Atomic Displacement Induced by Valence and Core Level Excitation in Solids

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abstract

I review, from a microscopic view point, the dynamics of local structural change of bonds in solids induced by various types of electronic excitations. In most cases, these processes are thermal origin, namely due to heating. However, there are evidences that athermal processes are often induced directly by the electronic excitation. The microscopic theories for such processes are reviewed together with the spectroscopic experimental data. In the last half, a recent topic on the recoil effects in the hard X-ray photoelectron spectra is also reviewed.

Keywords: athermal processes, Jahn-Teller instability, Inner core excitation, Recoil effect of photoelectrons

1. Introduction

The lattice structures of crystals in the ground state are determined by the balance of force due to the electronic interaction. The valence electrons play a role of "glue" in material bonding. Under the electronic excitation in the valence levels, the balance of force may be destroyed, and the atoms may relax to new quasi equilibrium points, which are different from those in the ground state as shown in Fig.1. One of the dreams of material scientists is, therefore, to manipulate the microscopic structures of materials at will by the electronic excitation. This scenario is, however, not always realized. On the contrary, most of the materials are stable against electronic excitation. A diamond crystal never changes into graphite under the UV light. Even defect formations are quite rare. In contrast to this, defects are introduced quite easily by illuminating UV light to a class of alkali halide crystals. Also, amorphous materials often show photo induced microscopic structural changes. Then, a question arises. What is the criterion for an efficient atomic displacement induced by electronic excitation (ADIEE) to occur?

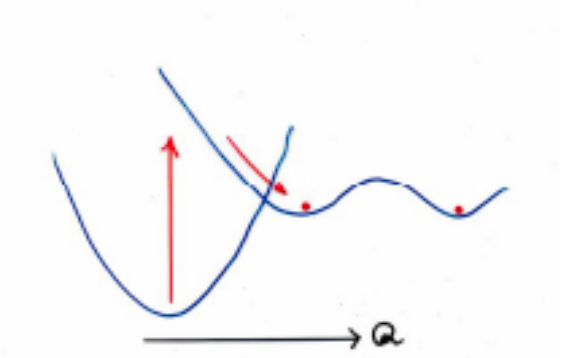


Fig.1. Schematic adiabatic potential curve indicating the atomic displacement in the excited state.

Because of the diversity of phenomena and materials, it seems hopeless to establish a unified framework to classify the mechanism of ADIEE. Here, I present some typical examples of the ADIEE in solids as a case study, with a hope it provides a clue to a unified theory and a hint to actual application in material sciences.

On the other hand, core electrons do not participate in the material bonding. But they sustain the valence electrons like foundations of buildings by Pauli's principle. Therefore, the inner core excitations often give rise to dramatic atomic processes. Usually the relaxation processes of the core excited states are very complicated, involving Auger decays and X-ray emission, but recent developments in the X-ray spectroscopy revealed microscopic mechanism of the atomic processes in the core excited states in some cases. I show the experimental data and theoretical calculations in the X-ray spectroscopy indicating the existence of strong atomic displacement in the core excited states.

As a very hot topic, I will also mention about the recoil effect of photoelectrons recently found in solids. The emitted electron kicks the atom from which it was ejected. This results in remarkable shift and broadening of the photoelectron spectra in the case of hard X-ray excitation.

2. Off-center instability

One of the most deeply understood ADIEE is the radiation induced defect formation in ionic crystals[1]. In the typical case like KCl, Frenkel pairs of color centers called F-centers and H-centers are created by the irradiation of UV light. This is definitely an athermal process, namely, the Frenkel pairs are created as a exothermic reaction in the electronic excited state. After a long history of confusion and controversy, the mechanism of ADIEE in alkali halides is now almost completely understood. It is closely related with the formation of self trapped excitons (STE) following the above-band-gap photo excitation. As shown in Fig. 2(a), the STE in the KCl-type alkali halides spontaneously undergoes an off-center relaxation with the change of symmetry from D_{2h} to C_{2v}[2]. Note that this off-center STE is nothing but a nearest neighbor pair of F-center and H-center, so that it evolves into a permanent pair of defects by the excess momentum gained in the relaxation process. The driving force of this atomic motion is the Coulombic repulsion between the deeply trapped electron and the central halogen ion pair which trapped a hole[3]. Paradoxically, the electron and the hole repel each other in the excited state of ionic crystals. The mechanism may also be understood from a view point of quasi Jahn-Teller instability in the excited state[1].

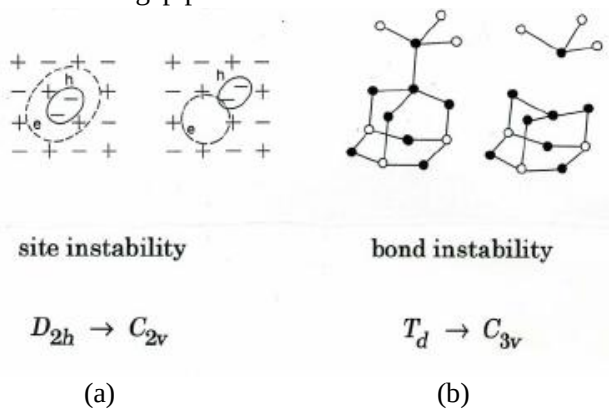


Fig. 2. Off-center instability in the self-traped exciton in alkali halides (a), and in the deep level of covalent semiconductors (b).

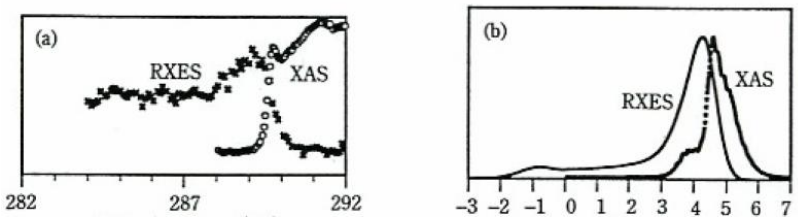
Analogous off-center instability has been observed in covalent materials. In Fig. 2(b), a schematic view of a model of DX center in GaAlAs crystal is shown. At present, the most convincing model of the DX center is a deep donor with negative *U*[4]. It is considered that the donor undergoes an off-center displacement in the negatively charged state. The bond changes from sp^3 to sp^2, with the symmetry breaking from T_d to C_{3v}. The driving force of this off-center instability is the bond breaking in the deeply trapped electron in the anti-bonding orbitals. Note that the conduction bands in covalent semiconductors are formed by the anti-bonding orbitals of sp^3 hybridized states. This mechanism may also be understood by a model of quasi Jahn-Teller instability. It is believed that essentially the same mechanism works also in the EL2 centers of GaAs[5], and N centers in Si[6].

Although the origin of the crystal bonding force of alkali halides (I-VII) and GaAs (III-V) is quite different, the mechanism of the off-center instability can be understood formally in the same way, namely the quasi Jahn-Teller instability and the spontaneous symmetry breaking. The bistability between the shallow center (on center state) and the deep center (off-center) is also a common feature.

2. Dynamical symmetry breaking in core exciton state in diamond and graphite

As shown above, even in covalent semiconductors, local bond breaking due to electronic origin occurs if the electron is strongly localized. Recently, spectroscopic evidence were obtained to establish this picture. In 1993, Ma *et al*.[7] observed resonant X-ray emission spectrum (RXES) from core exciton state of diamond. They excite 1s core electron of diamond to the core exciton state at the edge of the conduction band, and measured the recombination emission spectrum from the core exciton. The RXES shows a long low energy tail down from the Rayleigh scattering peak as shown in Fig. 3(a). Since the core hole lifetime is generally very short, as short as femto second order, due to the ultra fast Auger decay process, it had been believed that

all atomic processes induced by the core excitation occur only after the Auger decay of the core hole. Therefore, it was a little surprise that the RXES in diamond has an anomalous long tail, which is a signature of large lattice relaxation in the excited state.



(a) (b)

Fig.3. Observed X-ray absorption spectrum and the resonant emission spectrum in diamond (a), and the calculated spectra (b).

In Fig. 3(b), the theoretical results [8] for the RXES and the X-ray absorption spectrum are shown. The spectra are calculated by a cluster model which takes into account the vibronic interaction in a cluster of five carbon atoms including the core excited atom as shown in Fig. 4. The excited electron is trapped by the Coulombic potential of the core hole, and travels among the four sp^3 hybridized orbitals. Since these are anti-bonding orbitals as noted before, the electron may localize to one of them by breaking the bond, i.e. by forming a dangling bond.

In Fig. 5, the adiabatic potentials for the core exciton state is plotted, which are obtained by our vibronic cluster model. It should be noted that the core exciton state of diamond is electronically equivalent to the neutral nitrogen donor state. This is called the Z+1 equivalent-core approximation. Namely, the creation of the core exciton in diamond is nothing but a sudden photo doping of nitrogen donor. It is well known that a nitrogen donor in diamond has a deep level with accompanying off-center deformation corresponding to the change from sp^3 to sp^2 configuration[9]. Thus we may conclude that the long low energy tail in the RXES of diamond is a hot luminescence from the off-center adiabatic potential in the excited state, as shown in Fig. 5.

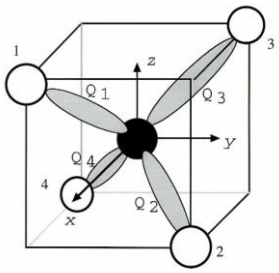


Fig. 4. Vibronic cluster model for diamond.

Recently, a more elaborate experimental work was done by Harada *et al*.[10] in SPring-8. They measured the RXES from the 1s σ–core exciton state of graphite. Harada *et al*. succeeded in measuring the polarization dependence of the RXES. In Fig. 6(a), the observed RXES are shown for different energies of the incident X-ray. The open circles (uuper ones) and the closed circles (lower ones) correspond to the case of polarized emission and the depolarized emission, respectively The polarized emission contains the component of photos with the same polarization as the incident X-ray. On the other hand, depolarized emission is composed only photons with components of polarization perpendicular to the incident light.

In Fig. 6(b), the theoretical spectra calculated by the vibronic cluster model for the σ–core exciton are plotted. In the case of resonant excitation, there appears a long tail in the RXES, just like the case of diamond. This is a signature of the existence of a strong atomic displacement in the core excited state before Auger decay. The existence of the depolarized emission itself is an evidence of the symmetry breaking in the core excited state, in this case from D_{3h} to $D_{2h.}$ This corresponds to the breaking of the σ–bond of the graphite. The central carbon atom moves in the graphite plane to form a dangling bond.

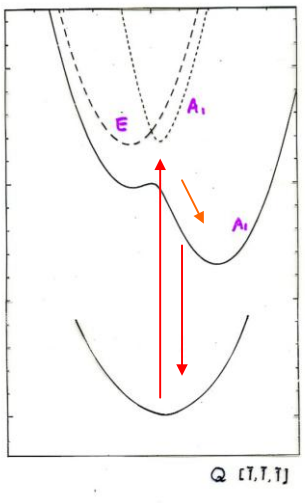


Fig. 5. Adiabatic potential curves for the core excited state in diamond.

The fact that the amplitude of low energy tail is relatively large in the depolarized emission as compared with the polarized emission is understood from the absence of a strong Rayleigh component in the former, because at least one phonon must be emitted in order to rotate the polarization vector. As the excitation energy is changed to off resonant values, the low energy tail disappears. This is because the effective lifetime of the excited electron decreases due to the uncertainty principle (in the lower detuning) and the quantum diffusion to the conduction band (in the upper detuning). All these spectral features are well reproduced by the theoretical calculation given in Fig. 6(b).

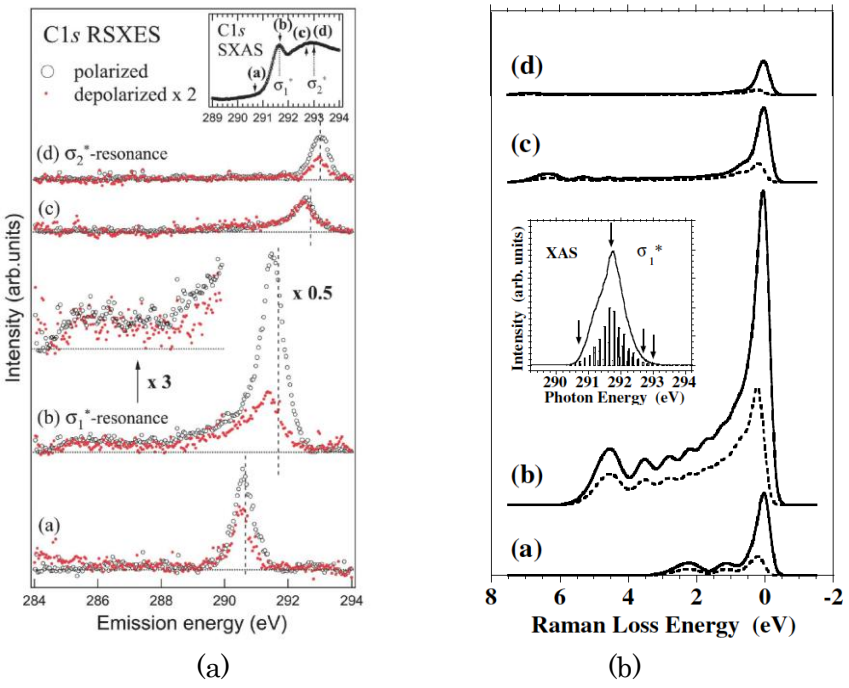


Fig. 6. The observed resonant X-ray emission spectra of graphite (a), and the theoretical curves (b) calculated by a vibronic cluster model (b) (reproduced from Ref.[10]).

3. Possibility of bond manipulation by ADIEE

Here I have shown a typical example of ADIEE due to the inner core excitation of covalent materials. Note that these materials are generally quite stable against the excitation of valence electrons. The story of ADIEE in the core excited state of diamond and graphite indicates that if the excited electron is strongly localized, even the bond of diamond may be broken. It is pointed out that the site selectivity of the core excitation may give rise to a possibility of selective bond breaking of molecules, a molecular scalpel. The main process of bond breaking would proceed after the Auger decay driven by the Coulombic instability in the two-hole or multi hole state. Even in that case, the ADIEE will play a role to initiate the selective bond breaking. The X-ray source has an advantage of possibility of high energy excitation by a one-photon process. However, the total fluence of the energy is low. On the other hand, extremely high fluence of energy can be attained by laser excitation, although the one photon energy is low. Therefore, a concerted use of the two sources may be useful to realize bond manipulation by ADIEE.

4. Recoil effect of photoelectrons

Quite another topic of athermal atomic process induced by the electronic excitation is the recoil effect of photoelectrons in the hard X-ray photoelectron spectra. The photoelectron spectroscopy is a powerful tool to obtain the information on the electronic states of material. The binding energy of the initial state of the electron E_B is given by a simple formula

$$E_B = h\nu - E_k \quad ,$$

where $h\nu$ is the energy of the incident photon and E_k is the kinetic energy of the emitted electron. In the above equation, the recoil energy of the atom is not included. In a model of a single atom at rest in vacuum, the recoil energy ΔE is evaluated by the conservation of momentum as

$$\Delta E = E_k \times (m/M) \, ,$$

in which m and M are the mass of the electron and the atom, respectively. This recoil energy gives rise to the high energy shift of the apparent binding energy. Because of the enormous difference between the electron mass and the atomic mass, the recoil effect is usually negligible in the UV and soft X-ray region. Note that the momentum of the incident photon is much smaller than the momentum of the photoelectron even in the hard X-ray region.

Quite recently, however, Takata *et al.* [11] found an anomalous deformation of the X-ray photoelectron spectra for carbon 1s core level in graphite. As shown in Fig. 7(a), the photoelectron spectra plotted against the apparent binding energy show a high energy shift depending on the incident photon energy. (The peak shift of the spectrum for the excitation by 340eV photon is due to the surface effect.) Furthermore, the spectra show an asymmetric broadening. These anomalies are due to the recoil effect. In solid, the recoil momentum is absorbed by the phonon bath resulting in the excitation of phonons. The photoelectron spectra are calculated by approximating the phonons in graphite by an anisotropic Debye model. In Fig. 7(b), theoretical curves of the photoelectron spectra are shown[11]. As shown in the figure, the theory reproduces the experimental curve quite well. It should be noted that there is essentially no adjustable parameters in the theory. The spectral broadening is due to the Doppler effect in the thermal as well as zero point vibration of the phonons.

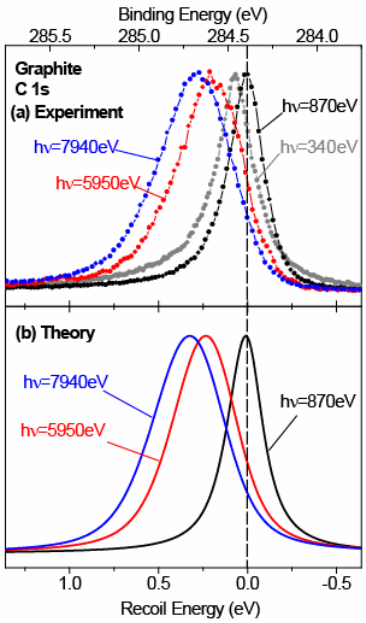


Fig. 7. Observed (a) and calculated (b) photoelectron spectra for 1s core level in graphite.

Furthermore, the dependence of the spectrum on the relative angle of the emitted electron with respect to the surface of graphite has been measured. As shown in Fig. 8, the emission angle can be controlled by using the linearly polarized light of the synchrotron radiation, since the photoelectron is ejected dominantly toward the direction of the electric field vector of the incident photon. In Fig. 9(a) is shown the emission angle dependence of the photoelectron spectrum for the excitation energy 7940eV at room temperature. As can be seen in the figure, the spectrum for the emission toward the grazing angle has slightly larger width than the spectrum in the normal angle emission. This spectral feature is also well explained by the anisotropic Debye model, as shown in Fig. 9(b). As is well known, the lattice vibrations in graphite have a strong anisotropy. The spring constant for the atomic displacement in the direction of the graphite sheet is roughly twice as large as that toward the normal direction. The dispersion relation also has a strong anisotropy. In fact, the phonon propagation in graphite can be regarded essentially as a two-dimensional one. The theoretical model takes into account these features in the anisotropic Debey model

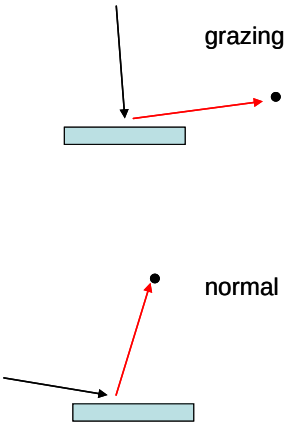


Fig. 8. Emission angle of the photoelectron.

The recoil effect reminds us of the Mössbauer effect[12]. In fact, the theory of photoelectron recoil effect can be formulated analogously to that
of the Mössbauer effect[13]. The anisotropy of the line shape comes from the quantum nature of the phonons. After the report of the recoil effect in graphite, the photoemission recoil effects in solid have been observed in other materials such as 2p level of Al and 1s level of MgB_2[14]. Recoil effect is universal since it originates simply in the conservation of momentum. As shown above, the spectrum indicates the solid state effect, namely the anisotropy of the lattice vibrations. This

suggests the possibility to utilize the photoelectron recoil effect as a tool to measure local vibrational coupling.

Recoil effects in photoelectron spectra are observed not only in the core level spectroscopy. Very recently, it was found that even the conduction electron in simple metals shows a recoil effect. Takata *et al.* [15] observed a remarkable shift and broadening of the Fermi edge of Al in the case of 7940eV excitation. This is a little surprising because the Bloch electrons in metals have wave functions delocalized all over the crystal, so that it may considered, at first glance, that the recoil momentum is shared by all of the atoms in the crystal. The theory developed by us[15], however, tells us that the recoil effect near the Fermi edge does exist, and is observable. The recoil effect becomes now an essential part of the photoelectron spectroscopy in the hard X-ray region.

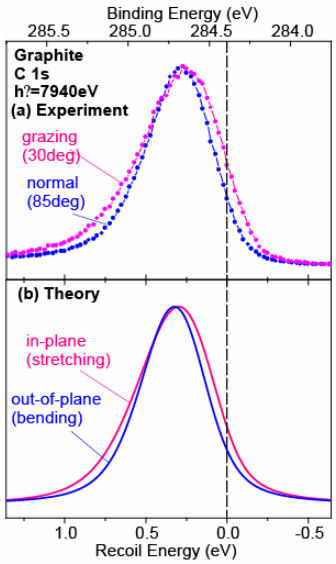


Fig. 9.. Experimental data (a) and the theoretical curves (b) of the dependence of the photoelectron spectra on the emission angle.

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Bibliography

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