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Dynamics of self-trapped hole processes in AgCl

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Abstract

A set of phenomena involving the self-trapped hole (STH) in AgCl have been studied in crystals doped with hole sources, traps for holes and electrons and providers of cation vacancies. An energy barrier was demonstrated in the self-trapping process; its energy was related to appropriate phonon energies, and tunnelling appeared in the temperature range predicted by Mott and Stoneham. Migration of the STH can occur either by phonon-assisted hopping or by tunnelling. From the temperature dependences, one obtains the activation energy (0.062 eV), the trap depth (0.12 eV) and the temperature exponent for quantum migration (1.3). The structures and energetics of two centres involving an STH bound to a vacancy have been deduced. Also, it was shown that low-temperature capture of a hole by substitutional Fe^{2+} causes production of a Frenkel pair, as well as ultimately leading to formation of the (interstitial Fe^{3+})—(multivacancy) defect that was first characterized by Hayes *et al.*

1. Introduction

In silver chloride, the free photohole is unstable relative to a self-trapped state, the properties of which are interesting not only because of their relevance to the small-polaron problem in general, but also because of the unusual structure of the valence band. In the silver halides, a strong mixing of the silver d states with the halide p states results in the top of the valence band appearing at the L-point instead of at the zone centre; this also brings the band gap down into the short-wavelength end of the visible, a property very useful to the performance of the classical photographic process.

In AgCl, the self-trapped hole (STH) is centred on a cation, not an anion; this is a result of the presence of the silver d states at the top of the valence band. The resulting Ag^{2+} centre has a tetragonal Jahn–Teller extension along [100] and strong molecular bonding with the four in-plane chloride ions [1]. Thus, this is quite different from the STH in alkali halides, the V_k centre, in which the hole is shared between two halide ions to form a molecular ion along a [110] axis.

The present paper summarizes an experimental study of processes involved in the formation and migration of the STH in AgCl, research that grew out of the discovery, in Bill Hayes' group at the Clarendon Laboratory, of an unusual new type of lattice defect: an interstitial Fe^{3+} bound to four halide ions and four cation vacancies [2]. The subsequent

experiments at Chapel Hill all employed AgCl single crystals, doubly doped with various cations chosen to serve as sources of holes or vacancies, or as traps for photo-carriers. Defect structures and populations were monitored by electron paramagnetic resonance (EPR) measured as functions of irradiation temperatures and subsequent annealing.

2. Formation of the interstitial ferric defects

The interstitial ferric ion defect identified in the Oxford study had originally been seen by Hennig [3], and was shown by Hayes *et al* to consist of an interstitial Fe^{3+} , partially covalently bonded to a tetrahedron of chloride ions, plus a tetrahedron of silver vacancies. This structure was later confirmed by ENDOR measurements [4, 5]. Also, Hay *et al* [6] showed that low-temperature irradiation with band-gap light could also produce a trigonally symmetric centre, $\text{Fe}_{\text{trig}}^{3+}$, with only three cation vacancies bound to the interstitial Fe^{3+} ; at higher temperatures, this converts to the cubic centre $\text{Fe}_{\text{cubic}}^{3+}$, described above. The cubic centre is apparently stabilized by the binding energy of the tetrachloroferrate ion; it has also since been seen in other hosts, such as Fe-doped NaCl [7–9].

To address the question as to how, at low temperatures, this centre acquires the extra vacancy necessary to its production, Laredo *et al* [10] monitored the EPR spectra produced by irradiating $\text{AgCl}:\text{Fe}^{2+}$, Pd^{2+} with band-gap light, at temperatures ranging from 4.5 to 220 K. The Pd^{2+} acts as a deep trap for photoelectrons, thereby preventing recombination with holes.

At temperatures much below 50 K, the mobility of the STH is quite low (see section 4, below), and although irradiation produces an intense EPR spectrum due to these STH, one sees no evidence of production of any ferric centres. If, however, the temperature exceeds about 60 K, then the STH is sufficiently mobile that Fe^{2+} can now be converted to Fe^{3+} . For temperatures between 60 and 120 K, the mobility of the cation vacancy is so low that only $\text{Fe}_{\text{trig}}^{3+}$ is produced. Nevertheless, this centre has one more cation vacancy than that available from the original $\text{Fe}^{2+}(\text{Ag}_{\text{vac}}^+)$, plus that created when the Fe^{3+} jumped from a substitutional to interstitial site. It seems most likely that the additional vacancy must have been formed upon the capture of a hole, presumably by conversion of a neighbouring substitutional Ag^+ into a mobile interstitial. The possibility of such Frenkel defect production upon photohole trapping was earlier proposed by Mitchell [11], and the present observations constitute good evidence for this process.

At temperatures above about 100 K, the mobility of cation vacancies in the bulk of the crystal begins to become significant [12, 13]. The $\text{Fe}_{\text{trig}}^{3+}$ centre can now complete the tetrahedron of vacancies characterizing the more stable $\text{Fe}_{\text{cubic}}^{3+}$ centre. Indeed, from the known diffusivity of the vacancy [12, 13] and a reasonable estimate of the concentration of ferric centres, one calculates that a cation vacancy will reach the trigonal centre within the 20 minute irradiation time for temperatures at least approximately 135 K. Experimentally, it was found that the production rate of the cubic centre increased with increasing irradiation temperature most rapidly just above 150 K, constituting satisfying agreement with the estimate.

For irradiation temperatures exceeding 195 K, however, the production of cubic centres drops sharply with increasing temperature. Since the photoelectrons trapped at Pd^{2+} are in a centre stable to considerably higher temperatures [14], and since $\text{Fe}_{\text{cubic}}^{3+}$ at these temperatures decays only slowly in the dark, we conclude that the drop in concentration above 195 K must be a result of combined effects of optical excitation and thermal activation during the ultraviolet irradiation. Consistent with this proposal was the experimental observation that using shorter irradiation times shifted the temperature of maximum production of cubic centres to higher irradiation temperatures.

3. The activation energy for the self-trapping transition

Because a three-dimensional potential well has no bound state unless it is sufficiently deep, a free hole cannot be self-trapped until the lattice has first undergone a sufficient local distortion. It has been pointed out [15–17] that if the hole–phonon coupling is not very strong, then an activation energy barrier must be surmounted in the self-trapping transition. For the case at hand, one can estimate the order of magnitude expected for the activation energy by noting that it consists mainly of components of short-wavelength transverse acoustical lattice modes, which in AgCl have energies in the range 4 to 8 meV [18]. One might then expect that if there is indeed an energy barrier to the transition, its height should be of the order of a few meV. In addition, the trapping rate for the hole would then decrease as the temperature is decreased, in contrast to the usual trapping behaviour of photocarriers.

All of these expectations were established in a determination of the temperature dependence of the number of photoholes in irradiated AgCl that become self-trapped before being captured by an added dopant ion [19, 20]. In one experiment, the AgCl crystal was treated so as to contain both Cu^+ (to serve as stationary traps for photoholes) and Cu^{2+} (to serve as a source of holes under illumination with sub-band-gap light [21]). A second experiment employed crystals containing both $\text{Pd}^{2+}(\text{Ag}_{vac}^+)$, which is a hole trap at low temperatures [14], and unassociated Pd^{2+} , which traps electrons and thereby prevents recombination upon exposure to band-gap radiation.

In each case, it was found that the number of STH produced by irradiation was greater for higher irradiation temperature. The range of temperature was limited by the onset of slow migration of the STH (for temperatures above about 30 K), resulting in capture at Cu^+ ions, and—at the lower end—by the appearance of an athermal transition below about 10 K. Presumably, this represents a tunnelling to the self-trapped state

The analysis of the data assumes that the free holes travel ballistically and that the cross-section for capture at a dopant ion does not depend significantly on temperature. With these premises, one concludes that the probability of the hole becoming self-trapped before reaching a dopant (either Cu^+ or $\text{Pd}^{2+}(\text{Ag}_{vac}^+)$, in the two different systems) should be proportional to $T^{-1/2} \exp(-E/kT)$, where E is the activation energy for the self-trapping transition.

In each of the two experiments, the data were found to fit the expected temperature dependence very well. For the Cu-doped crystal, the activation energy E was found to be 1.7 ± 0.1 meV. For the Pd-doped crystal, the data were less accurate because of overlap of lines of the EPR spectra, but this second experiment was nevertheless a useful test of the model because it involved a different hole trap and because it involved bandgap, rather than sub-bandgap, irradiation energy. The results obtained with this system gave an activation energy of 2.0 ± 0.3 meV, consistent with the more precise result from the AgCl:Cu crystal.

Regarding the onset of a tunnelling transition at the lower temperatures, Mott and Stoneham [16] had earlier estimated the tunnelling rate to be about $10^{12} \text{ s}^{-1} \times \exp[-E/(h\nu/4)]$. If one takes the phonon energy $h\nu$ to be 5 meV, then the tunnelling and thermally activated rates would be equal at about 10 K, in good agreement with our observations.

4. Migration of the self-trapped hole

The hopping rate of the STH was monitored [20] by following the decay of its EPR signal, after UV irradiation of AgCl crystals containing 40 ppm of Pd^{2+} . Much of the dopant was present in association with a cation vacancy; this centre acts as a deep trap for the migrating STH. During the decay period, the concentration of centres formed by the trapping of holes increased (e.g. small amounts of Fe^{2+} impurity were gradually converted to the trigonal Fe^{3+} centre). This

demonstrates that the decrease in concentration of STH was due to their migration and capture at stationary traps, rather than a result of the release of electrons from other centres.

It was found that, with this large concentration of hole traps, the decay followed first-order kinetics reasonably well (presumably, because with a high density of immobile traps and a diffusive hopping of the STH, the holes see, on average, an unchanging distribution of traps). The temperature-dependence of the decay rate showed two very distinct regimes: above 35 K the time constant decreased with increasing temperature according to an Arrhenius relation, while below 30 K, at which temperature it exhibited a maximum, the time constant was almost athermal, and actually decreased slowly with decreasing temperature. These two regions were sharply delineated and are now considered individually.

The decay in the high-temperature regime must be due to phonon-assisted hopping, rather than thermal escape from the self-trapped state, because the trap depth is expected to be significantly greater than the activation energy for hopping [22–24]. The time constant for the decay was found to have an activation energy of 61 ± 3 meV and a pre-exponential factor (for the trap concentration employed) of approximately 10^{-5} s. From the value of the activation energy, one can obtain an estimate of the trap depth for the STH. The short-wavelength acoustical phonons which are presumably involved have values of $(\text{Debye } T)/3$ ranging from 16 to 52 K; hence, a substantial fraction of them are almost classically excited at temperatures of 35 K and above. Then to a good approximation [22–24], the trap depth is twice the hopping activation energy, or about 0.12 eV. It is interesting that this value is very close to the 0.1 eV activation energy for the high-temperature mobility of the photohole in AgBr, a process interpreted by Sumi and Toyozawa [17] as being limited by thermally activated transitions between the free hole and the metastable (in AgBr) self-trapped state. It also agrees with a calculated value [29] of about 0.1 eV for AgCl.

We can obtain a rough estimate of the electron transfer integral from the pre-exponential factor of the time constant. Writing the time constant to be equal to $1/4\pi rND$, where we take the capture radius r of an uncharged trap to be of the order of 10^{-8} cm and the trap density N of order 10^{18} cm³, we obtain a value for D_0 , the diffusivity pre-exponential factor, of about 7×10^{-7} s⁻¹. But this must also equal $\lambda^2 z \nu_0 P/6$, where λ is the jump distance (3×10^{-8} cm), z is the coordination number (=12) and the attempt frequency ν_0 is taken to be 3×10^{12} s⁻¹. The factor P is the probability that the hole executes the hop within one vibrational period if the lattice locally has the necessary thermally excited relaxation. We obtain a very small value for P , 10^{-4} . From Emin [22], and including the fact that there are 12 equivalent jump directions, one obtains a value of the electron transfer integral of about 1% of the relevant phonon energy, or about 0.06 meV, and a bandwidth for the STH states of only about 2 meV. These numbers are underestimated, however, because their calculation ignores the question as to the geometric suitability (for a hop) of the ionic relaxations. Nevertheless, it would seem that their very low values are consistent with our expectation that the STH state is very localized.

The results for the range of temperature below 30 K, where it appears that tunnelling becomes increasingly important, are much less well defined. The STH decay process in this region was then examined in more detail [25] on AgCl:Cu and AgCl:Pd crystals. The experiments proved difficult to interpret because of several factors: (a) the decay kinetics at low temperature, where there is presumably a mixture of hopping and ballistic trajectory, were complex; (b) there was a large variation among the specimens, perhaps because of dislocations introduced by thermal strain of the very soft AgCl, and to which the tunnelling is expected to be sensitive; (c) the range of study could not be extended below 10 K because of a sharp drop in the decay rate, which appears to be the effect of traps a few meV in depth.

Nevertheless, by taking the initial rate of decay (after each irradiation) as a measure of the STH mobility, it was found that the migration rate over the range 10 to 30 K varied as T^{-n} ,

where $n = 1.3 \pm 0.2$. This may be compared with $n = 3.3$ and 2.7 for quantum migration of muonium atoms in two other ionic crystals, KCl [27] and CuCl [28], respectively. This field has recently been reviewed by Storchak and Prokof'ev [26], in which it is argued that any value of n lying between 2 and 7 is consistent with quantum diffusion limited by two-phonon scattering. It is tempting to suggest that our value of 1.3 is lower because the softness of AgCl promotes production of dislocations upon cooling. Clearly, we do not yet see the end of the story.

5. 'Diffusion-limited' decay kinetics

The progress of a chemical reaction, $A + B = C$, taking place in a fluid, is generally described by the standard second-order kinetics equation. This 'works' because for typical chemical reactions the success probability of any given collision is far less than unity; random diffusion can thus maintain a homogeneous mixture of the reactants. As a result, the joint spatial distribution function maintains a constant shape during the reaction, changing only in amplitude.

For diffusion-controlled defect reactions in a solid, however, the success probability in an encounter can be very near to unity, and the population of close A, B pairs becomes preferentially depleted, changing the shape of the joint probability function and causing a deviation from the standard second-order kinetics equation. The resulting behaviour is commonly referred to as 'diffusion-limited kinetics' (a perhaps unfortunate terminology, since even standard second-order processes may be controlled by diffusion).

Although these considerations should be applicable to a great variety of defect interaction processes in solids, there have been very few quantitative demonstrations of the expected deviation from standard kinetics. An early analysis of diffusion-limited kinetics was provided by Waite [30], who obtained a decay equation that is readily applicable to defect reactions, and is subject to experimental verification.

As a test of the validity of the Waite equation, a detailed study [31] was made of the decay of photo-produced STH in AgCl doped with both Cu^{2+} (a source of holes upon irradiation with sub-bandgap light) and Cu^+ (an immobile hole trap). One could argue that the deviation from standard chemical kinetics would be particularly pronounced with low concentrations of the trap: as the diffusion radius of the mobile STH increases (as $(\text{time})^{1/2}$) the incorporation of traps into the diffusion 'sphere' would be more evidently discontinuous. Hence, in these experiments, only a small concentration of Cu^+ , 1–2 ppm, was employed.

Twelve decay runs, over the temperature range 20 to 50 K, were carried out, three in the quantum migration range and nine in the classical phonon-assisted hopping regime. Above 50 K, the decay was too rapid to be monitored by scanning any of the EPR lines.

It was found that although standard second-order kinetics could be made to give approximate fits to the decay curves, there were nevertheless systematic deviations, outside experimental error. On the other hand, Waite's formulation provided excellent fits for all 12 runs, with no systematic deviations and with a set of fitting parameters that took reasonable (although not very sharply defined) values. These results thus appear to constitute a convincing, quantitative demonstration of the validity of Waite's treatment.

One would expect this kinetics to be of widespread occurrence in such solid state phenomena as the aggregation of impurity–vacancy complexes in ionic crystals, which thus far has been discussed only in terms of standard chemical kinetics. One recent appeal to a diffusion-limited treatment, however, is a study of the decay, after pulsed irradiation, of optical absorption and excitonic luminescence in AgCl [32]. It was found that, for temperatures above 80 K, the data could not be fitted by chemical kinetics equations, but could be treated in terms of a diffusion-controlled recombination.

6. Trapping of STH at cation vacancies

An unexpected result of the decay runs described in the previous section was the observation that after annealing out the STHs at 50 K there still remained a small population that was stable up to significantly higher temperatures. Moreover, several earlier authors had suggested that Coulombic attraction between the hole and a cation vacancy might stabilize a bound pair, thereby providing an explanation of various phenomena, such as long-lived photoconductivity and persistent optical and EPR signals (references are cited in [33]).

It therefore seemed desirable to conduct an EPR study that was specifically designed to establish the existence and structure of such a defect in AgCl [33]. Oriented single crystals were doped with approximately 100 ppm of divalent cation, in order to provide an excess of cation vacancies, and also either Cu^{2+} or Fe^{3+} , to serve as a source of holes under sub-bandgap irradiation at 20 K. The irradiation was followed by a series of 10 min anneals at successively higher temperatures; after each anneal, the EPR spectrum was recorded at 20 K.

As a control, one specimen was prepared with only Fe^{3+} , but no significant divalent dopant, present. Since the ferric ion acts as a net vacancy binder, rather than donor (as described in section 2), the concentration of cation vacancies in this crystal must have been unusually low. As might be expected, 20 K irradiation of this crystal produced the EPR spectrum of the STH, but this rapidly disappeared upon annealing at temperatures above 40–50 K. For the other crystals, however, which contained a large concentration of cation vacancies, annealing at 40 K or above converted the original spectrum into a less intense one which was very similar to, but by no means identical to, that of the unperturbed STH. Upon extending the isochronal anneals to higher temperatures, it was found that at 70–80 K there was a further sudden drop of intensity and a further change in the shape of the spectrum (as manifested by changes in the ratios of intensities of some of the lines). This more stable centre then disappears at temperatures of 110–120 K.

The fact that these two ‘high-temperature’ centres have EPR spectra that are only slightly perturbed from that of the STH argues that they must each involve an association of the STH with another defect. Further, it was found that the properties of these centres are independent of which divalent dopant had been used to introduce excess vacancies; hence, the perturbing defect cannot be a dopant ion. Finally, application of the mass-action law to the equilibrium between free and associated vacancies showed that the concentration of these new centres was correlated with the concentration of free, not dopant-bound, vacancies.

It may thus be concluded that these high-temperature centres are two different configurations of an STH bound to a cation vacancy. Further, by fitting computer simulations to the experimental spectra, the configurations could be deduced as follows. When the STH begins to migrate at 40–50 K, it binds to a cation vacancy located at a next-nearest-neighbour position in the equatorial plane of the STH (recall that in AgCl the STH has a [100] axis). At a temperature of 70–80 K, this centre rearranges to a more stable configuration, by a hop of either the hole or the vacancy so that the vacancy, while still in the equatorial plane, is now in a nearest-neighbour position. One can estimate the trap depths of the hole in these two centres from their thermal bleaching temperatures and the approximate value of the trap depth for the unperturbed hole (section 4), obtaining 0.24 and 0.31 eV for the two configurations. It is interesting that Grigorjeva *et al* [32] were able to interpret their excitonic luminescence decay at temperatures above 80 K in terms of these new centres. Also, earlier ODMR studies of AgBr [34] yielded a binding energy for a hole–vacancy complex in this material of 0.30 eV, close to our estimate of 0.31 eV for the more stable centre in AgCl. Unfortunately, although EPR studies were made [33] on double-doped AgBr, similar to those described above for AgCl,

no hole-related spectra were ever seen in AgBr. Perhaps the lifetimes of any such centres in AgBr are too short to be visible in an EPR study.

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