TRANSPORT ATOMIQUE ET THERMODYNAMIQUE DES DÉFautsLATTICE DEFECTS IN IONIC CRYSTALS

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LATTICE DEFECTS IN IONIC CRYSTALS

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1. Introduction. — The object of this review is to set the scene for the conference as a whole, although it must be recognised at the outset that any brief review of such a wide field must be based on a rather personal selection of illustrations. We do not, therefore, claim completeness but only to highlight some of the important areas. The other invited papers provide additional guidance to the subject. As starting points we may take the International Conference on Colour Centres in Ionic Crystals (Reading, England, 1971; unpublished) and the Europhysics Conference on Atomic Transport in Solids and Liquids (Marstrand, Sweden, 1970; [1]), although only a part of this second conference was concerned with ionic crystals. There appear to have been no comparable meetings on dislocations in ionic crystals; thus it was one of the objects of this conference to highlight those aspects of the subject common to dislocations, colour centres and transport and to emphasise the interplay between concepts in these different but related areas (1).

One may divide the interests and material of the present conference into the following areas

(i) Defect States, Structures and Energies,

(ii) Point Defects in or near Thermodynamic Equilibrium,

and (iii) Production of Defects by Irradiation and Radiation Damage Phenomena.

Under (i) we include theory, spectroscopy and new techniques, especially electron microscopy and the study of defect clusters. Under (ii) we include atomic and ionic transport, the solution and precipitation of impurities and space charges at dislocations and interfaces. Lastly, under (iii) we comment upon the production of defects by radiation, the observation of radiation damage and its effect upon mechanical properties. Of course, any such division of the field is somewhat arbitrary and one could find themes running across these sub-divisions. For example, one sees currently a wide extension of interest and understanding to new materials (e.g. the fluorites, CdF₂, KMF₃, etc.) which only a few years ago were very imperfectly understood. We shall, however, use the above division of the subject as being the most fundamental division convenient for this meeting.

2. Defect states, structures and energies. —

2.1 Theory. — There are two parts to the theoretical problem in general:

(i) the calculation of the electronic states for a given defect structure and lattice configuration,
(ii) the evaluation of the response of the lattice to forces exerted on it by the defect, which may be calculated in (i).

For the first of these we need to have a good idea of the principal features of the defect structure in order to limit the calculations to a practicable number of structures, while to evaluate the lattice response we need good physical models of the perfect solid itself. Both calculations are generally quite difficult although in any given situation one may be more so than the other. Thus for the F-centre the most sophisticated part of the effort has up till now largely gone into calculating the electronic states since, with these often rather compact wave-functions, it is a relatively simple matter to handle the lattice relaxation and polarisation. By contrast, in calculations of Schottky or Frenkel formation energies, part (i) is answered by the assumptions of the ionic model so that part (ii) has attracted the most mathematical effort. Although, in general, problems do not divide as sharply as these two examples, it is convenient to order our remarks against these two parts of the problem. For the electronic part we can take Stoneham's review at the Reading Conference as our starting point [4], while for the lattice relaxation calculations the review by Lidiard and Norgett [5] dating from the same time will be found pertinent.

Possibly the most basic question engaging colour centre theorists at present is the description of the low-lying excited states of F-centres and the way these depend upon and couple to lattice relaxation. The states of major interest are (i) the unrelaxed excited state obtained by F-light absorption from the cubic 1s-like ground state and (ii) the relaxed excited state obtained from this by subsequent lattice relaxation, and from which luminescent emission eventually occurs. Experimentally it appears that the 2s-like state lies above the 2p-like state in the unrelaxed configuration while in the relaxed excited state the order is reversed, the 2s-like level lying lower. The problem is to identify the nature of these states more closely and to explain the manner of this cross-over. One significant step taken since the Reading Conference is Ham's demonstration [6] that one can solve exactly a vibronic model suggested by the experimental work on Stark effects in F-centre luminescence, namely (non-degenerate) 2s and 2p electronic states interacting via a coupling to a triply-degenerate $\Gamma_{1v}$ vibrational mode. Explicit results have so far been given only for the strong-coupling limit, but these do show how a crossing of s- and p-like excited states can occur, while other features of the model are also in qualitative agreement with experimental results on the effects of stress and other perturbations on F-centre luminescence.

Calculations on the thermal activation energies for F-centre motion by Brown and Vail [7] broke new ground and have recently been extended to the discussion of the motion of F$_{\alpha}$-centres and to the stability of the « saddle-point » configuration of the type II F$_{\alpha}$-centres in their relaxed excited state [8]. Although the agreement with experiment is qualitative rather than quantitative these calculations must be regarded as a successful first attack on a group of rather complex colour centre problems. It is to be hoped that they will encourage others to tackle other complicated centres containing foreign ions, e. g. Z-centres.

Trapped hole centres were reviewed by Itoh at the Reading Conference in both their experimental and theoretical aspects [9]. On the theoretical side, the description of these centres (V$_{\alpha}$, H, V$_{\beta}$, etc.) as halogen molecule-ions $X^-$ embedded in a crystal lattice appears to work well on the whole, although a rigorous description of the remaining small covalent interactions with the ions of the lattice has yet to be provided.

As already noted, the evaluation of the lattice relaxation caused by the presence of a centre is often rather simple, e. g. for the ground states of F-centres and their aggregates. But this is also often far from being a good or allowable approximation, as in the case of defects bearing a net electric charge or having large elastic misfit (e. g. interstitials). For these defects there are various methods in use [4], [5], most notably (i) the Kanzaki Fourier transformation method (*), (ii) the Green's function method of Tewary and (iii) generalised Mott-Littleton methods. All three are in principle general methods but all detailed applications of the first two have so far involved particular assumptions about the symmetry of the defect, although the formulation by Stoneham and Bartram [59] allows the description of symmetry lowering via the Jahn-Teller effect. An important development of the last year or two is the production by Norgett of a general computer program « package » based on the third method (« HADES ») which is able to handle a wide variety of defects and models. It has so far been used notably for (i) rare gas impurities [5], [10], (ii) Schottky and Frenkel defects [5], [11], (iii) defect clusters [12] and (iv) V$_{\alpha}$-centres [13]. Its considerable value comes from its ability to handle accurately and economically very low symmetry defects and it can do this because it employs very efficient energy minimisation procedures (« variable metric » methods). An example illustrating this comes from the use made of it by Catlow [12] who shows how it allows us to understand the rather unusual interstitial structures seen in neutron diffraction studies of fluorite compounds. One broad conclusion coming out of this work is the readiness of anions in this structure to relax in $<111>$ directions towards the centres of the empty anion cubes ;

(*) Sometimes called the method of lattice statics though this title has really a wider meaning.
this can easily lower the symmetry of defects below one's immediate naive expectation.

Just as these point defect calculations have given considerable insight into structures and processes, so we should expect similar calculations for dislocations to be equally valuable, e.g. in answering some of the questions raised in Whitworth's review [14] (core structure, jog energies, dislocation-impurity interaction, etc.). Here the recent work of Granzer et al. [15] should be particularly mentioned, while the development of a flexible program package for dislocations by Norgett et al. [16] should also be noted. Since the models used by the two groups are different, it will be interesting to compare the sensitivity of the predictions of dislocation properties to variations in the assumed physical model. Point defects work has confirmed what has been known for some time in lattice dynamics, namely that polarisable point-ion models are bad and that it is necessary to include explicitly the dependence of the Born-Mayer overlap forces upon the state of polarisation of the ions and vice versa, as is done in shell models. Recent work [10], [11] also shows how one can (and sometimes must) get away from purely empirical analyses of interatomic forces (such as those of Fumi and Tosi [17] by including information from quantum mechanical calculations of greater or lesser sophistication [18]. In general, now that the accurate prediction of the response of any given lattice model is feasible, greater attention will inevitably shift towards the determination of better physical models.

In concluding this section on the theory of defect structures, attention should be drawn to related calculations on planar defects [19], [20]. The work by Stoneham and Durham [20] is a discussion of the interesting phenomenon of the ordering of shear planes which occurs in many non-stoichiometric oxides and which has been of considerable interest to solid state chemists. It brings out clearly that, because the ordering results from elastic interactions, this phenomenon is analogous to some other macroscopic ordering phenomena, e.g. void lattice formation and the formation of interstitial solute superlattices in certain bcc metals [21]. Figure 1 shows an example of the void lattice seen in irradiated Mo. Although void formation is currently of major interest only in metals, there is no fundamental reason why voids should not also be seen in other materials, including ionic crystals, wherever a mechanism exists for producing a steady state excess of vacancy over interstitial defects [22].

2.2 EXPERIMENT. — The greater part of the experimental material bearing directly on defect states and structure presented at this conference is spectroscopic in nature and exploits the well-tried techniques of optical and microwave spectroscopy.

We have already mentioned in section 2.1 the interest in the nature of the relaxed excited state of the F-centre. At the Reading Conference Mollenauer and Baldacchini presented data on the ENDOR spectrum of this state in KI [23], although unfortunately there are no theoretical predictions with which to compare their results for this material. At the present conference they present similar results on KBr, giving clear proof of the diffuse nature of the relaxed excited state in this material too, in agreement with some theoretical predictions. These experiments do not in themselves tell us whether the state is mainly 2s-like or 2p-like.

In this spectroscopic field there are also a number of interesting contributions on Z-centres (i.e. those colour centres in alkali halides involving divalent cation impurities), particularly the so-called Z1 and Z3 centres. The interest in these goes back to the early days of colour centre physics, but although the Z1-centre has been well established [24] as an associate of an F-centre with an impurity-cation vacancy pair the structure of the Z3-centre remains uncertain. This centre can be produced by purely thermal conversion in the dark and appears quite definitely to be a two-electron centre [25], despite earlier work [26] on the thermal partition between F- and Z3-centres which appeared to show that it could only involve one F-centre (Fig. 2). Perhaps this work should be repeated in order to establish the consistency (or otherwise) with the two electron models.

Another area in which divalent cations are important is in the thermoluminescence of LiF : Mg$^{2+}$ and especially dosimeter grade LiF : Mg$^{2+}$. The
For all defects the macroscopic volume change caused by a random distribution of molar fraction \( c \) in a cubic crystal is

\[
\frac{\Delta V}{V} = \frac{c}{3V_e} \kappa \operatorname{Tr} P
\]

(3)

where \( \kappa \) is the compressibility of the crystal and \( V_e \) is the cell volume. Techniques for measuring \( P_{ij} \) have been developed particularly at several centres in Germany and at the present Conference Balzer et al. [30] show how \( P_{ij} \) for H- and V\(_c\)-centres are obtainable from macroscopic dimension changes when the defects are aligned optically. These and other results bearing on \( P_{ij} \) should be of direct interest to theoreticians in view of their close relation to the forces on the atoms around the defect and thus to the basic potential models used (eq. (1)). One can point to current conflicts between theory and experiment here. First, the inference that the interstitial anion is a tetragonal centre [31] is difficult to understand even though explicit calculations have only been made for cubic and trigonal configurations [32]. Secondly, the inferred net outwards relaxation around anion vacancies [31] appears to conflict with the long-range nature of the electrostatic forces exerted by such a defect on the ionic lattice [33].

One of the most important recent experimental developments I believe is the elegant work of Hobbs et al. [34] on the application of electron microscopy to the study of radiation damage in alkali halides, made possible by their development of the liquid helium stage. Although electron microscopy has played a major role in the study of lattice defects and radiation damage in metals and other materials, its application to the alkali halides has been effectively prevented by the very highly damaging effect of the electron beam on these materials arising, of course, from their sensitivity to ionisation. The liquid helium stage not only significantly reduces damage rates in some halides but, more importantly, it so inhibits interstitial mobility that the point defects produced do not aggregate in the times needed to make good electron microscope observations. These studies of the structure and formation of dislocation loops in irradiated alkali halides are likely to have a substantial impact on many parts of the subject (e. g. interstitial aggregation, effect of irradiation on mechanical properties, etc.). One of the surprising results is the observation that the dislocation loops formed by defect aggregation at both room temperature and very low temperatures are perfect interstitial loops (Fig. 3), even though all the defects produced by ionisation are produced in the anion sublattice. It simply does not seem possible to account for the observed absence of stacking faults in these loops on the basis of anion interstitials alone. The authors have thus proposed a mechanism of loop growth in which cations also join the extra half-plane in such a way that the resultant effect is the growth of the loop...
The suggestion therefore seems both necessary to explain the electron microscope observations and to be energetically feasible. It should be of considerable interest to both theory and experiment as providing another «molecule-like» colour centre, the identification of which would do much to confirm the suggested process.

3. Point defects in or near thermodynamic equilibrium. — The study of point defects in or near thermodynamic equilibrium ranges widely and includes:

(i) atomic and ionic transport, e.g. ionic conductivity, self- and impurity-diffusion, motional effects in nuclear magnetic resonance, etc.,

(ii) relaxation phenomena associated with thermally activated reorientation of complex defects, e.g. dielectric and inelastic relaxation of impurity-defect pairs,

(iii) the solution and dissolution of impurities,

(iv) space charges at dislocations and interfaces, important for charged dislocations, the photographic process, ionic thermopower, etc.

All these aspects are represented at the present conference. This area of study has made considerable progress over the years on the basis of rather simple ideas of defect structure, often only the basic geometrical features of co-ordination and symmetry being required. As we turn to more complex materials, however, these simple models may need modification, especially when paired or clustered defects are involved, e.g. in \( \text{UO}_2 \) or \( Y^{3+} \)-doped alkaline earth fluorides and in \( \text{Fe}^{2-1} \_\text{O} \).

3.1 Transport. — Basic transport properties such as ionic conductivity, self- and impurity-diffusion depend on products of defect mobility with defect concentration or, more generally, with some function of defect concentration. Defect mobilities and jump rates are largely intrinsic properties of the defect, rather little influenced by interactions at long range and sometimes even surprisingly little affected by the presence of another defect close by \(^*\). Mostly, defect jump rates are represented by an Arrhenius formula

\[
\nu = \nu_0 \exp\left(-\frac{\Delta g}{kT}\right)
\]

where \( \Delta g \) is the free energy barrier between the neighbouring sites available to the defect. Such a formula follows from a generalised rate theory based on classical statistical mechanics; it would thus be expected to hold at high temperatures \( T \gg T_0 \) where the distributions of atomic positions and velocities conform to classical statistical mechanics. A number of examples exist where \( \nu \) has been observed

\(^*\) Compare e.g. the jump frequencies of free cation vacancies in alkali halides with those of cation vacancies moving around divalent cation impurities in the first co-ordination shell \([35]\).
to conform to (4) over a wide range of temperature. The present conference heard again, however, of the inconsistency of the high- and low-temperature data on anion vacancy migration rates with (4), a problem first raised by the measurements of Hartel and Lüty [37] several years ago (Fig. 4). It is perhaps still not absolutely clear whether the circumstances of the anion vacancy migration observed in these low-temperature colour centre conversion experiments are such that the inferred mobilities should correspond exactly with those obtained by analysis of the high temperature transport measurements. But if not, a quantitative explanation which preserves the agreement with (4) has still to be provided.

In this connection, we should recall that we do not expect (4) necessarily to hold in the region of the Debye temperature and below; and very many defect jump processes do of course take place in this low-temperature region. Despite some initial attempts, a satisfactory quantum theory of barrier-limited motion is still lacking. A satisfactory quantum theory of small polaron hopping does, however, exist and this formalism has been applied to $V_T$-centre motion and to the motion of light interstitial impurities in bcc metals [38]; in these cases the hindrance to motion is the energy of self-localisation of the particle (electron hole, interstitial hydrogen, etc.) and not the existence of a large potential energy barrier between initial and final sites. Figure 5 shows the dependence of jump rate upon temperature for hydrogen in bcc Ta; this is one well substantiated case of quantum diffusion.

So far we have said nothing about defect concentrations except to note the dependence of macroscopic transport coefficients upon them. This functional dependence is mostly direct as, for example, in ionic conductivity, self-diffusion and diffusion of substitutional impurities by means of vacancies: the greater the appropriate defect concentration the larger the macroscopic coefficient. In the case of interstitial solutes, however, vacancies can act as traps, so that the relation of diffusion coefficient to vacancy concentration is inverse in this case; the most important systems of recent interest showing this behaviour are rare gas impurities in ionic solids [39]. In all cases, however, the concentrations of defects in thermodynamic equilibrium are strongly dependent on purity through (i) the existence of Schottky and Frenkel product relations between the concentrations of conjugate defects and (ii) the electroneutrality requirement imposed everywhere except in the immediate vicinity of sources and sinks of defects by the long-range and strength of Coulomb forces between defects carrying net charges. This, predictable, dependence on purity allows one to separate out the different contributions to diffusion, conductivity, etc., by deliberate doping; elegant examples of the utility of this technique in the present conference will be found in the contributions by Bénieré [40], by Félix [39] and a number of others.

3.2 Statistical mechanics. — To proceed from the basic knowledge of defect and atomic mobilities and concentrations to observable macroscopic quantities requires a kinetic theory. This has been reviewed...
in detail in recent years [41]-[43]. It may be noted, however, that the correspondence of these treatments with the generalised phenomenological flux equations of the type used in the thermodynamics of irreversible processes has not yet been fully worked out, despite the useful insights which this can bring. This approach can be especially useful when diffusion involves the interplay of solute and defects and the defect population is separately affected; examples are provided by Fredericks’ work on double doping [44] and by the effect of surfaces on defect population and consequently upon solute behaviour [45], [46].

One of the important tests of these kinetic theories provided by ionic crystals is through the ratio of ion mobility to diffusion coefficient, $\lambda_i/D$, which in general is not given by the simple Nernst-Einstein value $q/kT$ (where $q$ is the ion charge). The departure of $\lambda_i/D$ from $q/kT$ depends on the mechanism of transport and has been calculated for the commonly studied lattices and defect mechanisms [43]. A particularly satisfying comparison of this sort obtained from the work of Corish and Jacobs [47] is shown in figure 6. This shows Ag self-diffusion coefficients in AgCl (i) calculated from an analysis of the ionic conductivity of a single specimen of AgCl. (After Corish and Jacobs [47].)

![Fig. 6. — An Arrhenius plot of the self-diffusion coefficient of Ag in AgCl. The solid circles (●) are experimental points of Weber and Friauf [57] and the open circles (○) are those of Reade and Martin [58]. The solid line is a theoretical line calculated using parameters obtained by analysis of the ionic conductivity of a single specimen of AgCl. (After Corish and Jacobs [47].)](image)

by an application of the Bjerrum-Fuoss theory of liquid electrolyte solutions, i.e. one separates out the neutral defect pairs and then treats the long-range Coulomb interactions among the defects bearing net charges by Debye-Hückel theory. This appears to work well in practice but it is intuitive in formulation. Allnatt et al. [48] have recently developed more fundamental analyses based on cluster expansion methods: this shows when one may expect the simpler analysis to be accurate and when one should expect to find departures from it.

From the point of view of statistical thermodynamics, defect complexes are merely part of the distribution function. But they are generally strongly bound and remain together for many jump-times of the component defects so that they have a separate physical identity as we see in many phenomena, e.g., $Z_1$-centre formation, impurity diffusion, dielectric relaxation, etc. Knowledge of impurity complexes built up in this way provides the basis for understanding the kinetics of impurity aggregation and precipitation.

3.3 SURFACES AND DISLOCATIONS. — We have already remarked that the requirement of overall electroneutrality imposed on the concentrations of defects in the bulk does not hold near to sources and sinks of defects [49]. In these regions a space charge exists as a result of the generally different energies of formation of defects of opposite sign. The thickness of these regions, the Debye screening length, is very simply related to the defect concentrations: it is

$$\lambda_D \equiv \kappa^{-1} = \left( \frac{4 \pi \sum n_i q_i^2}{\varepsilon_0 kT} \right)^{-1/2}$$

where $n_i$ is the number concentration of defect $i$ bearing net charge $q_i$ and $\varepsilon_0$ in the static dielectric
constant. Some typical results are shown in figure 8. These ideas have been used to provide theories of space charges at surfaces and at dislocations, generally assuming that these can act as infinite sources and sinks, i.e. that there are effectively no limitations associated with jog formation (on dislocations) or step formation (on surfaces). Surface space charges contribute to the thermolectric power of ionic crystals [50] and there appear to be no limitations on the infinite sink model here. An important prediction of the infinite sink models is the existence of an isolectric temperature, $T_{\text{iso}}$, where the space charge vanishes; this depends directly on the presence of aliovalent impurities and the sign of the charge cloud is different above and below $T_{\text{iso}}$. This is an important prediction of the model and one confirmed in a number of experiments. However, an infinite sink model is certainly a simplification and the consequences of making more realistic assumptions are described notably in Whitworth's review [14]. There is a need to extend the precision of experiments which can give information about isoelectric points. On the theoretical side, we need to know more about the interactions of point defects and dislocations in these materials. Little has been done here apart from the early calculations of Bassani and Thompson [51]. Developments such as those now being made by Granzer, Norgett and co-workers should, in due course, be capable of making the necessary predictions.

4. Production of defects by irradiation. — So far we have discussed defects in alkali halides and other ionic crystals together, since the principles governing their properties are the same. When we come to their production by irradiation, then the singular nature of the alkali halides sets them apart, however. This sensitivity of the alkali halides to ionisation to give halogen interstitials and vacancies as the primary defects, is still incompletely understood. The basic idea of the Pooley-Hersh mechanism provides a phenomenological explanation of a number of important facts. This mechanism postulates the production of the primary defects as the result of an $<110>$ replacement collision sequence along a row of anions following upon the radiationless recombination of an electron with a $V_{\text{e}}$-centre (self-trapped hole). It provides a model showing how atomic displacements arise in the anion sublattice as a result of ionisation (electron and hole ($V_{\text{e}}$) production) and explains the different temperature dependence of damage production in the different materials and the effect of electron trapping impurities (e.g. Pb) in reducing damage rates. Also, at the present conference, Townsend provided an explanation of the so-called Rabin-Klick diagram for the efficiency of $F$-centre production on the basis of this mechanism. However, there are some important difficulties. Firstly, actual calculations of the minimum energy necessary for the propagation of a $<110>$ replacement collision sequence in the anion sub-lattice gave values several times higher than the maximum available from electron-$V_{\text{e}}$ recombination. Secondly, the very beautiful fast pulse (~nanosecond) irradiation experiments show that the primary products are not anion vacancies and anion interstitials, as in the Pooley model, but instead are principally $F$-centres and $H$-centres [52]. At the present conference, Itoh and Saidoh [53] suggest a means by which the replacement sequence can carry the hole along with it, so that the end product is an $H$-centre with an $F$-centre remaining at the site of the original $V_{\text{e}}$-centre. In this proposal, actual electron-$V_{\text{e}}$ recombination does not occur. It will be very interesting to see if this proposal can be made quantitative.

Turning now to secondary processes, we have already commented on the importance of the direct observation of clusters of interstitial defects by Hobbs et al. [34]. The consequences for the understanding of the effect of radiation on mechanical properties are further described at the present conference by Hobbs and Howett. In particular, it is very interesting to see the explanation of previously reported dependence of flow stress on $F$-centre density in terms of the observed morphology of the loops. This dependence, seen as $[F]^{1/2}$ in some materials and $[F]^{1/4}$ in others, differs according to whether the loops are round and circular as in KI or whether they are elongated (i.e. effectively linear defects) as in some other alkali halides.

5. Conclusion. — In this brief introductory review, we have touched on a number of important topics — though by no means all — in the study of lattice defects in ionic crystals. The interaction between
the different parts of this study is real and fruitful and will undoubtedly become more so as fundamental understanding of defect structure, production, mobilities and mutual interactions extends. The stimulus provided by new theoretical techniques (e.g. the computer simulation of defect structure) and new experimental techniques (e.g. fast-pulse irradiations, low temperature electron microscopy) show that this study remains an exciting area of fundamental solid state physics.

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DISCUSSION

R. V. HESKETH. — Would you regard a curved Arrhenius plot for self diffusion as a symptom of quantum effects, quite generally?

A. B. LIDIARD. — No, not generally since there are many well understood effects which can lead to greater or lesser curvature in Arrhenius plots. My object in showing the results for H diffusion in bcc...