier capture mechanism for defect reaction [15].

We are living in a world filled with background radiations from materials around (300 K), Sun (6000 K) in addition to high energy cosmic ray. Then all materials must have structures G which are stable against these radiation: at least stable against single electronic excitation. (This must be also for M). This is a reason why electronically induced structural changes have not been so frequently met. Then multiple electronic-excitation

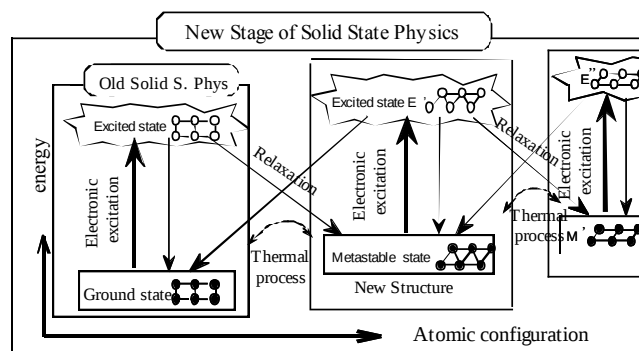


Fig. 7 New stage of Solid State Physics by electronic Excitation.

would be effective because the induced force is proportional to the electronic charge change Δn and the relaxation energy is proportional to Δn^2 . Thus, multiple excitation and also co-excitation using several different excitation would be very effective tools to fabricate new materials and nanostructure.

Acknowledgments

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