

STRONG LATTICE RELAXATION AT LOCALIZED DEFECTS

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A survey of the most characteristic phenomena resulting from strong defect-lattice coupling is given. Among the topics discussed are: influence of lattice relaxation on photoionization and capture processes with the main emphasis put on the defects exhibiting metastable phenomena and recombination induced defect reactions such as defect creation and defect motion.

I. Introduction

It is well known that the strength of defect-lattice coupling depends critically on the localization of the electron or hole wavefunction at the defect. If during any transition this localization changes substantially (e.g. in transition from a localized to a delocalized defect bound state or in charge transfer involving a localized defect), the lattice around the defect usually undergoes strong rearrangement. This is called strong lattice relaxation.

The strength of the vibronic coupling is characterized by the Huang-Rhys parameter S . For a single dominant vibrating mode $\hbar\omega_0$, the product $S\hbar\omega_0$ is called the relaxation energy (Fig. (1)). If more than a one vibronic mode is involved, an average S parameter is introduced [1]. Its value depends on the type of coupling (e.g. Fröhlich, deformation potential [2]) and for the delocalized objects is usually less than unity. In this review we shall discuss only the case of defects characterized by a large value of S ($S \gg 1$). Since S inversely depends on the radius of the electron wavefunction (optical coupling) or its square (acoustic), such a large value of S implies strong electronic localization. This in turn indicates coupling mainly to the large $\vec{k}$ - vector phonons, for which there is no essential difference between acoustic and phonon modes. There are some experiments, however, in which a preference is observed (e.g. coupling to TA modes in spectra of transition metal impurities in II-VI compounds [3]).

A direct consequence of the large value of S is that the final states in transitions are states characterized by a large vibronic number n . Therefore, a semiclassical description of the processes is often possible. A configuration coordinate diagram is commonly used, which allows a good visualisation of the most characteristic phenomena due to the strong defect-lattice coupling. The total energy of the system E (electronic plus elastic, usually taken in a harmonic approximation) is plotted versus the local lattice displacement represented by the so-called configuration coordinate Q (Fig. (1)). It should be pointed out, however, that Q very seldom

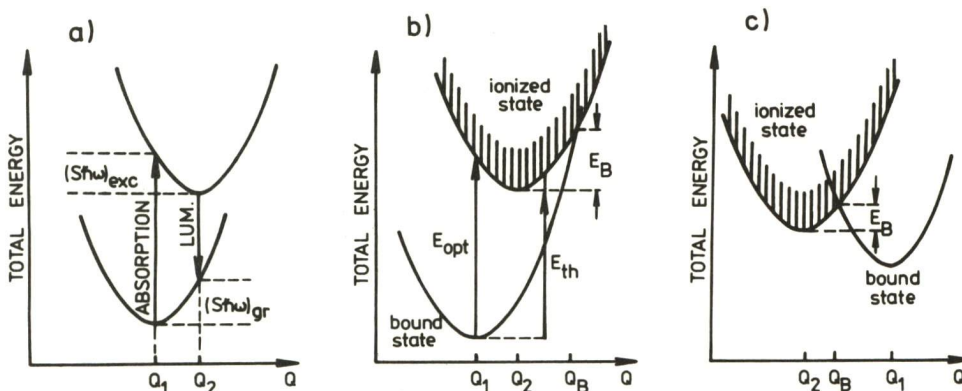


Fig.1 Typical configuration coordinate diagrams in solids: a) intra-defect b), c) charge transfer transitions

can be ascribed to a real displacement. Usually it is a fictitious parameter characterizing vibronic interactions in the system [4]. A simple inspection of the c.c. diagram shows that a strong vibronic coupling must influence all recombination processes at the defect. The most trivial consequences are differences between thermal and optical transition energies and the Stokes shifts in optical spectra. Among the others are vibronic broadening of the optical transitions, vibronic barrier effects in recombination and especially the existence of the metastable defect states. The next two chapters contain a concise survey of the recent results pertaining to the above phenomena. The extreme case of a strong defect-lattice relaxation - the recombination induced defect reactions is discussed at the end of this review.

II. Photoionization and Vibronic Coupling

The role of a vibronic coupling in optical spectra of localized defects in solids has been recognized quite early, especially in connection with the study of intradefect optical transitions. A good example of the evolution of this subject and the state of both theory and experiment is the treatment of the Jahn-Teller effect in solids [5].

The vibronic coupling of the localized defect and the lattice is expected to affect the ionization and capture processes much more than the intradefect transitions. This is because the force acting on the defect neighbours and causing their redistribution depends on the change of the charge distribution at the defect. Due to carrier ejection or trapping by a defect such a change is usually much more drastic than an internal transition. Accordingly, the S-factor for most of the internal transitions is less than 10 (e.g. in transition metal impurities the product Shw_0 , the Jahn-Teller energy, is of the order of 50 meV or less [3,5]). Notable exceptions are the F-centres for which Shw_0 is about 1 eV [6]. This reflects the fact that the excited states of these centers are delocalized effective-mass states and the change of localization of the electronic wave-function is almost as large as in the case of total ionization. This example serves as the argument for the necessity of inclusion of the vibronic coupling in the analysis of all the charge-transfer transitions involving localized centers, thermal and optical. The most widespread analysis of this process using only pure electronic models (see [7] for their up to date critical review) is evidently

erroneous. In the case of a relatively weak coupling the treatment proposed by Monemar and Samuelson [8] is satisfactory. In the case of a stronger coupling ($S > 10$) the semiclassical approximation may be used leading to the following formula for the total photoionization cross-section which is just a convolution of the electronic and vibronic components [9]:

$$\sigma(h\nu) = \frac{1}{\sqrt{\pi}} \int_{-\beta}^{\infty} dz e^{-z^2} \sigma_{el}(E_{opt}, h\nu + \Gamma z) \left(1 + \frac{\Gamma z}{h\nu}\right), \quad (1)$$

where β is the reduced energy

$$\beta = (h\nu - E_{opt})/\Gamma, \quad (2)$$

and broadening Γ equals

$$\Gamma = (\omega_{exc}/\omega_{gr}) \sqrt{2E_{relax} h\omega_{gr} \coth(h\omega_{gr}/2kT)}. \quad (3)$$

Here ω_{gr} and ω_{exc} are the frequencies of the dominant vibronic modes of the lattice in the ground and ionized defect states, respectively, E_{relax} is the difference between $E_{opt} - E_{th}$. A very serious problem is the proper choice of the electronic part σ_{el} of the photoionization cross-section. The effective mass models [7] are obviously inadequate. Some alternatives have been proposed [10,11,12,13] but the subject is still open for a serious, although perhaps laborious, study.

According to eqs. (1-3) a temperature dependent broadening of the photoionization spectrum, especially in the vicinity of E_{opt} is expected. A full analysis of this process has been attempted only for just few defects strongly coupled to the lattice [9,14-18]. Such an analysis allows a direct determination of the vibronic frequency ω_{gr} [14,15] and at least an estimate of E_{relax} if ω_{exc} is not known or its direct determination from both optical and thermal ionization processes is not possible [15]. It must be pointed out, however, that anharmonic effects complicate slightly the above analysis introducing additional multiplicative factor in the eq. (3). Determination of ω_{exc} is less straightforward. The best way would be a study of resonant Raman scattering at $h\nu > E_{opt}$. Due to the strong vibronic coupling, an enhancement of the scattering process is expected (good examples are F-centers in the alkali halides [19] and $CdF_2:In$ [20,14], where up to 7 phonon replicas were observed).

III. Vibronic Barrier and Trapping Processes

The defect-lattice coupling affects in the same way the process which is the reverse of the photoionization i.e. carrier capture. In the case of strong coupling the capture process is most efficient at the carrier energy at which the accepting level enters the band states (the vicinity of E_B at Fig.(1b)) [21,22]. Since this process requires thermal activation, it must be temperature dependent. At high temperatures [21,23] the Mott limit is reached and the capture cross-section is given by the expression:

$$\sigma(T) = \sigma_{\infty} \exp(-E_{act}/kT); \quad E_{act} \leq E_B \quad (4)$$

At low temperature the $\sigma(T)$ dependence flattens because of the dominant tunnelling and direct processes [23]. The σ_{∞} is of the order of 10^{-15}cm^2 [21].

The relative positions of the c.c. parabolas is a crucial parameter, leading to either normal (Fig.(1b)) or metastable (Fig.(1c)) states. Such states are called large-lattice-relaxation (LLR) states and are believed to be responsible for a broad class of metastable phenomena recently observed in many doped semiconductors [24]. A typical example is the persistent photoconductivity. At low temperatures the lifetime of the photoinduced state is immeasurably long, indicating a presence of a high potential barrier. We must point out, however, that the observation of persistency is not enough to classify the defect responsible for it as LLR. A potential barrier can be electrostatic in origin and be due to dislocations [25] or to an inhomogeneous spatial impurity distribution [26]. The recent paper by Queisser and Theodorou [27] presents convincing arguments in favour of such a situation.

Table 1: The characteristic energies for four defects exhibiting LLR

	InSb:"O"[28]	GaAlAs:Te[29,30]	CdTe:"Cl"[31]	CdF ₂ :In[9,14]
E_{opt}	> 0.25 eV	0.85 eV	0.95 eV	1.95 eV
E_{th}	- 0.15 eV	0.10 eV	- 0.05 eV	0.25 eV
E_{B}	0.30 eV	0.18 eV	0.50 eV	0.17 eV

The defects characterized by the LLR usually have a very large difference between the optical and thermal ionization energies (E_{opt} and E_{th}). Their capture cross-section is unusually low ($\sigma \lesssim 10^{-30} \text{ cm}^2$) and thermally activated. Table 1 summarizes these parameters for the four most representative examples. A much more extensive discussion is presented in [24]. The most puzzling is that similarly behaving states can be found in both highly covalent and highly ionic solids. Anyhow one can expect that the microscopic model should be different in these classes of materials. In my opinion, there are just two general groups. One of them found only in crystals with predominantly ionic bonding, is a symmetrical local lattice collapse due to change of the core screening after ionization of the defect. A corresponding local distortion is of the order of 10% of the n.n. distance. The examples are: In in CdF₂ crystals [9,14], F-centers in alkali halides [6], self-trapped exciton states in alkali halides [32] (here the lattice distortion need not to be symmetrical) and maybe transition metals in II-VI compounds [15]. The second group consists of defects in which LLR is a local rearrangement in which the atoms move even from one lattice site to another (e.g. substitutional to interstitial). I believe that all the bizarre defect states found in the more covalent crystals are of this nature. The key argument in favour of any of these models, pictured in Fig.(2), comes from a comparison of the c.c. model parameters: E_{opt} , E_{th} and E_{B} and the analysis of the temperature dependence of the barrier crossing [24]. For a single c.c. model of LLR states to be valid a tunneling process should dominate at the experimentally accessible temperatures (the time constant cannot be larger than a few hours). Therefore, an effective barrier must be smaller than the geometrical one. Due to the population effect, it should be temperature dependent [24,14]. Moreover, a preexponential factor in the $\sigma(T)$ dependence must be much smaller than σ_{∞} since it is just a product of σ_{∞} and the vibronic overlap at the energy corresponding to the most efficient tunnelling below the barrier. Such a behaviour has been observed in CdF₂:In [14], supporting the validity of the local collapse model. In the other cases (e.g. in InSb:"O" [28] or CdTe:Cl [31].), $\sigma(T)$ is exponential

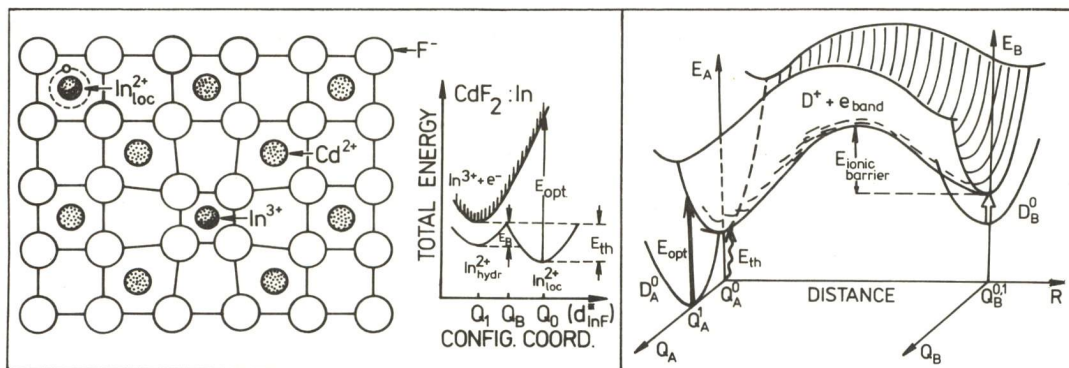


Fig.2 a) A single C.C. model of the LLR effect in $\text{CdF}_2:\text{In}$, b) a two dimensional c.c. diagram applicable in most covalent materials [9,14,24]

over many decades and the preexponential factor is of the order of σ_{∞} . The validity of the Mott model implies an inefficiency, of the tunneling process, hence a very thick barrier or in other words, a large distance motion, as shown in Fig.(2b) [24]. The crucial problem is the construction of a reasonable microscopic model of such defects. It is quite obvious that it cannot be just a single impurity. Complexing with some native defect is most probable. Lang and Logan proposed that these defects come from the pairing of the anionic vacancies with an appropriate dopant [30,33,18]. Although the symmetry of these defects has been determined recently in a ballistic phonon attenuation experiment [34] and it was shown to correspond well to the model predictions, there are serious arguments against it [35].

Another very unusual aspect of the LLR is the quenching of the autoionization [24]. A substantial diminishing of this process is expected since the resonant states have a different lattice equilibrium position than that of the ionized state, and an electronic factor is strongly quenched by small vibronic overlaps. Its effectiveness is best exemplified for $\text{CdTe}:\text{Cl}$ [31]. A localized "Cl" level is resonant at the ambient pressure ($E_{\text{th}} = -50$ meV). An application of pressure moves the level into the gap and causes its population. After pressure is released at a low temperature the level becomes again resonant remaining populated and can be emptied only optically ($E_{\text{opt}} \approx 1$ eV). Due to a very high barrier ($E_b \approx 0.5$ eV), autoionization does not occur.

Quite often the defect states are being connected with specific points of the band structure, usually the subsidiary minima. The assignment is based mostly upon the pressure dependence of their ionization energies. In the case of the coupling of a defect to the lattice, it may lead to a serious mistake since the separation of the electronic and lattice relaxation components in dE/dp is far from being straightforward. On the other hand, simultaneous analysis of the pressure dependence of photoionization and thermal ionization provides direct information on dE_{relax}/dp , which allows estimation of the magnitude of the local distortion [14].

IV. Localization and Defect-Lattice Coupling Discontinuity

All defects in solids can be divided into the two groups characterized either by weak or strong vibronic coupling. Another words a discontinuous change of the localization of the electronic wave function

at the defect is observed. This problem has been discussed by several workers on the basis of different models of electron-phonon coupling [36,37,38]. Here we repeat some key arguments given by Toyozawa [1,32,37]. In the continuum approximation the energy functional of a defect is given by:

$$E(\lambda) = E_{\text{kin}} \cdot \lambda^2 - E_L \cdot \lambda - E_S \lambda^3, \quad (5)$$

where λ is the degree of electron localization ($\lambda = a_0/a: a_0$ - n.n. distance, a - electron effective radius), E_L is the sum of all long range forces (Coulomb) and E_S - short range forces (localized potential + acoustic phonon coupling). It is obvious that depending on the relative strength of E_L and E_S we get either a delocalized ($\lambda \ll 1$ for $E_L \gg E_S$) or a localized ($\lambda > 1$ for $E_L < E_S$) state. The former is just an effective mass Coulomb state, the latter the so-called extrinsic self-trapped state. In the case of comparable binding energies of the two states they are separated by a barrier. Although the validity of the model is restricted to $\lambda < 1$, it can be simply extended to $\lambda > 1$ by an appropriate defect potential scaling ($m^* \rightarrow m_0$, $\epsilon^* \rightarrow \epsilon_\infty$) and a proper inclusion of the local lattice distortion [39] (theoretical papers on the ground state of F-centers are good examples [6]). Electron localization means a strong lattice relaxation around the defect (as in the case of In^{2+} in CdF_2 [9,14]). Such a localized state may exist only if the electronic binding energy is larger than the energy of the local lattice distortion. For most single impurities in covalent semiconductors this is not the case (the exceptions are the 3d impurities), and the only stable state is the delocalized effective mass state with a relatively weak coupling to the lattice. In contrast, missing atoms or defect aggregates provide a potential strong enough to bind electrons on a localized orbit with a resultant large local lattice distortion.

V. Recombination Induced Defect Reactions

The recombination-induced defect reactions, such as defect transformation: defect production or enhanced defect diffusion are extreme cases of the strong defect-lattice interaction. Defect reactions are usually temperature-controlled processes. The reaction enhancement is observed if the activation energy, equivalent to some energy barrier for the process, can be diminished, or even cancelled (the process becomes athermal). The subject of recombination enhancement of a defect reaction has recently been reviewed by Bourgoin and Corbett [40], Kimmerling [41] and Stoneham [42], therefore we shall concentrate only on some basic principles giving just two experimental examples.

There are two broad classes of mechanisms leading to the enhanced defect reactions in solids. The recombination energy usually comes from the electronic degrees of freedom. There are two classes of the recombination induced defect reactions. The first class is when the recombination energy may be transferred directly into the vibronic energy in the reaction coordinate. The reaction activation energy may be then diminished by a fraction of the recombination energy in proportion to the temporal localization of the vibronic excitation at the defect. The weaker is the coupling of the local modes to the crystal vibrations (e.g. in the solids with weak bonds, like molecular crystals or some amorphous materials), the higher is the probability for the reaction to take place [43]. Ingenious junction experiments on recombination induced defect annealing performed at the Bell Laboratories (see [44,41] for a review), show that for many defects a thermal annealing is enormously enhanced by a nonradiative recombination of the carriers at these defects. For smaller gap materials the process remains thermal but with the activation energy reduced by

an almost total achievable recombination energy. For the crystals with the larger gaps, such as GaP, the process becomes athermal. The second kind of reaction occurs when the defect is in its excited electronic state. The different potential energy surface of the excited state with a smaller or even zero barrier at the reaction coordinate, allows for an enhanced defect migration or defect production. Among reactions of this type occurring in semiconductors are the following: the charge-state dependence of the diffusion rates in Si [45] and photostructural reactions in amorphous solids [46]. The best documented example of this mechanism in solids is an F-center production by annihilation of excitons in alkali halides [47,48,49,36,1]. The excitons in ionic crystals are usually self-trapped, with a self-trapped hole being the main source of relaxation [36,48,42]. A relaxed triplet excited state of the exciton is a precursor of a further instability, causing annihilation of the relaxed exciton into a pair of defects (F and H centres) propagating further in the [110] direction. It is important to note that the triplet relaxed exciton state is not the source of the defect production per se. An additional, although much smaller than in the ground state, barrier along the [110] axis has to be overcome to produce a defect pair. It can be done either via nonradiative recombination after a second light pulse [47,50] at low temperatures, or just by an increase of temperature which would help to overcome the barrier in a normal activation process.

The importance of all these defect reactions is quite obvious, since different degradation phenomena in solid state devices, especially at high injection levels, probably originate from them.

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