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Atomic processes induced by relaxation of excitons in the bulk and on the surfaces of non-metallic solids

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Abstract

Atomic processes induced by electronic excitation in the bulk and on surfaces of insulators are surveyed, emphasizing the difference in the atomic processes induced in different types of solids. The phenomena treated involve local lattice modification in the bulk and atomic emission from the surfaces. First the relaxation of holes and excitons in halides and oxides are compared and the way how the self-trapping of excitons leads to formation of defects is discussed. It is argued also that the self-trapping of holes and excitons is favorable in amorphous materials and the difference in the behaviors of holes and excitons in crystalline and amorphous SiO_2 is discusses. The relaxation of excitons on surfaces of ionic crystals and consequent atomic emission processes are argued. The relaxation of densely generated excitons and electron-hole pairs in the bulk is also discussed.

§1. INTRODUCTION

It is well established that fundamental excitation of some insulators leads to local lattice modification, including the formation of Frenkel pairs or vacancy-interstitial pairs, initiated by the self-trapping of excitons (1), which arise from the exciton-lattice coupling, one of the fundamental problems of solid state physics. Most intensive works on self-trapping of excitons and subsequent local lattice modificatin have been carried out for alkali halides. Recently, it has been recognized that the self-trapping is induced in a variety of solids not only in the bulk but also on surfaces. Thus, formation of excitons and their self-trapping are considered to be the cause of a variety of local lattice modification or atomic processes induced by electronic excitation.

A variety of photon-induced atomic processes have been found and practically used in the regime of materials science. Examples of these includes laser-induced ablation of solids (2), laser-induced interface reactions (3), photo-enhancement of epitaxial growth (4), laser-induced surface composition change (5) and laser-induced defect-initiated atomic emission (6). The mechanisms of these processes have not been understood satisfactorily. The primary interaction of photon beams with non-metallic solids produces fundamental electronic excitation or creation of electron-hole pairs and excitons. Furthermore a substantial fraction of the energy imparted to solids by interaction with ionizing radiation (electron beams and γ rays) and even with ion beams is dissipated to these excitations. Thus understanding of the consequence of the excitation in a variety of solids on the microscopic basis is of use to make clear the mechanism of these atomic processes induced by electronic excitation.

It is the purpose of the present paper to review the present understanding of the electron-lattice interaction that can induce atomic processes following primary excitation in insulating solids. For the electronic energy possessed by electron-hole pairs or by excitons to be converted to the energy of local lattice deformation, the localization of the electronic energy is necessary. The self-trapping of excitons and that of holes followed by electron trapping induce localization and are often the primary step of the following lattice rearrangements particularly in insulators. Emphasis is placed on the difference in these atomic processes in different materials and in the bulk and at surfaces. The possible consequence of dense electronic excitation is also surveyed.

§2. PRIMARY EXCITATION AND ELECTRON-LATTICE INTERACTION

Photons above the band-gap energy produces primarily electron-hole pairs unless the photon energy is in resonance with the exciton peak energy. Similarly ionizing radiation produces electron-hole pairs with an yield of

$$n=\frac{W_{abs}}{\mathscr{E}} \tag{1}$$

where W_{abs} is the absorbed energy and $\mathscr{E}$ is an energy 2-3 times the band-gap energy (7). Evidently, 1/2-1/3 of the absorbed energy is dissipated to formation of electron-hole pairs and the other for lattice phonons through the interaction of the free electrons and holes with phonons. Electron-hole pairs generated in solids can combine to each other to form excitons. In insulators, in which the exciton binding energy is much higher than the phonon energy, ionization of excitons to electron-hole pairs is practically prohibited.

Electrons and holes generated are coupled with phonons, or induce local lattice modification. Two cases in the electron-phonon and hole-phonon coupling may be differentiated: when the coupling is weak, the electrons and holes, called polarons, are still mobile with an effective mass slightly larger than that without coupling. If the coupling is strong, the electrons or holes are not mobile, namely trapped by the lattice distortion induced by their presence, or self-trapped. Although electrons are self-trapped only in limited materials (1), holes and also excitons in some materials including alkali halides are known to be self-trapped. Electrons and holes can be trapped separately by defects or their recombination can take place on a defect: in this case an electron is trapped by the defect, which subsequently traps an electron or *vice versa*.

The relaxation of the lattice at an electronically excited state can be expressed in terms of configuration coordinate diagram, as shown in Fig. 1. In Fig. 1, we describe two cases: (a) a luminescent decay from the excited state to the ground state is feasible and (b) a thermally activated process is needed to restore the ground state. The latter may be referred to as formation of defects or of metastable state, depending on the lifetime of the relaxed configuration. Non-radiative transition from the excited state to the ground state can take place in the former case particularly at high temperatures.

The criterion for self-trapping has been given by (8,9)

$$E_{LR}>B \tag{2}$$

where E_{LR} is the lattice relaxation energy and B is the transfer energy of the particles from the site to a neighboring site. Eq. (2) compares the energy gain due to lattice relaxation with that due to the translational motion of a hole or exciton. In order to derive the criterion in the time scale, we define time t_T in which the wave packet representing a hole or exciton stays on a lattice point:

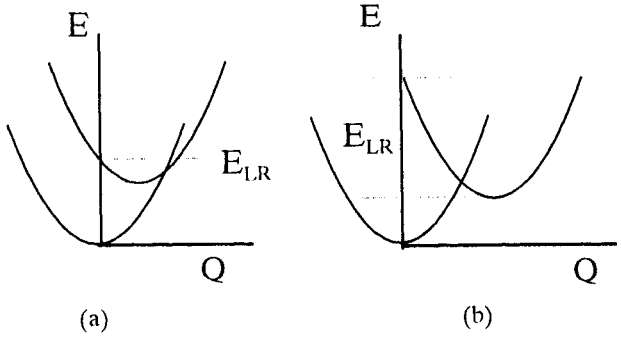


Figure 1. The configuration coordinate diagram describing formation of (a) a luminescent relaxed state and (b) a metastable state. The upper and lowerr curves are ground and excited states.

$$t_T=\frac{\hbar}{B} \tag{3}$$

Thus the distance Q_T of the relaxation within t_T is given by

$$Q_T=\frac{\omega^2 t^2}{2}Q_R=Q_R\frac{\hbar^2\omega^2}{2B^2}=\frac{Q_R}{2S}\left(\frac{E_{LR}}{B}\right)^2 \tag{4}$$

where ω is the angular frequency, Q_R is the distance of relaxation (see Fig. 1) and S is the Huang-

Rhys factor and is $E_{LR}/\hbar\omega$, the number of the vibrational quanta included in E_{LR}. According to Eq. (4), the criterion Eq. (1) is equivalent to the following new criterions:

$$Q_T > \frac{Q_R}{2\sqrt{S}}, \quad t_T > \frac{1}{\sqrt{S}\omega} \tag{5}$$

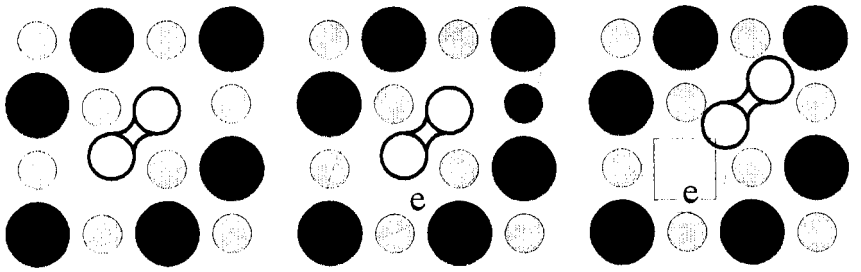
The former compares the distance of the relaxation within the transfer time of a hole or exciton with the distance of the relaxation before a vibrational quantum is emitted and the latter compares the lifetime of a hole or exciton on a site with the lifetime of a specific vibrational state. The concept described above suggests that self-trapping is favorable in amorphous materials.

In many insulators MX, where M is a cation and X is an anion, the valence band consists of anion p orbitals; thus a hole may be described as $X^{-(z-1)}$, where z is the valency, and an relaxed exciton may be $X^{-(z-1)} + e$, where e denotes an electron. The hole and exciton of these configurations are called sometimes one-center hole and exciton, respectively. Generally speaking three types of lattice relaxation from these configurations are conceivable (10): the symmetrical (breathing) and asymmetrical (Jahn-Teller) relaxation modes Q_A around the exciton or hole wave packet, the relaxation mode Q_I forming a bond with one of the neighboring anions and the mode Q_D that displace the atom on which the exciton or hole wave packet is located, forming a Frenkel pair.

A hole in a core orbital can be transformed by an Auger process into multi-holes in the valence band localized on a lattice point. It has been suggested first by Varley (11) that the localized multi-holes cause an instability and excite the Q_D mode, forming Frenkel pairs or interstitial-vacancy pairs. In this case, the localized holes should stay on a lattice point long enough for atomic displacements to be induced. It has been argued that the time of the hole localization is relatively long if the Coulomb repulsion energy between two holes exceeds the width of the valence band (12). So far there is no direct evidence for formation of defects in the bulk by core excitation (13,14). The potential energy possessed by a core hole is also converted to the energy of Auger electrons, which are emitted from a single lattice point. Thus the effects of dense electronic excitation, as discussed later, may play a role in producing the 'core-hole effects'. It should be noted that the instability of the multi-holes formed from a core hole produces only a single defect, but the Auger electrons produces many number of defects according to Eq. (1). Core holes on the surfaces of insulators leads to emission of ions, as reviewed by reference (15).

§3. RELAXATION OF HOLES AND EXCITONS IN THE BULK OF INSULATORS

The optically detected electron spin resonance (ODEPR) studies (16) have shown that the self-trapped hole (STH) in alkali halides is a halogen molecular ion, the center of which is located at the center of a square formed by two cations and anions on a (100) plane, as depicted in Fig. 2a. The STH in alkali halides is called V_k center and evidently the Q_I mode is effective for the relaxation. It has been shown recently that about 10 ps is needed for the relaxation to form the V_k center in alkali bromides (17) and iodides (18) and that the other relaxed configurations appear before the relaxation to the V_k center in the latter. The configuration of the self-trapped excitons (STE) in alkali halides has been studied by the measurements of luminescence (19) and the optical absorption due to the electron and hole transitions (20,21), optically detected EPR (ODEPR) (22) and electron nuclear double resonance (ODENDOR) (23) and resonant Raman scattering (RRS) (24). The relation between the peak energies of the luminescence bands due to the recombination of the STEs of all alkali halides and the Rabin-Klick (25) parameter S/D, where S is the space between two neighboring halogen ions and D is the radius of a halogen atom, has been shown to fall on three different straight lines (26), suggesting that there are three types of STEs, named types I, II and III. The optical absorption bands due to the electron transition for the type I STE is in the infrared region (27), while those for type II and III are in the infrared or visible regions. The transition energy E_a of the latter two types of STEs follow the Ivey Mollwo relation (28): $E_a = E_a^0 a^q$, where a is the lattice parameter and E_a^0 and q are the parameters. In RbI the luminescence from all types are observed (29), type I is the singlet state and types II and III are the triplet states, suggesting that the types II and III STEs, if they exist in the same alkali halides, are on the same adiabatic potential energy surface (APES). It is now generally accepted that the APES for the lowest exciton



(a) (b) (c)

Figure 2. Schematic diagram of (a) the self-trapped hole, the self-trapped exciton of (b) type I and (c) type II and III in alkali halides.

is capable of possessing three local minima corresponding to the types I, II and III STEs (1), although all minima are not deep enough to show luminescence in many alkali halides.

Because of the low transition energy of the electron of the Type I STE (26), it is suggested to have a configuration near the (V_k+e) or an electron trapped by a V_k center (Fig. 2b). On the other hand, recent RRS studies (24) indicate most clearly that the type II and III STEs have a configuration of the nearest pair of an F center (halogen atom vacancy) and an H center (halogen interstitial atom): the stretching vibrational frequency of the molecular ion, obtained by RRS with resonance to the hole transition agrees with that of the H center and that with resonance to the electron transition is very similar to that of the F center. Furthermore the result that the electron transition energy follows the Ivey-Mollwo relation, which has been explained in terms of the point ion model (30), is in favor of the interpretation that the electron of the type II and III STE is trapped in potential fields similar to that of the F center but slightly different from each other. The ODENDOR experiment indicate that the hole is almost equally, but not exactly, populated on the two halogen atoms forming the halogen molecular ion. All of these arguments are in favor of the interpretation that the type II and III STE are more likely the nearest F-H pairs ($(F+H)$ configuration), as shown in Fig. 3c. The nearest F-H pairs are formed from the (V_k+e) configuration by displacement of the halogen molecular ion along a $<110>$ direction; this mode of the translation motion is a kind of the Q_D distortion.

Theoretical calculations of the STE, carried out using a cluster model by applying the semi-empirical approach (31), extended-ion approach (32,33) and ab-initio method (34-37), indicate that there is only a minimum in the APES. According to the calculation by Song et al. (31), the value of Q_2 at the minimum with respect to the lattice constant differs depending on the crystal: it increases with increasing S/D. The minimum for NaBr occurs at a deviation of only 10 % of the halogen-halogen distance, close to the (V_k+e) configuration, while that for KCl occurs almost at the $(F+H)$ configuration. Furthermore ab initio calculations indicate that the halogen molecular ion is strongly polarized, in contradictory to the experimental results of ODEPR and ODENDOR. As we have seen, experimental results appear to indicate that the APES has at most three minima, having different configurations; type I is more likely the (V_k+e) configuration and type II and III are more likely the $(F+H)$ configuration. Thus it appears that the theoretical studies are not at the situation where they can describe the STEs configuration satisfactorily. Recent calculation by Puchin et al.(37) suggests that the rotation of the axis of the molecular ion influences the energy substantially. The softness of the APES near the minimum (32) may make it more difficult to derive an definite theoretical prediction on the STE configuration. The possibility of the contribution of the configurational interaction has been also suggested (38).

It is of interest to compare the difference in the relaxation energy S_H of the STH and that S_X of the STE. Referring to Fig. 4 (39), of which the upper curve shows the APES of a non-interacting

electron-hole pair and the lower curve shows the APES of an exciton, we obtain

$$S_X - S_H = I_S - I_F - D_h \quad (6)$$

where I_S and I_F are the ionization energies of the self-trapped and free excitons, respectively, and D_h is the energy necessary to distort the lattice from STH to STE configurations. From Eq. (6), it is clear that S_X is larger than S_H by the difference in the gain of the electron energy by the STH-to-STE distortion and the loss of the distortion energy. The conversion from the (V_k+e) configuration to the nearest $(F+H)$ configuration is feasible only when the gain of the electron energy compensates the loss for the distortion. Similar arguments have been made by Sumi (8) and Toyozawa (40) in terms of the coupling coefficient of the electron and hole with the lattice; if their signs are opposite the $(F+H)$-type distortion is favored, if otherwise the (V_k+e) type distortion is favored. In NaBr and NaI, only type I STE is formed, while types II and III are formed in other alkali halides. This may be explained in terms of the large distortion energy for NaBr and NaI due to small S/D. It has been shown that the STE of alkaline earth fluorides is of the nearest $(F+H)$ configuration, although STH is similar to the V_k centers as in alkali halides.

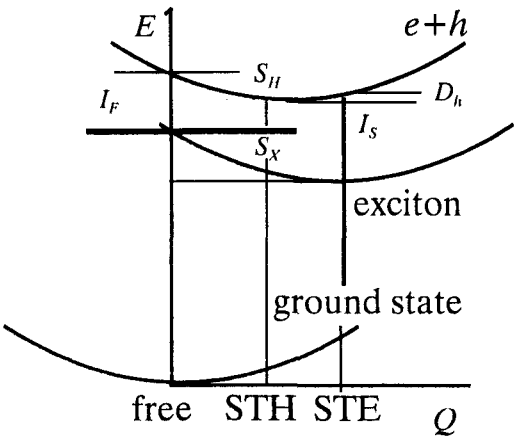


Figure 3. A schematic diagram of the APES describing STH and F-H pairs of alkali halides.

It is known that Ge-trapped holes are produced in Ge-doped SiO_2, indicating that holes in pure SiO_2 are mobile (not self-trapped) (41). ODEPR works have shown that the Ge-trapped hole is localized on an non-bonding p orbital of oxygen accompanied with Q_A -type distortions (42) (Fig. 4a). This trapping is what is called as extrinsic self-trapping; the nature of the relaxation is more likely irrelevant to the presence of the impurity, but the impurity helps to reduce the potential barrier for the self-trapping [43] or make the lifetime of the wave packet on a lattice point longer, according to Eq. (5). Thus, the fact that the STH is not formed but STE is formed in crystalline SiO_2 can be ascribed to the larger relaxation energy for an exciton than for a hole.

Formation of STE has been proved by ODEPR works in SiO_2 (44), Sc_2O_3 and Y_2O_3 (45). According to theoretical calculation of the atomic and electronic structures of the STE in SiO_2 carried out by Fisher et al. (46) and Shluger and Stefanovich (47), the schematic atomic structure of the STE in SiO_2 is as shown in Fig. 4b. Apparently, a Si-O bond is broken, resulting two dangling bonds, with the hole localized on the O dangling bond and the electron on the Si dangling bond. We note the difference in the configurations of the STE and STH: suppose that an electron is added to an STH, the energy gain by putting the electron into Si dangling bond from the STH+e state suffices to break the bond. STEs in SiO_2 are known to emit luminescence at 2.8 eV and to

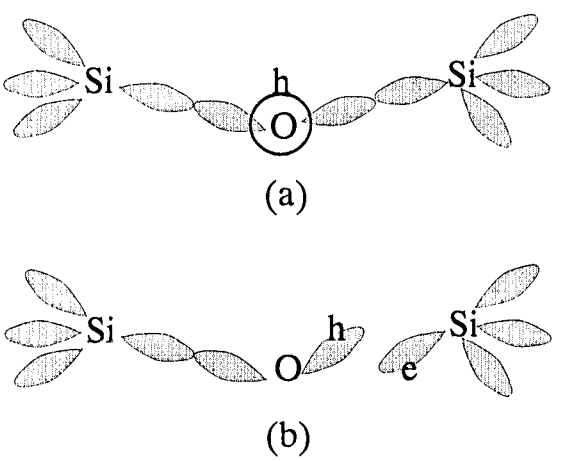


Figure 4. Schematic diagrams of (a) a self-trapped hole and (b) a self-trapped exciton in SiO_2.

exhibit an optical absorption band at 5 eV (48). Formation of the STEs exhibits a large macroscopic volume change (49). The properties of the extrinsic STE perturbed by Ge impurity are known to be similar to the STE in pure SiO_2 (50).

Recombination luminescence of free-excitons, exhibiting a sharp line, has been observed for MgO at low temperatures (51), indicating that self-trapping of exciton does not occur in MgO. It has been argued that a luminescence band in other oxides such as Al_2O_3 and YAl_2O_3, in which free exciton luminescence has not been observed, is due to recombination of STEs (52). However, the absence of sharp luminescence line and presence of broad luminescence band cannot necessarily be an indication of the self-trapping on excitons. Since a hole or O^- in oxides is bound by the Madelung potential to the lattice point, the self-trapping of excitons accompanied with the Q_D distortion may not be feasible in highly ionic oxides.

§4. FORMATION OF FRENKEL PAIRS BY BAND-TO-BAND EXCITATION

It has been known for a long time that the Frenkel pairs in the halogen sublattice is generated in alkali halides by ionizing radiation or by band-to-band excitation (53). Recent time-resolved spectroscopy with 100 femtosecond resolution after electron excitation of the lowest STEs of NaCl (54) has revealed that the evolution of the F centers at low temperatures takes place in the process of the vibrational de-excitation of vibrationally excited STEs on the lowest electronic state. The result demonstrates dynamical evolution of vibrationally excited nearest *F-H* pair to further distant *F-H* pairs. This dynamic evolution is known to be enhanced as the temperature increases (55). Furthermore the thermal conversion from the STE to the distant *F-H* pair has been observed near liquid nitrogen temperature in alkali halides for which the yield of Frenkel pairs by the dynamical process is extremely small (56-59). Thus it appears that the APES for the lowest STE is extended beyond a small potential barrier to the *F-H* pairs with larger separations (60).

Recent subpicosecond time-resolved spectroscopy of the evolution of the STE and *F-H* pairs in KBr and RbBr from electron-hole pairs (17) have revealed two channels of the *F*-center generation; one which occurs with the same delay time as that of the STEs and the other which occurs much faster than formation of the STEs. The former channel is the evolution during the vibrational de-excitation of the STEs, as discussed above. The latter channel bypasses the STE configuration and is branched before the Q_1 relaxation to form the molecular ion is initiated. The concept has been argued by Kabler (61) and Itoh and Saidoh (62): *F-H* evolution takes place from a highly excited state of exciton. The latter authors suggested that *F-H* separation may be larger if dynamic Q_2 relaxation occurs specifically at a hole-excited state.

Formation of the Frenkel pairs in oxides by ionizing radiation appears to be less significant than halides. In SiO_2, vacancies are known to be produced by ionizing radiation of amorphous phase, as we discuss later, but not in crystalline phase. New optical absorption bands in MgO and Al_2O_3 produced by ionizing radiation at higher temperatures are suggested to arise from defect pairs or STEs (63-65). The phenomena need further examinations by means of ODEPR or ODENDOR techniques: it is still too early to make any conclusion on the origin of these absorption bands. It is also of interest to note that photolysis is induced in Al_2O_3 at a certain condition (66,67).

§5. RELAXATION OF EXCITONS AND HOLES IN AMORPHOUS SOLIDS

As we discussed in §2, the amorphous phase appears to provide favorable sites for self-trapping. Thus it is of interest to compare the behaviors of the exciton and holes in the crystalline and amorphous phase of the same materials. SiO_2 is of particular interest for this purpose, since the behaviors of the holes and excitons are well established in both phases.

Recently Griscom (68,69) observed EPR spectra due a hole trapped center in amorphous SiO_2 at low temperatures, very similar to that formed by hole trapping by Ge impurity in Ge-doped crystalline SiO_2 (Fig. 4a), and ascribed it to STH. The results indicate that the type of relaxation is largely governed by the hole-lattice interaction and provide strong evidence for extrinsic self-trapping of the hole in amorphous SiO_2. The STEs in crystalline and amorphous SiO_2 are found to

be similar (70, 71): the optical absorption bands due to the electron transition of the STEs in both phases have almost the same peak energy and shape and the volume change induced by formation of STEs has been found almost to be the same. The lifetime and the luminescence band shape are found to depend on the phase: the lifetime is distributed in the amorphous phase showing a non-exponential decay, while it is unique in crystalline phase. The peak energy of the luminescence band in the amorphous phase is different from that in the crystalline phase by 0.3 eV, and furthermore the peak energy shifts as the delay time changes. These results are characteristics of the amorphous materials, of which the local structure varies depending on the site. These results indicate that the relaxed configuration around the electron of an exciton has nearly the same structure, irrespective of the site, giving rise to the same potential for the electron and almost the same amount of volume change, but the relative configuration between the electron and hole depends on the locality.

Oxygen vacancies (the *E'* centers (72)) are known to be produced in amorphous SiO_2 by ionizing radiation (48) (not in crystalline SiO_2) with a yield lower by a factor of about 1/100 than that of the STEs (73). The mechanism of creation of the *E'* centers is still controversial: one obvious interpretation is formation of vacancy-interstitial pairs from STEs, as it is the case for alkali halides. In fact Tsai and Griscom (74) have obtained experimental evidence for generation of the peroxy radical or interstitial oxygen by ionizing radiation. On the other hand, Imai et al. (75) have shown that the concentrations of the E' centers and of the non-bridging oxygen, or an oxygen dangling bond resulting from breaking of a Si-O bond, produced by ionizing radiation are in parallel and suggested that formation of the *E'* centers is simply due to bond breaking followed by migration of the non-bridging oxygen. Tsai and Griscom argued that formation of interstitial oxygen occurs only when the density of excitation is high, but the rate of exciton interaction is apparently overestimated in their papers (76).

Shluger and Stefanovich (47) have calculated the APES that leads from the STE to the oxygen interstitial-vacancy pair. They showed that the potential barrier from the STE to the nearest interstitial-vacancy pair is about 0.5 eV. Evidently, the energy is reduced tremendously from the formation energy of Frenkel pairs 8.4 eV at the ground state; the self-trapping process itself brings to a highly distorted configuration from which formation of a Frenkel pair becomes feasible.

Since the self-trapping is very likely in amorphous materials, the concept of self-trapping may be applied to other amorphous materials. Indeed ODEPR experiments (77) have shown that the initial state of the luminescence of chalcogenides is a triplet state similarly to SiO_2 and the model for this triplet state has been suggested (78). Shimakawa et al. (79) have suggested formation of Frenkel pairs from STE in order to explain the reversible photo-induced structural change. We emphasize here that the concept of self-trapping can explain in principle the luminescence, defect formation and structural change in amorphous materials.

§6. ATOMIC PROCESSES INDUCED BY DENSE ELECTRONIC EXCITATION

It is plausible that formation of STEs at a high density induces local lattice modification that is not seen when isolated excitons are formed. An experimental simulation of dense electronic excitation is made using RbI, which exhibits an exciton absorption band perturbed by STEs. Excitation of this absorption band eventually creates a new exciton in the proximity of an STE. Tanimura and Itoh (80) have shown that excitation at this band produces the F-H pairs at liquid helium temperature, where no F-H pair is produced by conventional ionizing radiation of RbI. The result indicates clearly that the relaxation of two interacting excitons can lead to a relaxed configuration that cannot arise from single exciton; thus demonstrating possible dense excitation effects. It has been also shown that excitation of the STE to further higher excited states leads to defect formation. This process can also be induced when excitons are formed densely.

The registration of heavy ion tracks in some insulators is known since long time ago (81). The phenomenon, which occurs above a critical local density of energy deposition by electronic encounters, was first known as track etching, since the tracks are etched by chemical agents. It has been recognized recently that amorphization or heavy radiation damage is induced along the path of

heavy ions (82). Three types of mechanisms have been suggested: dielectric breakdown (80), heating (83) and STEs (84). In the context of the present paper, we discuss the last mechanism. Since almost all atoms along the path of heavy ions are excited at the critical density of excitation, a cluster of STEs are produced after the passage of a heavy ion. In crystalline SiO_2, in which the recombination of isolated STEs restore the perfect sites, the recovery may not be complete if the density of the STEs is extremely high: crystal-to-amorphous phase change is feasible since each STE is accompanied by the bond breaking. A correlation between the materials in which track registration occurs and in which STEs are produced have been pointed out (84). Although both the heating and the STE mechanisms are due to electron-phonon coupling, the difference is that the electronic excitation energy is transferred preferentially to the mode leading to defect formation in the STE mechanism, but it is distributed to all phonon modes in the heating mechanism.

§7. RELAXATION OF EXCITONS ON SURFACES

Band-to-band excitation near surfaces of alkali halides is known to cause the emissions of both halogen and alkali atoms (85), of which that of halogen atoms is considered to be primary, since the surface is gradually enriched with alkali (86) near room temperature. The yield of emission is relatively high: it has been estimated to be 14 molecules per 500 eV electron. Taking the range of the electron into account, the probability that an electron-hole pair ends up with the emission is close to unity. Recently, Li et al. (87) and Puchin et al. (88) have obtained the APES for an exciton on the surface top layer (Fig. 5), indicating the emission of a halogen atom leaving an *F* center on the surface, equivalent to the Q_0 distortion in the bulk. The latter authors have obtained also the APESs for STEs formed within the first five layers from the surface and showed that they are decomposed into an *F* center and an emitted atom. Thus it is most likely that the formation of excitons or electron-hole pairs near the surface of alkali halides leads to the emission primarily of halogen atoms. Emission of alkali atoms may be induced by various processes: thermal evaporation, excitation of the *F* centers (89) and formation of excitons near defects. The emission of alkali from excitons on the perfect sites on the surface still cannot be completely excluded. It has been pointed out that surface and interface processes of SiO_2 is related to the self-trapped excitons (90).

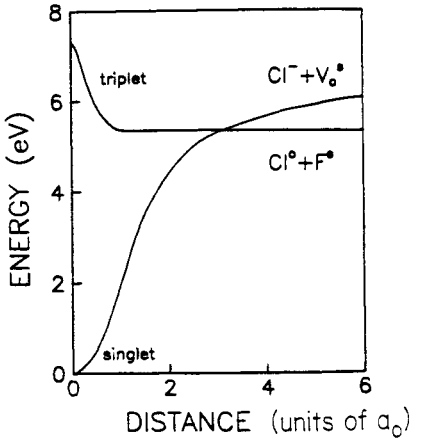


Figure 5. The APES for an exciton on the surface top layer for NaCl. The abscissa is the distance of the emitted Cl atom from the surface.

CONCLUSION

In this paper we have treated the consequences of formation of excitons in insulators in the bulk and on surfaces. It is point out that localization of electronic excitation energy can be the cause of local lattice modification. It is pointed out the relaxation of an exciton in several solids leads to Q_0 distortion leading to formation of Frenkel pairs and emission of atoms from the surface. The concept of extrinsic self-trapping is extended to amorphous materials: it explains the difference in the STH and STE in crystalline and amorphous SiO_2. Finally the effects of dense electronic excitation is discussed and the track registration process is interpreted in terms of the formation of dense STEs. We emphasize that the formation of STE is the most fundamental process in solids in which the exciton-lattice coupling is strong. Thus the consequence of formation of STEs should be examined carefully to understand atomic processes in these materials.

Atomic processes induced in the materials in which the exciton-lattice coupling is weak and no STE is formed is substantially different than those described in this paper. Since the localization of

the electronic excitation energy is essential for the atomic processes to be induced, the atomic processes that occur in these materials are defect-related. The modification of the defect atomic structures induced by electronic excitation or by change in the charge state in semiconductors has been demonstrated, for example the As anti-site defects in GaAs (91). Laser-induced emission at low laser fluence has been shown to be defect related (92). In this case the yield is a power function of the fluence with power indices larger than 2. It has been suggested that single excitation is not sufficient to break bonds of atoms on surfaces and that re-excitations from the relaxed state reached after the previous excitation are necessary to break bonds ultimately. These problems are treated separately (93).

References

1. K. S. Song and R. T. Williams, *Self-Trapped Excitons*, Springer Verlag, Berlin (1993).
2. J. C. Miller and R. F. Haglund (eds.), *Laser Ablation, Mechanisms and Applications*, Springer Verlag, Berlin (1991)
3. T. R. Jervis, M.Nastasi and J-P. Hirvonen, *Materials Research Society Symposium Proceedings vol 279 Beam-solid Interactions: Fundamentals and Applications*, p. 665, ed. M. Nastasi, L. R. Harriot, N, Herbots and R. S. Averback, Materials, Research Society, Pittsburgh (1993)
4. J. F. Schetzina, *Proceedings of first International Conference on Photo-Excited Processes and Application* (Sendai, 1993) to be published.
5. P. D. Brewer, J. J. Zinck and G. L. Olson, *Materials Research Society Symposium Proceedings, vol 201, Surface Chemistry and Beam-Solid Interactions*, p. 543, eds. H. A. Atwater, F. A. Houle and D. H. Lowndes, Material Research Society, Pittsburgh (1991)
6. Hattori, K. Hattori, A. Okano, Y. Nakai and N. Itoh, *Phys. Rev. B* **45**, 8424 (1992)
7. W. Shockley, *Czech. J. Phys.* B 11, 81 (1961).
8. Y. Toyozawa, *Physica B+C* **117/118**, 23 (1983) and M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa and E. Hanamura, *Excitonic Processes in Solids*, Springer Verlag, Berlin (1986)
9. E. I. Rashba, *Excitons*, p. 543, ed. E. I. Rashba and M. D. Sturge (North Holland, Amsterdam (1982)
10. A. L. Shluger, R. W. Grimes, C. R. A. Catlow and N. Itoh, *J. Phys. Condens. Matter* 3, 8027 (1991)
11. J. H. O. Varley, *J. Nucl. Energy* 1, 130 (1954)
12. M. Cini, *Phys. Rev.* B **32**, 1951 (1985)
13. N. Itoh, J. Sharma and R. Smoluchowki, *International Conference on Color Centers in Alkali Halides* (1965) abstract 95.
14. F. C. Brown, B. R. Sever and J. P. Stott, *Phys. Rev. Lett.* **57**, 2279 (1986)
15. P. J. Feibelman and M. L. Knotek, Phys. Rev. B 18. 6531 (1978)
16. M. N. Kabler, *Point Defects in Solids*, p. 291, eds. J. H. Crawford and L. M. Slifkin, Plenum, New York (1972)
17. T. Shibata, S. Iwai, T. Tokizaki, K. Tanimura and N. Itoh, *Phys. Rev. B*, in press
18. A. Nakamura, unpublished
19. M. N. Kabler, *Phys. Rev.* **136** A1296 (1964)
20. R. T. Williams and M. N. Kabler, *Phys. Rev. B* **9**, 1897 (1974)
21. K. Tanimura and N. Itoh, *J. Phys. Chem. Solids* **45**, 323 (1984)
22. M. J. Marrone, F. W. Patten and M. N. Kabler, *Phys. Rev. Lett.* **31**, 467 (1973), and A. Wasiela, G. Ascarelli and Y. Merle D'Aubigne, *J. Phys. (France)* **34**, C9, 123 (1973)
23. D. Block, A. Wasiela and Y. Merle D'Aubigne, *J. Phys. C* **11**, 4201 (1978)
23. K. Tanimura, T. Suzuki and N. Itoh, *Phys. Rev. Lett.* **68**, 635 (1992), and T. Suzuki, K. Tanimura and N. Itoh, *Phys. Rev.* B **49** 7233 (1994)
25. H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960)
26. K. Kan'no, K. Tanaka and T. Hayashi, *Rev. Solid State Sci.* **4**, 383 (1990).
27. S. Hirota, K. Edamatsu and M. Hirai, *Phys. Rev. Lett.* **67**, 3283 (1991) and K. Edamatsu, M. Sumita, S. Hirota and M. Hirai, *Phys. Rev.* B **47**, 6747 (1993)
28. K. Tanimura and N. Itoh, *Phys. Rev. B* **45** 635 (1992)
29. T. Eshita, K. Tanimura, N. Itoh and H. Nishimura, *J. Phys. Soc. Jpn* **54**, 4418 (1985) and K. Tanimura, N. Itoh, T. Hayashi and H. Nishimura, *J. Phys. Soc. Jpn* **61**, 1366 (1992)
30. R. F. Wood, *J. Phys. Chem. Solids* **26**, 615 (1965)
31. K. S. Song, C. H. Leung and R. T. Williams, *J. Phys. Condens. Matter* 1, 683 (1989)
32. G. Brunet, C. H. Leung and K. S. Song, *Solid State Commun.* **53**, 607 (1985)
33. C. H. Leung, G. Brunet and K. S. Song, *J. Phys. C* **18**, 4459 (1985)
34. R. C. Baetzold and K. S. Song, *J. Phys. Condens. Matter* **3**, 2499 (1991)
35. K. S. Song and R. C. Baetzold, *Phys. Rev.* B **46**, 1960 (1992).
36. A. L. Shluger, N. Itoh, V. E. Puchin and E. N. Heifets, *Phys. Rev.* B **44** (1991) 1499.
37. V. E. Puchin, A. L. Shluger, K. Tanimura and N. Itoh, *Phys. Rev.* B **47** (1993) 6226^R
38. A. Shluger, V. E. Puchin, K. Tanimura and N. Itoh, to be published.
39. N. Itoh, K.Tanimura, A. M. Stoneham and A. H. Harker, *J. Phys. Condens. Matter* 1, 3911 (1989)
40. A. Sumi, *J. Phys. Soc. Jpn* **43** (1977) 1286
41. W. Hayes and T. J. L. Jenkins, *Crystal Lattice Defects and Amorphous Materials* **16**, 13

(1987)
42. W. Hayes and T. J. L. Jenkins, *J. Phys. C* **19**, 6211 (1986)
43. Y. Shinozuka and Y. Toyozawa, *J. Phys. Soc. Jpn* **46**, 505 (1979)
44. W. Hayes, M. J. Kane, O. Salminen, R. L. Wood and S. P. Doherry, *J. Phys. C* **17**, 2943 (1984)
45. W. Hayes, M. J. Kane, O. Salminen and A. I. Kuznetsov, *J. Phys. C* **17**, L383 (1984)
46. A. J. Fisher, W. Hayes and A. M. Stoneham, *Phys. Rev. Lett.* **64**, 2667 (1990) and A. J. Fisher, W. Hayes and A. M. Stoneham, *J. Phys. Condens. Matter* **2**, 6707 (1990)
47. A. Shluger and E. Stefanovich, *Phys. Rev. B* 42, 9664 (1990)
48. D. L. Griscom, *Proceedings of the Third International Frequency Control Symposium* (Electronic Industries association, Washington, D. C., 1979) p.98
49. K. Tanimura, T. Tanaka and N. Itoh, *Phys. Rev. Lett* **51**, 423 (1983)
50. W. Hayes and T. J. L. Jenkins, *J. Phys. C* **21**, 2391 (1988)
51. Ya. A. Valbis, K. A. Kalder, I. L. Kuusmann, Ch. B. Lushchik, A. A. Ratas, Z. A. Rachko, M. E. Springs and V. M. Tiit, *Sov. Phys. JETP Lett.* **22**, 36 (1975)
52. A. I. Kuznetsov, V. N. Abramov, V. V. Myurk and R. B. Namozov, *Sov. Phys. Solid State* **33** 1126 (1991)
53 J. H. Schulman and W. D. Compton, *Color Centers in Solids*, MacMillan, New York (1962)
54. T. Tokizaki, T. Makimura, H. Akiyama, A. Nakamura, K. Tanimura and N. Itoh, *Phys. Rev. Lett.* **67**, 2701 (1991)
55. R. T. Williams, J. N. Bradford and W. L. Faust, *Phys. Rev. B* **18**, 7038 (1978)
56. D. Pooley and W. A. Runciman, *J. Phys. C* **3**, 1815 (1970)
57. R. T. Williams, K. S. Song, W. L. Faust and C. H. Leung, *Phys. Rev. B* **33**, 7232 (1986)
58. N. Itoh, T. Eshita and R. T. Williams, *Phys. Rev. B* **34**, 4230 (1986)
59. T. Eshita, K. Tanimura and N. Itoh, *Phys. Status. Solidi (b)* **122**, 489 (1984)
60. N. Itoh and K. Tanimura, *J. Phys. Chem Solids* **51**, 717 (1990)
61. M. N. Kabler, *Proceedings for NATO Advanced Study Institute on Radiation Damage Processes in Materials*, p.171, ed. C.H.S.Dupuy, Noordhoff International, Leyden (1975)
62. N. Itoh and M. Saidoh, J. Phys. (France) **34**, C-9, 101 (1973)
63. Z. A. Rachko and J. A. Valbis, *Phys. Status. Solidi (b)* **93**, 161 (1979)
64. M. J. Springis and J. A. Valbis, *Phys. Status Solidi (b)* **125**, K165 (1984) and A. I. Kuznetsov, T. E. Jyesaar, B. R. Namozov and T. V. Uibo, *Opt. Spectrosc.* **52**, 438 (1982)
65. J. Valbis and N. Itoh, *Radiat. Eff. Defects Solids* **11**, 171 (1991)
66. E. R. Hodgson, *Radiat. Eff. Defects Solids* **18**, 169 (1990) and *J. Nucl. Mater.*179-181, 383 (1991)
67. Y. Chen, F. W. Clinards, B. D. Evans, R. F. French, R. Gonzalez, J. J. O'Dwyer, F. Wiffen and X. F. Zong, unpublished
68. D. L. Griscom, *Phys. Rev. B* **40**, 4224 (1989)
69. D. L. Griscom, *J. Non-Cryst. Solids* **149**, 137 (1992)
70. N. Itoh, K. Tanimura and C. Itoh, *The Physics and Technology of Amorphous SiO2*, p. 135, ed. R. A. B. Devine, Plenum, New York (1988)
71. C. Itoh, K. Tanimura, M. Georgiev and N. Itoh, *Rev. Solid State Sci.* **4**, 679 (1990)
72. R. A. Weeks, *J. Appl. Phys.* **27**, 1376 (1956)
73. N. Itoh and K. Tanimura, *Radiat. Effects* **98**, 435 (1986)
74. T. E. Tsai and D. L. Griscom, *Phys. Rev. Lett.* **67**, 2517 (1991)
75. H. Imai, *J. Non-Cryst. Solids*, to be published
76. N. Itoh, T. Shimizu-Iwayama and T. Fujita, *J. Non-Cryst. Solids*, to be published
77 L. H. Robins and M. A. Kastner, *Phys. Rev.* B **35**, 2867 (1987)
78. J. Ristein and G. Weiser, *Solid State Commun.* **66**, 361 (1988)
79. K. Shimakawa, S. Inami and S. R. Elliot, *Phys. Rev. B* **42**, 11857 (1990)
80. K. Tanimura and N. Itoh, *Phys. Rev. Lett.* **60**, 2753 (1988)
81. R. L. Fleisher, P. B. Price and R. M. Walker, *Nuclear Tracks in Solids* (Uuniv. California Press, Berkeley, 1975)
82. J. P. Duraud, F. Jollet, Y. Langevin and E. Dooryhee, *Nucl. Instrum. Methods B* **32**, 248 (1988)
83. M. Toulemonde, S. Bouffard and F. Studer, *Nucl. Intrum. & Methods* B **91**, 108 (1994).
84. N. Itoh, Radiat. Effects Defects Solids **110**, 19 (1989)
85. M. Szymonski, *Fundamental Processes in Sputtering of Atoms and Molecules*, p. 495 ed. P. Sigmund (Munksgaard, Copenhagen, 1993)
86. D. J. Elliot and P. D. Townsend, *Phil. Mag.* **23**, 249 (1971)
87. X. Li, R. D. Beck and R. L. Whetten, *Phys. Rev. Lett.* **68**, 3240 (1992)
88. V. E. Puchin, A. L. Shluger and N. Itoh, *Phys. Rev. B* **47**, 10760 (1993)
89. T. Kubo, A. Okano, J. Kanasaki, K. Ishikawa, Y. Nakai and N. Itoh, *Phys. Rev. B* **49**, 4931 (1993)
90. C. Fiori and R. A. B. Devine, Phys. Rev. Lett. 52, 2081 (1984) and Akazawa, Y. Utsumi, J. Takahashi and T. Urisu, *Appl. Phys. Lett.* **57**, 2302 (1990) and H. Akazawa, M. Nagase and Y. Utsumi, *Nucl. Intrum. & Methods B* **91**, 644 (1994)
91. D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **60**, 2187 (1988)
92. K. Hattori, A. Okano, Y. Nakai and N. Itoh, *Phys. Rev. B* **45**, 8424 (1992)
93. N. Itoh, J. Kanasaki, A. Okano and Y. Nakai, *Annual Review of Materials Science*, to be published.