The lifetime of electrons, holes and excitons before self-trapping

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Abstract. In this paper we discuss the self-trapping of a carrier or exciton in an insulator. The qualitative differences between small self-trapped molecular polarons and dielectric polarons are stressed. We point out that, for the formation of a molecular polaron or self-trapped exciton, a potential barrier must be penetrated or surmounted by the configuration coordinate, leading to a delay in the self-trapping process. This does not exist for dielectric polarons. The observable consequence of the delay time before self-trapping is discussed, and applications are made to alkali halides and to SiO_2.

1. Introduction

Two kinds of polaron are known in the literature: the 'dielectric' polaron, which occurs for electrons or holes in a polar lattice, and the 'molecular' polaron in which self-trapping is caused by short-range interactions. It is the purpose of this paper to show how the two types differ both in their rates of formation when a free carrier is excited and in their observed behaviour.

The properties of the dielectric polaron result from the Coulomb interaction of the carrier and the polar lattice. As argued by Landau (1933; see also Mott and Gurney 1940), the electron or hole is thought to create for itself a potential hole of the form for large r,

$$- e^2/\kappa_{\text{eff}} r, \qquad \kappa_{\text{eff}}^{-1} = \kappa_{\infty}^{-1} - \kappa_0^{-1}, \tag{1}$$

where κ_0 and κ_∞ are the static and optic dielectric constants. Since this is a Coulomb field, self-trapping is always possible, and the orbital of the self-trapped electron is of order

$$\hbar^2 \kappa_{\text{eff}}/m_{\text{eff}} e^2. \tag{2}$$

Equation (1) is only valid for values of r greater than this and the polaron is only called 'small' if (2) is comparable with the lattice constant. If it is greater, only weak trapping is expected and, as m_{eff} decreases, there should be a continuous transition to 'large' polaron behaviour, with no activation energy for motion. Though we know of no detailed treatment of the rate at which such small polarons form round free carriers, it appears likely that, for a carrier injected into a solid, equilibrium will be established within the time of a very few lattice vibrations.

The main point of this paper is to stress some of the differences for the other kind

of self-trapped carrier, the molecular polaron, or for self-trapped excitons. Typical of these are the V_K centres in alkali halides; here a hole in the valence band is self-trapped because a halogen atom forms a bond with a neighbouring halogen ion, the two attracting each other so that the distance between them falls well below that in the undistorted lattice. A similar phenomenon occurs in solid and liquid argon (Miller *et al* 1968), and, as we shall argue, for holes in SiO_2. Similar mechanisms can give self-trapping for excitons too. The 'molecular' polaron is *only* formed for fairly large effective mass, and if this is not large enough nothing happens; there is nothing analogous to the dielectric 'large polaron'.

The reason for this critical change of behaviour has been pointed out by Toyozawa (1962, 1963) and Emin (1972, 1973). Our version of the argument is illustrated in figure 1.
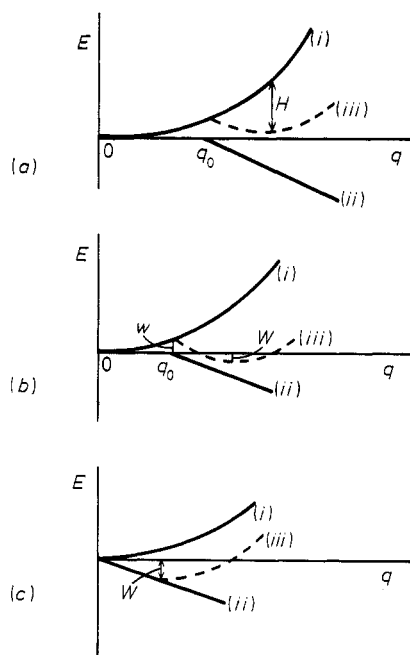
Figure 1. Self-trapping mechanism for a hole. (i) is the elastic energy, (ii) the electronic and (iii) the total. In case (a) no polaron is formed, in (b) the trapping energy is W, (c) is for a hole trapped by a defect.

For a V_K centre q denotes the change in the distance between the two halogens concerned, and curve (i) the elastic energy. The potential well formed for the carrier is *not* of coulomb type (1), and therefore only for a finite value q_0 of q will it be able to trap an electron. This is because in three dimensions a potential well of radius a and depth V can only trap a carrier if

$$2mVa^2/\hbar^2 > \tfrac{1}{4}\pi^2. \tag{3}$$

When it does, the energy of the electron will be lowered as in curve (ii). The total energy (iii) will have a minimum, but only if this lies below zero can self-trapping occur. This case is shown in figure 1(b) and the binding energy of the polaron is W.

Perhaps the most striking evidence for self-trapping when the polaron binding energy W is positive but not when W is negative comes from the study of radiation emitted by excitons in $AgBr_xCl_{1-x}$. Here it is a question of self-trapping of excitons rather than

free carriers, which we shall treat below, but the principles are the same. In this system there is at a certain value of x a sudden change from narrow lines due to untrapped excitons to a much broader line displaced to longer wavelengths due to trapped excitons (Kanzaki and Sakuraki 1970).

Several other points are worth making here. First of all, it is only in two or three dimensions that short-range forces like chemical bonding give rise to the critical behaviour shown in figures 1(a) and (b) for a molecular polaron. This has been discussed by Sumi and Toyozawa (1973) and by Emin and Holstein (1976). In Holstein's (1959) important paper on hopping polarons, using a molecular model, he took a one-dimensional array of molecules, and since, in one dimension, any potential well will trap a carrier, our q_0 must be zero (figure 1(a)) and the present considerations do not apply. Secondly, it is possible for both types of polaron to coexist in the same system if the coupling parameters are suitable (see, e.g., Emin 1972 or Emin and Holstein 1976). This is important in some transport properties (e.g., Sumi 1973), where most carriers may be present as the slowly diffusing small molecular polarons, yet transport may be dominated by the faster-moving large dielectric polarons. We shall treat the interaction between the two kinds of polaron later in this paper. Thirdly, in simple treatments of small dielectric polarons, the hopping energy for diffusive motion, W_D, is related to the polaron binding energy, W, and approximately $W_D = \frac{1}{2}W$. This result has only limited validity in any case. But it can be seen from figure 1 that for molecular polarons there is no relation at all between W and the hopping energy ($W_D = H/2$), quite apart from any limitations of the usual simple treatments.

The new point that we want to bring out in this paper should be clear from figure 1. If the electron is in thermal equilibrium at the point O in figure 1(b), and self-trapping is to occur, the system must first pass through a potential barrier[†], of height marked w. At high temperatures the probability of this happening will be $C\exp(-w/kT)$ per unit time. At low temperatures it can tunnel through the barrier and the probability will be $C\exp(-w/\frac{1}{4}\hbar\omega)$. Here ω is the frequency of the vibration of the quantity denoted by q in figure 1; C is probably of order $10^{12}\,\mathrm{s}^{-1}$. We shall discuss the observable consequences of the barrier w.

Emin and Holstein (1976) discuss the case when dielectric and molecular polaron formation are possible together (cf § 3), as they must be for holes in alkali halides. We think, in terms of the model of figure 1, that a dielectric polaron (large or small) will be formed round a hole at O in a few multiples of 10^{-12} s, and that this will have the effect of increasing the effective mass of the hole (m in equation (3)). This will clearly decrease q_0 in figure 1 and so make self-trapping easier. The effect should not be so marked when the hole is part of an exciton, since the electron will screen the hole from the surrounding dielectric.

2. Consequences of a barrier to self-trapping

When a molecular polaron is formed, its effects are observed spectroscopically and in transport phenomena. Optical spectroscopy is a particularly useful tool, for self-trapping leads to broad lines with a large Stokes shift, whereas transitions involving only weakly-localised states are often sharp. Thus there may be sharp absorption to a diffuse state

[†] The existence of a potential barrier was pointed out by Toyozawa (1962), but its consequences were not analysed.

followed by a broad emission band from a self-trapped state. The transport properties of a small polaron show a characteristic thermally-activated form which can be identified more closely by measurements of the thermopower and Hall effect.

We are concerned with a barrier to self-trapping, and hence with a delay before the characteristic features of a molecular polaron appear. The delay time will usually be temperature-dependent, but tending, as we have seen, to a constant value at low T, and there may be a period for which (in ionic materials) both small molecular and large dielectric polaron behaviour can be seen together. In this section we discuss the experimental evidence from transport measurements in SiO_2 and from optical work on alkali halides.

2.1. Self-trapped holes in SiO_2

Evidence of delay in the formation of self-trapped carriers can come either from the mobility of injected holes in, say, films of solid argon, or from the behaviour of excitons formed from an electron bound to a hole, as in NaCl. For free holes the only evidence known to us comes from the work of Hughes (1973, 1975, 1977) on thermally-grown SiO_2. This substance is amorphous; the valence band, formed from lone-pair oxygen 2p-orbitals, is calculated to be ~ 3 eV wide. The hole mobility is found to be activated, the electron mobility not. It seems unlikely that discrete traps are present for holes but not electrons and the rather large activation energy found, 0·37 eV, is in all probability due to self-trapping. One possibility is (see Mott 1977) that a 'hole' on one oxygen ion forms a bond with another neighbouring oxygen ion, and as in the V_K centre the two pull together.

Hughes finds also an initial mobility with an activation energy of 0·13 eV (his 'prompt' mobility), settling down to a final value of 0·37 eV after a time of order $\sim 10^{-5}$ s. We suggest that this is the time needed for self-trapping, and that, due to the high Debye temperature, this should be $(1/C)\exp(+w/\frac{1}{4}\hbar\omega)$; with $\hbar\omega \sim 0\cdot1$ eV, $C \sim 10^{12}$ s^{-1}, this gives $w = 0\cdot4$ eV, which seems reasonable. We have however to explain the smaller value (0·13 eV) for the 'prompt' mobility. This could well be the energy for excitation to a mobility edge; for holes in amorphous As_2Te_3 this, according to Nagels *et al* (1974; see also Mott *et al* 1975), is 0·1 eV, so 0·13 eV is reasonable for SiO_2. But we have to ask whether, if states at the valence band edge are localised by disorder in the Anderson sense, a delay time for self-trapping is still to be expected. If the states are strongly localised, within a distance comparable to the lattice parameter, a delay time is not to be expected and the distortion should occur within the time of a few lattice vibrations. But localised states leading to a mobility edge at only 0·13 eV from the valence band edge should have a spatial extent of ~ 10 atomic spacings, and under these conditions the activation energy and hence the delay in self-trapping will be only slightly reduced. A simple way of showing this is to represent the localised state by a sphere of radius b at which ψ vanishes, and the well produced by distortion by a potential $-V$ extending over a radius a, with $b/a \gg 1$. For small V, the change in the energy is Va^3/b^3, but when V becomes deep enough for a bound state to occur for $b = \infty$, the change in the energy is little affected by b. Thus, except that the discontinuity in the slope of E versus q is no longer there, the essential features of figure 1 are retained.

2.2. Self-trapped excitons

We turn now to excitons. In alkali halides a direct gap exciton is expected (Kunz and

Lipari 1971). For these materials the concept of exciton self-trapping, and a finite life-time before trapping, goes back quite a long way (see for instance Sumi and Toyozawa 1972, Sakoda and Towozawa 1973), and it is generally supposed that the mechanism is the same as for holes. However, there are two main differences: the mechanisms which determine the free-particle bandwidths are different for excitons† and for holes, and the coupling to the lattice is modified by the electron component of the exciton. Thus the value of q_0 in figure 1 will be different and may also be larger than for the free hole.

We think, then, that for an exciton we may draw the ground and excited states in various ways, shown in figure 2. In (a) B lies above A. The exciton absorption line will
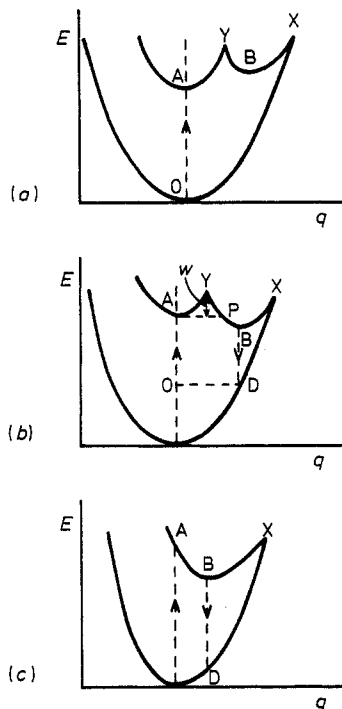

Figure 2. Self-trapping mechanism for an exciton. In case (a) no self-trapping occurs, in case (b) it occurs after a time delay; case (c) is for a trapped exciton.

be sharp, and a sharp line with the same frequency should be reradiated. In figure 2(b), B lies below A. Self-trapping is then possible with the time delay given as for holes; after self-trapping, we have either a broad luminescence band or multiphonon emission where at low temperature the transition probability will be (Englman and Jortner 1970)

$$ C \exp\left(-\gamma E/\hbar\omega\right) \begin{cases} \gamma \sim 1 & \text{for strong interaction} \\ \gamma \sim 2 & \text{for weak interaction.} \end{cases} \qquad (4) $$

Here E is the energy radiated, C is of order $10^{12}\,\text{s}^{-1}$ and γ depends weakly on the distance OD. As the temperature increases towards the Debye temperature, (4) should be multiplied by $[\exp\left(-\hbar\omega/kT\right) + 1]^{-E/\hbar\omega}$; and at higher temperatures recombination occurs

† For a discussion of the transport mechanism of excitons, see for instance Haken and Reineker (1972).

by exciting over the crossing point X, as first suggested by one of us (Mott 1938); the recombination coefficient then behaves as

$$C \exp\left(-W/kT\right). \tag{5}$$

In this non-radiative multiphonon transition, the energy released may be dissipated by interaction with other phonons or by causing radiation damage. Whether the system shows luminescence or decays non-radiatively depends largely on the form of the curves in figure 2(b) or (c). Dexter *et al* (1955) first suggested that if X lies below A (in figure 2(c)), then the system would swing directly to X and recombine in a time $\sim 1/\omega$. But this is only true in the low T regime when the system tunnels from A to P; if self-trapping occurs after excitation *over* the barrier, then the condition is that Y lies above X.

Evidence for a delay in the formation of self-trapped excitons can take several forms. By far the clearest data are the results of Kuusmann *et al* (1976). Their results for NaI show both the luminescence of the self-trapped exciton at 4·2 eV and the band-edge luminescence at 5·55 eV characteristic of an unrelaxed exciton. The temperature-dependence of the luminescence indicates a barrier $w \sim 0\cdot02$ eV against self-trapping. The edge luminescence and self-trapped exciton luminescence were both observed in KI and RbI too, although barrier heights were not quoted. They conclude on the basis of excitation of luminescent centres that in NaI the exciton 'migrates hundreds of lattice constants before being self-trapped'. There is similar evidence for solid rare gases, summarised by Jortner (1974). Also Nishimura and Tomura (1975) show that in alkali halides excitons can migrate up to 75 Å before producing F-centres.

Earlier work which suggested a barrier relied mainly on the temperature dependence of luminescent efficiency, either of the self-trapped exciton itself or of some other luminescent centre to which energy is transferred. Whilst these data (Kink and Liid'ya 1969, 1970, Vasil'chenko *et al* 1970, Fontana *et al* 1968, 1969, Lushchik *et al* 1972) may indicate a barrier, other possibilities cannot be ruled out. These authors consider, on the basis of excitation of luminescent centres, that the exciton migrates. However, the rapid exciton motion could occur not only in the unrelaxed exciton state with a delay before self-trapping but also in the states of an instantly self-trapped exciton in which the hole is excited (Wardle and Murray 1973). Further, the efficiency of self-trapped exciton luminescence can have a temperature dependence of a similar type arising from the thermal population of different spin states from which spin-allowed transitions can occur (Purdy and Murray 1975, Song and Stoneham 1975). A detailed analysis is needed to identify the precise mechanism involved. But it remains a real possibility that the activation energies indicated are associated with a barrier to self-trapping. There is here the question of whether excitons can decay to the (presumably) lower triplet state before decaying.

Turning now to SiO_2, one of us (Mott 1977) has discussed the evidence that the peak in the absorption spectrum at 10·2 eV observed in crystalline and amorphous SiO_2 is due to an exciton, and it was pointed out that the sharpness of the peak contrasts with the very broad band due in the glass to the non-bridging oxygens associated with sodium ions. If as we suggest here holes can be self-trapped, it is likely that excitons can be too. If so, the sharpness of the line implies that there must be a barrier to self-trapping, and thus that in the crystals the exciton is mobile and in the glass that it can move within a weakly localised state. We conjecture that the mechanism of recombination is that of Dexter *et al* (1955), occurring after the coordinate q penetrates the barrier; if so, recombination rather than self-trapping must be the normal event. Self-trapping would lead to fluorescent radiation, which is not observed in the pure material (Sigel 1973).

3. Analogues of self-trapping

Several systems behave in a way which resembles the dielectric and self-trapped polaron case we have described. One system shows an especially close analogy: the V^--centre in simple oxides like MgO, CaO, SrO, ZnO, BeO and Al_2O_3. Here a hole is trapped by a cation vacancy. The analogue of the large polaron corresponds to a hole shared equally among the nearest-neighbour oxygen ions. The analogue of the small polaron, which is actually observed experimentally, has a hole localised on a single oxygen neighbour. The gain in lattice polarisation and distortion energy exceeds the advantage in kinetic energy when the hole is shared (see, e.g., Norgett *et al* 1977). Thus the physical basis of the behaviour parallels the polaron case closely. However, the analysis of Schirmer (1976) indicates no barrier. This difference can be understood from the following argument. Emin and Holstein's analysis of self-trapping concentrates on questions of scale, that is on how the energy of a carrier changes when a scale length is altered. The result involves competition between the enhanced kinetic energy and lowered potential energy as the scale length is reduced. Very similar relations appear in the bound polaron problem (Larsen 1969). However, the V^--centre does not involve a scale length in the same way, and this is the reason that it does not show a barrier to self-trapping. Suppose the hole to be in its lowest state when there is no self-trapping distortion. In this state the hole wavefunction has equal weights from the oxygen ions next to the vacancy. For a small self-trapping distortion, the weight associated with one of the oxygens is enhanced by a factor f. Both the kinetic energy and polarisation and distortion energies change by order f^2. If the polarisation energy term dominates, the centre can move spontaneously towards the self-trapped state; if the kinetic energy term is dominant, the system does not self-trap. One simply compares two terms of order f^2, and no question of a barrier arises. This may be contrasted with the scaling arguments of Emin and Holstein, where the kinetic energy varies with scale length Λ as $+\Lambda^{-2}$ and the other terms as $-\Lambda^{-\delta}$, with $\delta > 2$. It is the difference between the powers -2 and $-\delta$ of the two terms which can lead to large and small polaron extrema, separated by a barrier. The V^- centre, with both terms in f^2, is an analogue of $\delta = 2$, which would only give a single solution, without an intervening barrier.

The present arguments are relevant when there is disorder, as mentioned in § 2.1. Only if the small and large polarons differ in scale, that is in mean square radius, is a barrier expected.

Two other cases appear analogous to self-trapping: the hindered-rotor problem, and its complex relation, the Jahn–Teller effect. In both cases, as potential barriers are raised, the observed properties move more to those of a localised system. However, this is mainly a question of the relative sizes of a tunnelling time and a time characteristic of the observation. It is quite distinct from self-trapping.

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