COLOUR CENTRES IN ALKALI HALIDE CRYSTALS

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1. Introduction

A REMARKABLE wealth of information of interest and significance extending well beyond the field of solid-state physics has recently been forthcoming from studies of the spectrophotometric and magnetic properties of colour centres in ionic crystals.

It is our aim here to describe and discuss the simplest of these systems, namely, additively coloured alkali halide crystals, and to give some indication of the situation in other systems. Our treatment will be brief and selective. The reviews by Seitz[1,2] are outstanding and exhaustive: other major works dealing with specific aspects will be referred to when appropriate.

In general, colour centres are found whenever a new species is incorporated into the alkali halide crystal to give what may be described, crudely, as a solid solution. However, the geometry of the crystal imposes severe limitations on the size, shape, and charge of the solutes.

We can distinguish two classes of "solutes": (*a*) Those which are derived from the cations or anions of the host crystal (sections 2 and 3), and (*b*) those which are unrelated to the host crystal (section 4). Alkali halide crystals have two great advantages as host crystals: they are transparent from the far infrared to the far ultraviolet region (about 2000 Å) where the fundamental absorption of the crystal begins. In addition, the simplicity of the lattice geometry and the nearly complete ionic character of the bonding greatly simplify the interpretation.

When considering colour centres of class (*a*), it is convenient to describe those which are derived by addition of metal as electron-excess centres and those derived from halogen as electron-deficit centres. Experimentally, these can be formed separately, by treating the crystal with metal or halogen vapour, or together, by exposure to high-energy radiation. Since such exposure can be carried out at low temperature, several spectral features occur which are lost on warming and are not formed by the addition procedures. Additions give rise to relatively simple spectra and will be considered in the greater detail.

The situation can be pictured in a simple way by considering what chemical reactions are to be expected for alkali-metal and halogen atoms in a fluid medium and then how they are likely to be modified by the crystal lattice.

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[1] Seitz, *Rev. Mod. Phys.*, 1946, **18**, 384.

[2] Seitz, *Rev. Mod. Phys.*, 1954, **26**, 7.

Alkali-metal atoms have one overriding tendency, namely, to donate electrons to any available acceptor. In the absence of an acceptor they may dimerise, but this bonding is very weak and at room temperature condensation to metal will normally occur. In contrast, halogen atoms, besides being powerful electron-acceptors, can dimerise to give relatively stable molecules. In the presence of halide ions an equilibrium involving trihalide ions would be established:

$$\mathrm{Hal}_2 + \mathrm{Hal}^- \rightleftharpoons \mathrm{Hal}_3^- \quad . \ . \ . \ . \ (1)$$

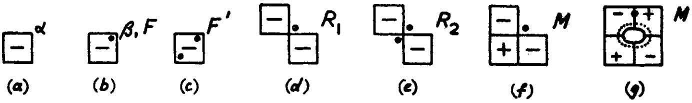
If the concentration of halide ions is large compared with that of halide atoms, dihalide radical-ions can be formed:

$$\mathrm{Hal}\cdot + \mathrm{Hal}^- \rightleftharpoons \mathrm{Hal}_2^- \quad . \ . \ . \ . \ (2)$$

The bonding must be weak, but there is evidence that these radical-ions are important intermediates in the flash photolysis of halide ions in water.[3]

Within the lattice, in the absence of impurities, the simplest electron-acceptors are anion vacancies, which have an effective positive charge centred on the vacancy. It can be shown theoretically that alkali-metal atoms cannot exist as such in an undistorted lattice site and therefore they must be trapped interstitially, combine to form metallic units, or ionise in such a way that the electrons are trapped in anion vacancies and the resulting cations occupy cation vacancies. An electron in an anion vacancy, termed an *F*-centre, is the simplest electron-excess centre [Fig. 1 (*b*)].

FIG. 1. *Models for electron-excess centres.*



⊟ and ⊞ *represent anion and cation vacancies.* ⊟ *represents an electron in an anion vacancy.* (*f*) *and* (*g*) *are alternative models for the M-centre.*

Other varieties of electron-excess centres formed by combination of electrons and vacancies are discussed in section 2.

Similarly, a halogen atom in an alkali halide crystal cannot exist at a regular lattice point. An interstitial atom would probably combine with a neighbouring ion to form a dihalide anion or migrate to a more stable site. If spatial requirements are satisfied, formation of molecular halogen and trihalide negative ions would be expected. However, it is commonly supposed that the most fundamental and simplest of electron-deficit centres would be the antimorph of an *F*-centre, that is, a system of similar configuration but with a reversal of sign. Such a unit, termed a V_1 centre by Seitz[1,2] and symbolised in Fig. 2 (*a*), consists of a cation vacancy and a "hole", symmetrically distributed around the vacancy. That is to say that,

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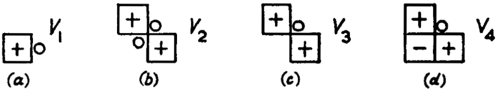
[3] Grossweiner and Matheson, *J. Phys. Chem.*, 1957, **61**, 1089.

at any given instant, one could picture one halogen atom and five halide ions around the cation vacancy, but that, on average, all the six surrounding halide ions share the "hole" created by the absence of an electron, and hence the unit has spherical symmetry.

FIG. 2. *Models for electron-deficit centres* (*after Seitz*[2]).



o *represents the absence of an electron from one of the halide ions surrounding the vacancy.*

Since the spectra of several of these electron-deficit units, such as the trihalide ions, are known, they can be compared with the bands observed in additively coloured crystals. These bands, found in the near-ultraviolet region, and generally described as *V*-bands, are discussed in section 3.

2. Electron-excess centres

Alkali halide crystals prepared with a stoicheiometric excess of alkali-metal either by heating them in the presence of the metal vapour[4] or by electrolysis just below the melting point[5] may exhibit a variety of optical absorption bands. In general these electron-excess bands occur in the lower-energy half of the region of transparency of the host crystal. The particular type of coloration observed depends in detail upon the optical and thermal treatment to which the crystal is subjected after introduction of the metal. Although a large variety of such colour centres exists they may be conveniently grouped according to their mode of formation in additively coloured crystals.

The F-Centre.—When a crystal is heated in the presence of alkali-metal vapour and then quenched rapidly, a single narrow absorption band, the *F*-band, is found. The excess of alkali-metal ions is incorporated in the crystal and causes the formation of cation vacancies, in which, according to de Boer's model of the *F*-centre, the excess of electrons is trapped.[2] This vacancy model which has been generally accepted for some time, has now been established beyond reasonable doubt by the results obtained from magnetic resonance studies. In view of these results, which are discussed briefly below, there seems little point in considering alternative models for the *F*-centre, such as those discussed by Seitz.[2] Detailed wave functions, all based on the vacancy model, have been presented, and recent experimental studies have been designed to give results which probe the suitability of these treatments. We will mention some of the most significant properties of *F*-centres and then give a brief resume of the basic features of the

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[4] Rogener, *Ann. Phys.*, 1937, **29**, 386.
[5] Heiland, *Z. Physik.*, 1950, **127**, 530.

mathematical treatments. For details the reader is referred to a comprehensive and critical treatise by Gourary and Adrian,[6] and to a review by Dexter[7] in which the optical properties are discussed in detail. One of the most interesting features of the *F*-bands in alkali halides is that the wavelengths of the band maxima are a simple function of the nearest-neighbour distance *a*. Ivey[8] has given an empirical equation for the wavelength, $\lambda_{\text{max.}}$ (Å) $= 703a^{1 \cdot 84}$, which reproduces the experimental data within 7%. It is noteworthy that the electron-affinity of the cations does not seem to be an important parameter, and any theoretical treatment should reproduce this dependence upon the nearest-neighbour distance.

Another important yardstick against which wave functions for the *F*-centre must be judged is the wealth of detailed information obtained from the application of electron-spin resonance[9,10,11,12] and electron-nuclear double resonance techniques.[13] When crystals containing *F*-centres are placed in an intense magnetic field the two-fold degeneracy of the electron spin is removed and transitions between these levels can be induced by suitable irradiation with microwave energy. The resulting absorption curve is generally broadened or split into components (described as hyperfine structure) by interactions with the magnetic moments of the surrounding nuclei. It is this hyperfine structure which provides the most useful information since one can deduce from the number of lines and their relative intensities the number of equivalent nuclei interacting, and it is generally a simple matter to identify the nuclei involved. At the same time the separation of individual lines derived from a given nucleus is a function of the time the unpaired electron spends near that nucleus and hence a very detailed picture of the electron distribution can be built up. The results show that the unpaired-electron density is quite high on the six cations which define the vacancy. Somewhat surprisingly, it is also appreciable on the first shell of anions, although it is only just detectable on the second shell of cations.

Early wave-functions for the *F*-centre were calculated on the assumption that the crystal could be treated as a polarisable continuum, the ionic nature of the lattice and the characteristic periodic potential being largely ignored. This approximation can be correct only if both the ground and the first excited state are diffusely spread over many ions in the vicinity of the vacancy. In fact the simple models based on this approximation prove to be inconsistent since the resulting wave functions are far too compact for the continuum model to be a valid approximation, and hence this simplification must be rejected.[6] Indeed, the results of electron-spin

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[6] Gourary and Adrian, *Solid State Physics*, in the press.
[7] Dexter, *Solid State Physics*, 1958, **6**, 353.
[8] Ivey, *Phys. Rev.*, 1947, **72**, 341.
[9] Hutchinson, *ibid.*, 1949, **75**, 1769.
[10] Schneider and England, *Physica*, 1951, **17**, 221.
[11] Kahn, Kittel, Levy, and Portis, *Phys. Rev.*, 1953, **91**, 1066.
[12] Lord, *Phys. Rev. Letters*, 1958, **1**, 170.
[13] Feher, *Phys. Rev.*, 1957, **105**, 1122.

resonance show conclusively that the electron is closely confined to the vacancy and the first cation and anion shells; this volume is far too small to justify a continuum model.

The other extreme would be to use an infinitely deep square-well model, with a radius equal or close to the interionic distance. However, a better approximation is to use a well of finite depth with a constant potential inside it and a coulombic potential outside it. This semi-continuum theory has been greatly refined by various workers and is discussed in detail by Gourary and Adrian.[6] These more refined calculations give good agreement with experiment when applied to the calculation of the energies and intensities of the *F*-bands, and reasonable values for the hyperfine interactions can also be obtained, provided one includes the reasonable extension that, when close to an ion, the electron behaves like an *s*-electron in the outermost shell of that ion.

The linear combination of atomic orbitals (LCAO) molecular-orbital approximation has also been used to describe the cavity model of *F*-centres, and was particularly important in the development of the underlying theory of electron-spin resonance in *F*-centres.[11] However, by far the most satisfactory and versatile approximation for the *F*-centre is the "point-ion-lattice" approximation of Gourary and Adrian.[6,14] These authors have compared their treatment with the continuum and the molecular-orbital approximation in their review,[6] and have extended it to cover other electron-excess centres. Agreement with experiment is good, both for the energies of the *F*-bands and for the hyperfine splitting constants and other data derived from electron-spin resonance spectroscopy. The model uses the Hartree–Fock approximation in which the dipoles induced by the *F*-electron on the surrounding ions point to the centre of the vacancy rather than following the detailed motion of the electron.

In view of the success of these calculations, the following conclusions can be drawn with some confidence: (*a*) the *F*-electrons are to be found largely within the vacancy, and hence (*b*) polarisation of the surrounding ions is small, since the trapped electron will largely cancel the effect of the missing anion; (*c*) displacement of the ions surrounding an *F*-centre from the normal lattice position is small; (*d*) the electronic transition which gives rise to the *F*-band may be described as $p \leftarrow s$ to a first approximation, and even in the excited *p*-state the electron is closely confined to the vacancy.

Although the vacancy model satisfactorily accommodated most of the properties of the *F*-centre, until recently there was one notable exception. It can readily be shown that *F*-centres should luminesce on excitation, with high quantum efficiency at low temperature.[15,16] However, all evidence pointed to the contrary until, in 1954, Botden, van Doorn, and Haven[17]

[14] Gourary and Adrian, *Phys. Rev.*, 1957, **105**, 1180.
[15] Huang and Rhys, *Proc. Roy. Soc.*, 1950, **204**, *A*, 406.
[16] Pekar, *J. Exp. Theor. Phys.* (*U.S.S.R.*), 1952, **22**, 641.
[17] Botden, van Doorn, and Haven, *Philips Res. Reports*, 1954, **9**, 469.

published results which showed that the predicted luminescence was readily detected if crystals were used which contained only *F*-centres, and that the quantum efficiency was indeed high under these circumstances.[18] When there is appreciable aggregation the excitation energy is apparently dispersed by other processes involving these aggregate centres, and it was for this reason that luminescence from *F*-centres proved so hard to detect. This aspect is discussed in more detail in the section on aggregate centres.

F′-, α-, and β-Bands.—The *F*-band is always accompanied by a narrow band, β, in the ultraviolet region close to the long-wavelength edge of the first fundamental band of the crystal.[19] The band is therefore assigned to a transition involving the anions surrounding the *F*-centre. If the *F*-band is bleached by radiation of somewhat higher energy than the *F*-band maximum, the β-band is also bleached, and a new band, α, is found on the long-wavelength side of the β-band. Simultaneously a broad band, labelled *F′*, grows on the low-energy side of the narrow *F*-band. Since there is a decrease in paramagnetism as the *F*-band is bleached, and since quantum-efficiency measurements show that, in favourable circumstances, two *F*-centres are destroyed for every quantum absorbed,[20] the effect of irradiation seems to involve the ejection of one *F*-electron from its anion vacancy trap and its capture by another *F*-centre. The *F′*-centre is thus two electrons with paired spins, trapped at a single anion vacancy. The α-band is then due to the excitation of electrons on those anions which surround an anion vacancy, whilst the β-band is a similar transition when the vacancies contain *F*-electrons. These transitions may be similar in nature to that for anions in normal lattice sites, or they may be caused by electron-transfer from an anion into the vacancy to give, momentarily, an *F*-centre (α-band) or an *F′*-centre (β-band).

Aggregate Centres: R, M, N.—When light is absorbed within the *F*-band at room temperature numerous new absorption bands may be formed on the long-wavelength side of the *F*-band;[21] Seitz has suggested that the new bands are due to electrons trapped at aggregates of vacancies.[1,2] The criterion of simplicity, together with a consideration of possible formation mechanisms, led Seitz to suggest specific models for these centres (Fig. 1). The R_1 model is an electron trapped at a pair of adjacent anion vacancies, the R_2 model is two electrons trapped at a similar vacancy pair. Thus the models correspond to F_2^+- and F_2-centres. That is, if one compares the *F*-centre with a hydrogen atom, then the R_1 and the R_2 model are analogues of the hydrogen molecule ion and the hydrogen molecule respectively. Seitz's model for an *M*-centre is an electron trapped at a cluster of two anion vacancies and one cation vacancy. All of these centres have lower than cubic symmetry [Fig. 1 (*d*, *e*, and *f*)]. It should be emphasised that

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[18] van Doorn, *Philips Res. Reports*, 1958, **13**, 296.
[19] Delbecq, Pringsheim, and Yuster, *J. Chem. Phys.*, 1951, **19**, 574; 1952, **20**, 746.
[20] Pick, *Ann. Physik.*, 1938, **31**, 365.
[21] Petroff, *Z. Physik.*, 1950, **127**, 443.

there is still no convincing evidence that they are correct. However, most of the available evidence is consistent with these models.

Much of the data relating to aggregate centres is still based upon plausible formation mechanisms. An example of such arguments may be mentioned. The aggregate centres are not produced simultaneously.[21] The M-band appears first, followed by R_2. The rate of production of R_2-centres is proportional to the concentration of M-centres. Cole and Friauf[22] explain this genetic relation, using Seitz's models, as due to capture of an electron by an M-centre followed by the ejection of a positive ion vacancy.

This sort of reasoning can hardly be taken as establishing the models. More direct evidence on aggregate centres is obtained from symmetry studies. Ueta[23] has shown that polarised light absorbed in the M-band leads to dichroism, thus establishing that the M-centre has lower than cubic symmetry, in qualitative agreement with Seitz's model. Corroboration of this symmetry is obtained from measurements of the polarisation of luminescence excited by polarised light.[24,25]

The problem is complicated by evidence, presented below, that centres which are close together, but not adjacent, can interact strongly.[26] Some, at least, of the asymmetry detected by polarisation studies could be caused by such interaction between centres which in isolation might have cubic symmetry. Another experimental result which gives information about the symmetry of M-centres is the observation by Overhauser and Rüchardt[27] that no linear Stark effect could be detected in the M-band. One can conclude from this negative result that M-centres should have inversion symmetry, a conclusion which conflicts with Seitz's model. Knox[28] has suggested a modified model which, whilst being in accord with all other information relating to M-centres, also possesses inversion symmetry. This model can also be used to explain the otherwise puzzling absence of a dielectric loss peak.[29] Knox assumes that this configuration, shown in Fig. 1 (*g*), may actually be stabilised by lattice relaxation. Such a configuration may be thought of as a neutral alkali atom strongly distorted by the surrounding lattice. Since the composition of the M-centre in both Knox's and Seitz's models is the same, no reappraisal of formation and bleaching experiments is necessary. It should be possible to distinguish easily between the two configurations by using the new electron-spin double resonance methods[13] because of the difference in symmetry. Moreover, one would expect a considerable hyperfine splitting due to the central nucleus for Knox's model. Conventional electron-spin resonance

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[22] Cole and Friauf, *Phys. Rev.*, 1957, **105**, 1464.
[23] Ueta, *J. Phys. Soc. Japan*, 1952, **7**, 107.
[24] van Doorn, *Philips Res. Reports*, 1957, **12**, 309.
[25] Lambe and Compton, *Phys. Rev.*, 1957, **106**, 684.
[26] Compton and Klick, *Phys. Rev.*, 1958, **112**, 1620.
[27] Overhauser and Rüchardt, *Phys. Rev.*, 1958, **112**, 722.
[28] Knox, *Phys. Rev. Letters*, 1959, **2**, 87.
[29] Jacobs, *J. Chem. Phys.*, 1957, **27**, 218.

has already been observed in M-centres,[30] but the large, inhomogeneous broadening of the lines has prevented any detailed conclusions regarding the nature of the centre.

Seitz's models assign R_1- and R_2-bands to two different centres, consisting of one or two electrons trapped at two neighbouring anion vacancies. It has been observed, however, that the ratio of the intensity of the R_1-band to that of the R_2-band is constant over a range of concentrations. This has led Herman, Wallis, and Wallis[31] to suggest that the two bands represent different transitions of the same centre. Again it should be possible to distinguish between these alternatives by using electron-spin resonance since the R_1 model would give rise to paramagnetism, whereas the R_2 model would not.

Crystals containing aggregate centres exhibit a number of interesting phenomena which may be termed *interaction effects*. Of these we shall list only a few as being typical and particularly interesting. (*a*) The quantum efficiency of the conversion of F- into F'-centres on irradiation decreases with repeated bleaching and thermal reconstitution of the F-band.[32] (*b*) In a crystal containing both F- and M-centres irradiation with polarised "F-band" light gives rise to dichroism of opposite sign in the M-bands.[33] From the conditions of this experiment, it appears that reorientation of M-centres is involved. (*c*) Irradiation in the F-band produces luminescence characteristic of R- and M-bands in crystals containing aggregate centres.[28] (*d*) Irradiation, at 90°K, in any of the bands produces a temporary change in the bands, some being increased in intensity and others decreased.[28,29]

All these effects may be explained by the existence of an efficient interaction mechanism. Thus, (*a*) would simply require the energy absorbed by the F-centre to be transmitted to an R-centre, say, which could undergo a radiationless transition to its ground state. Alternatively the energy could be utilised by an R-centre for dissociation. Similarly, in case (*b*), the energy absorbed by the F-centre could be utilised by a neighbouring M-centre to reorient itself. The mechanism for preferential reorientation is obscure but may simply be that interaction with light is a minimum for one particular orientation which is thus favoured on irradiation. Case (*c*) involves energy exchange between centres followed by re-emission as light, a phenomenon well known in the general field of luminescence. The high efficiency of the process, however, suggests a greater proximity than would be deduced from the concentration of the various centres. This may indicate a segregation of all of the centres in specific regions of the crystals, possibly along dislocation lines. Such a segregation is known to occur in the later stages of coagulation.[34]

Case (*d*) provides striking evidence for interaction, for it was found that

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[30] Lord, *Phys. Rev.*, 1957, **106**, 1100.
[31] Herman, Wallis, and Wallis, *Phys. Rev.*, 1956, **103**, 87.
[32] Geiger, *Phys. Rev.*, 1955, **99**, 1075.
[33] van Doorn and Haven, *Phys. Rev.*, 1955, **100**, 753.
[34] Amelinckx, *Phil. Mag.*, 1956, **47**, 269.

irradiation in the infrared region (*M*-band) in sodium chloride produced changes in the absorption spectrum in the ultraviolet region. Since it is hardly likely that bands so widely spaced in wavelength could overlap appreciably, this observation is interpreted as implying a particularly close proximity of centres. As Compton and Klick have pointed out,[26] such strong interaction between centres may invalidate earlier conclusions regarding the symmetry of aggregate centres drawn from polarisation measurements. Interaction effects certainly complicate the analysis of the properties of aggregate centres. However they also offer a new intriguing field of study.

The Colloid Band.—The *F*-band, obtained by rapidly quenching hot additively coloured crystals, does not represent an equilibrium state. When the concentration of *F*-centres exceeds the solubility of the metal there is a tendency for the excess of metal to coagulate in the form of colloidal particles.

The *F*-band is then replaced by a new band at longer wavelengths. This band, which we shall describe as the "colloid band", is thought to be a property of the colloidal metal. All the known features of this band—position, width, shape, integrated intensity and the fact that its properties are independent of temperature—are determined by the optical constants of the metal and the index of refraction of the host lattice. It can be shown that this result is in accord with the concept that the colloid band is caused by transitions of electrons in the colloidal metal: the position of the band can be computed by using Mie's theory[35] for the absorption of light by metal spheres,[36,37] and by using the free-electron theory for alkali-metals it can be shown[38] that there is an intimate connection between the colloid band and the theory of collective modes of oscillation.[39] Thus the optical properties of colloid centres seem to be well understood.

A considerable body of independent evidence is available to show that colloidal particles of reduced metal are present in crystals when the colloid band appears, *e.g.*, electron-diffraction measurements,[40] *X*-ray scattering,[41] and nuclear magnetic resonance.[42] This evidence will not be described here, but a glance at the references enumerated would convince the reader that the identification of this band as a property of colloidal metal rests on firm ground.

The mechanism of colloid formation is not yet well understood. In particular, the action of light, and the rôle of impurities, deserve further study. It is known that concentrated arc light can cause coagulation of

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[35] Mie, *Ann. Phys.*, 1908, **25**, 377.
[36] Savostianova, *Z. Phys.*, 1930, **64**, 262.
[37] Scott, Smith, and Thompson, *J. Phys. Chem.*, 1953, **57**, 757.
[38] Doyle, *Phys. Rev.*, 1958, **111**, 1067.
[39] Pines, *Rev. Mod. Phys.*, 1956, **28**, 184.
[40] McLennan, *Canad. J. Phys.*, 1951, **29**, 122.
[41] Smallman and Willis, *Phil. Mag.*, 1957, **48**, 1018.
[42] Ring, O'Keefe, and Bray, *Phys. Rev. Letters*, 1958, **1**, 453.

electron-excess centres,[43] but only if the specimen is allowed to become warm under the intense illumination.[44] If in high concentration *F*-centres will coagulate in the dark.[45] A heterogeneous equilibrium, analogous to a vapour–solution reaction, exists between *F*-centres and colloid particles if light is excluded. The heat of the dark reaction was measured[45] and found to be in agreement with the cohesive-energy data for bulk metal.[46] Although light is unnecessary for coagulation in densely coloured crystals, Theisen and Scott[47] found that the rate of coagulation was enormously enhanced by illumination. Shatalov[48,49] has examined the effect of light alone, using small concentrations of *F*-centres so that thermal coagulation did not occur. Light within the *F*-band produced coagulation at 250°c, even in the absence of thermal coagulation. The *F*-band was replaced by a band, labelled *X*, which was displaced by about 0·5 ev to the low-energy side of the *F*-band. This is probably the same band which Scott and Bupp[44] called *R'*. Shatalov attributes it to the F_2 molecular centre, but its position and temperature-dependence seem to suggest that it is due to very small colloidal particles of reduced metal. The kinetics of formation and destruction of *X*-centres will bear closer examination since they are very early products in the coagulation process. They offer an interesting meeting ground between aggregate centres (*R*, *M*, etc.), which are produced optically at room temperature, and the larger colloidal particles which are formed in heavily coloured crystals by thermal coagulation.

The rôle of impurities in stimulating and suppressing colloid formation can throw light on the initial steps in coagulation. It is known that small quantities of bivalent cations can greatly inhibit colloid formation,[50] possibly by altering the equilibrium vacancy concentrations.[51] Conversely, hydroxyl ions may well be *necessary* for the formation of colloids in irradiated crystals,[52] but are not needed to promote coagulation in additively coloured crystals. However, hygroscopic salts, such as sodium bromide, are particularly hard to colour additively, suggesting that hydroxyl ions may assist coagulation even in additively coloured crystals. Hydroxyl ions are present in synthetic crystals unless special pains are taken to exclude water vapour. There is every indication that this impurity affects other properties besides the coagulation of colloids (cf. section 4).[53,54]

[43] Glaser, *Nachr. Akad. Wiss. Göttingen*, 1936, **3**, 31
[44] Scott and Bupp, *Phys. Rev.*, 1950, **79**, 341.
[45] Scott and Smith, *Phys. Rev.*, 1951, **83**, 982.
[46] Scott, *Phil. Mag.*, 1954, **45**, 610.
[47] Theisen and Scott, *J. Chem. Phys.*, 1952, **20**, 529.
[48] Shatalov, *Soviet Physics J.E.T.P.*, 1956, **2**, 725.
[49] Shatalov, *Optika i Spektrosk.*, 1957, **3**, 610.
[50] Heiland and Kelting, *Z. Phys.*, 1949, **126**, 689.
[51] Watson and Scott, *J. Chem. Phys.*, 1958, **30**, 342.
[52] Compton, *Phys. Rev.*, 1957, **107**, 1271.
[53] Rolfe, *Phys. Rev. Letters*, 1958, **1**, 56.
[54] Etzel and Patterson, *Phys. Rev.*, 1958, **112**, 1112.

3. Electron-deficit centres

In 1954, Seitz[2] made a strong plea for a systematic study of electron-deficit (*V*) centres, which at that time were not well understood. Since then some light has been thrown upon the problem, but much still awaits clarification.

Seitz[1,2] offered an interpretation of the various *V*-bands in terms of centres which are direct antimorphs of the electron-excess centres discussed in section (2). His V_1-model consists of a hole combined with a cation vacancy, symbolised as in Fig. 2 (*a*). By "hole" is meant the absence of a single electron from the outer shells of those halide ions directly surrounding this vacancy: the unit is therefore centrosymmetric. Seitz's V_2-, V_3-, and V_4-centres are also shown in Fig. 2. This approach failed to take note of the strong tendency of halogen atoms to form covalent bonds and it now seems clear that, in general, the *V*-bands are not so much properties of the imperfect solid as of isolated molecules or ions, trapped within the solid.

Certain bands in the ultraviolet region are always designated as V_1, V_2, V_3, etc., for specific crystals, but there is no certainty that the same centre is being described in different crystals. We therefore deal with each halide in turn.

Iodides.—Since no magnetic studies of *V*-centres in alkali iodides have yet been reported only spectrophotometric results can be discussed. Additive coloration with iodine invariably gives rise to two intense bands at about 3650 and 2950 Å.[55–57] These bands are found with about the same relative heights under different conditions, and the separation between them is approximately equal to the energy difference between the $^2P_{3/2}$ and the $^2P_{1/2}$ state of the iodine atom. It therefore seems likely that these bands are caused by a single centre. Hersh[57] has pointed out that tri-iodide ions in various solvents have two intense ultraviolet absorption bands with maxima close to the 3650 and 2950 Å bands of additively coloured crystals, and has suggested therefore that these bands are due to I_3^- ions incorporated in the crystals. This is in accord with chemical expectation. It is not clear, however, how the lattice changes to accommodate these ions. It is curious that the low-energy band is more intense than that of higher energy in the crystal doublet whereas the reverse is true for I_3^- in solution. It is possible that other bands are present in the crystal spectrum which are not resolved under the conditions used, or that distortion in the crystal considerably alters the relative intensities of the two transitions.

Uchida and Nakai[56] found a third band at about 2600 Å in potassium iodide crystals. No chemical analogue is known for this band and further study is required before an assignment can be made.

[55] Mollwo, *Ann. Phys.*, 1937, **29**, 394.
[56] Uchida and Nakai, *J. Phys. Soc. Japan*, 1954, **9**, 928.
[57] Hersh, *Phys. Rev.*, 1957, **105**, 1410; *J. Chem. Phys.*, 1957, **27**, 1330.

Molecular iodine has a fairly strong absorption band in the 5000 Å region. Since the formation of tri-iodide ion is energetically favoured, free iodine is not likely to be a stable species in the crystal, but Hersh has reported two bands in this region in potassium iodide under unspecified conditions.[57]

Bromides.—Potassium bromide coloured with bromine has been studied more extensively. An intense band in the 2700 Å region generally predominates. This is very close to the peak found for Br_3^- ions in various solvents and is probably due to these ions. Mollwo[55] found a weak band at about 4200 Å: this is close to the position expected for molecular bromine and the band shape is also similar to that found for bromine in solution. It therefore seems likely that both Br_2 and Br_3^- are formed. Another band at 2300 Å was found by Mollwo and also by Hersh:[57] it is unlikely that this band is due to Br_3^- since Teegarden[58] found an intense band at 2740 Å but no band at 2300 Å. Also, the spectrum of Br_3^- ions in solution is a single broad line rather than a doublet. Teegarden, however, did find a shoulder at about 3200 Å, which was also found by Dorendorf[59] in crystals exposed to *X*-rays at −140°. Since no simple molecular or ionic species is known with bands either at 3200 or at 2300 Å no clear identification can be made. A combined magnetic and optical study might prove helpful in this connection.

Teegarden[58] found that potassium iodide crystals, treated with bromine, gave spectra which were indistinguishable from those treated with iodine under similar conditions. This can be understood in terms of the concepts outlined in this section since bromine readily oxidises iodide to iodine:

$$Br_2 + 2I^- \rightleftharpoons I_2 + 2Br^- \quad \ldots \quad (3)$$

However, a similar result was found for potassium bromide treated with either bromine or iodine, and the reverse reaction (3) is not energetically favourable. It is more probable that, under these conditions, Br_3^- and BrI_2^- respectively are formed. Since these ions have bands at 2700 and 2600 Å respectively it would be difficult to distinguish between them. It is possible, however, that the large excess of bromide ions is sufficient to upset equilibrium (3) and that iodide ions are formed from iodine. Teegarden rejected this possibility on the grounds that no band for I^- was detected in the 2150 Å region. However, when iodide is incorporated in a potassium bromide lattice[60] the first excited band is strongly shifted towards the higher-energy region, being at 1930 Å at 77°K. This is outside the range studied by Teegarden.

Chlorides.—Unfortunately, it has not been possible to form *V*-centres in alkali chlorides or fluorides by additive coloration. Therefore we have to

[58] Teegarden, *J. Chem. Phys.*, 1956, **24**, 161.
[59] Dorendorf, *Z. Phys.*, 1951, **129**, 317.
[60] Delbecq, Robinson, and Yuster, *Phys. Rev.*, 1954, **96**, 262.

turn to the results obtained with high-energy radiation. At room temperature two bands are found both for sodium chloride and for potassium chloride, in the 2300 Å region (V_2) and the 2150 Å region (V_3). By analogy with solution spectra it is probable that the V_2-band is due to Cl_3^-, but the assignment is not clear cut since the V_2- and the V_3-band lie close together. One might expect to find spectrophotometric evidence for the presence of "free" chlorine whose ${}^1\Pi_u \leftarrow {}^1\Sigma_g$ transition lies at about 3330 Å. This is normally a weak transition and might well be too small for measurement, but a weak band at 3400 Å found by Hersh[57] for potassium chloride pellets could be due to free chlorine.

When alkali chlorides or bromides are exposed to high-energy radiation at low temperatures and the spectra measured at the same temperature, two new bands in the near ultraviolet region appear which are irreversibly lost on warming. Seitz[2] has speculated on the nature of the centres responsible for these bands (which are symbolised as V_1 and H), but there is still insufficient information concerning them to enable definite conclusions to be drawn.

However, electron-spin resonance studies have conclusively proved the presence of Cl_2^- ions in potassium chloride crystals *X*-irradiated at low temperature.[61] It was thought at first that the V_1-band was due to this radical ion[61] and it has also been suggested that the resonance was caused by V_3-centres[62] [Fig. 2 (*c*)]. In fact, neither postulate is correct and none of Seitz's models is suitable. The ions have an absorption band at 3650 Å in potassium chloride which had not been detected previously because of its proximity to the V_1-band ($\sim$ 3500 Å).[63]

The electron-resonance results are of great importance since the wealth of detail is such that identification is unambiguous. These ions represent the simplest possible electron-deficit centre in which a chlorine atom formed by loss of an electron has combined with any *one* of its neighbouring chloride ions: no lattice vacancies appear to be involved, and the absorption band is close to that attributed to Cl_2^- ions in aqueous solution.[3]

Thus the V_1-bands still remain enigmatic. There is no evidence against Seitz's model, but the inability to detect any electron-spin resonance which can be linked to this band is hard to understand in terms of this model. The band for potassium chloride is close to that for molecular chlorine, but the intensity is too great and studies with polarised light suggest that the centre has cubic symmetry.[64]

Cohen, Känzig, and Woodruff[65] recently identified the radical ion F_3^{2-} in irradiated lithium fluoride. They suggested that this unit was closely similar to Seitz's V_4-model and it would be of great interest to make a combined magnetic and optical study similar to that of Delbecq *et al.*[63]

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[61] Kanzig, *Phys. Rev.*, 1955, **99**, 1890.
[62] Bagguley and Owen, *Reports Progr. Phys.*, 1957, **20**, 304.
[63] Delbecq, Smaller, and Yuster, *Phys. Rev.*, 1958, **111**, 1235.
[64] Lambe and West, *Phys. Rev.*, 1957, **108**, 634.
[65] Cohen, Känzig, and Woodruff, *Phys. Rev.*, 1958, **107**, 1096.

The particular items discussed in this section establish conclusively that the formation of specific molecules plays a fundamental rôle in the field of electron-deficit centres. Many outstanding problems remain, and it is felt that these should be viewed in terms of interactions between vacancies and the molecular species whose formation now seem established. The results of Miessner[66] and Pick[67] are of great significance in this respect: their studies of mixed alkali halide crystals, whilst still lacking a complete interpretation, clearly show the difference between *F*-centres and *V*-centres.

4. Foreign ions

A remarkably large number of cations and anions can be incorporated in alkali halides to give crystals which are ideal for spectrophotometric and magnetic studies. Of these, we choose to discuss briefly hydride ions, hydroxide ions, alkaline-earth metal ions, and first-row transition-metal ions of low valency.

Hydride Ions.—Because it consists of only a proton and two electrons, the hydride ion can adapt itself to fit any alkali halide lattice, giving what is often described as a *U*-centre. Because of this flexibility, the *U*-band, which may be described as the first fundamental band of the hydride ion, depends strongly upon the lattice constant, just as does the *F*-band.

Other bands, associated with hydrogen, are found after high-energy irradiation of crystals containing hydride. A combined magnetic and spectrophotometric study[68] has greatly helped to elucidate the reactions involved and has established that hydride ions are photolysed with ultraviolet light to give *F*-centres and interstitial hydrogen atoms. A band (U_2) found on the long-wavelength side of the *U*-band after irradiation is thought to be due to these interstitial hydrogen atoms.[68]

Hydroxide Ions.—These ions can replace halide ions in certain crystals and are of great importance because this may well happen unintentionally, and hence phenomena caused by hydroxide ions may be ascribed to the pure crystal.[53,54]

On photolysis with ultraviolet light in the fundamental hydroxide band, hydrogen atoms (U_2) and *F*-centres are detected for potassium chloride, but for potassium bromide a prominent V_1-band is also found. Since the primary step probably gives H· and O·⁻, this difference can be understood in terms of the reaction:

$$O\cdot^{-} + Br^{-} \rightarrow O^{2-} + Br\cdot\ (V_1) \qquad \ldots \quad (4)$$

Whilst this is favoured in a bromide lattice the greater electron affinity of chlorine could well prevent its occurrence with potassium chloride.

Alkaline-earth Cations.—Any cation with an electron-affinity greater

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[66] Miessner, *Z. Phys.*, 1953, **134**, 567.
[67] Pick, *Z. Phys.*, 1953, **134**, 604.
[68] Delbecq, Smaller, and Yuster, *Phys. Rev.*, 1956, **104**, 599.

than that of the host cation is a potential electron-trap. This is certainly true for alkaline-earth cations, and the resulting centres, which are, to a first approximation, the corresponding singly charged cations (*e.g.*, Ca^+), give rise to characteristic optical spectra[69] and electron-spin resonance absorption.[70] These centres are generally designated Z_1, irrespective of the particular cation involved.

Transition-metal Cations.—Lithium fluoride has been used as host crystal for magnetic studies of ions such as Cr^+, Mn^{2+}, Fe^+, Co^{2+}, Co^+, and Ni^+ by Bleaney and Hayes,[71,72] the monopositive ions being formed by exposing crystals containing the corresponding bivalent ion to high-energy radiation. In many cases a measure of the covalent character of the bonds between impurity ions and the six neighbouring fluoride ions can be deduced because such interaction gives rise to a hyperfine structure in the electron-spin resonance spectra.

Univalent ions (Cr^+, Fe^+, and Co^+) are found to have cubic symmetry, but bivalent ions (Co^{2+} and Mn^{2+}) are in surroundings of less than cubic symmetry. This suggests that there is a cation vacancy close to the bivalent ions which migrates away during the irradiation.

Extensive studies of this sort have also been made by Wertz and his co-workers using magnesium oxide as host crystal.[73]

5. Conclusions

The most outstanding development in this field has been the application of electron-spin resonance methods, including double resonance. When this is combined with optical studies a great deal of information can be obtained which, besides establishing the basic characteristics of the centre being studied, provides data which the theoretician can use as a yardstick for detailed mathematical descriptions.

It is perhaps not always realised how many unusual compounds are studied in this field: we have already mentioned many, such as F_3^{2-}, Cl_2^-, Ca^+, and Fe^+, and doubtless many more will soon be discovered. These highly reactive species have not only been detected, but have often been subjected to more detailed structural analysis than is afforded to stable compounds.

Those interested in solution chemistry can also draw from the results of these studies. This has been done, for example, in the field of solutions of alkali metals in ammonia and other solvents,[74] and comparison with crystals may also be relevant when considering ionic solvation.[75]

[69] Pick, *Ann. Phys.*, 1939, **35**, 73.
[70] Kawamura and Ishiwatari, *J. Phys. Soc. Japan*. 1958, **13**, 574.
[71] Bleaney and Hayes, *Proc. Phys. Soc.*, 1957, **70**, *B*, 626.
[72] Hayes, *Discuss. Faraday Soc.*, 1958, **26**, 58.
[73] Wertz, Auzins, Griffiths, and Orton, *Discuss. Faraday Soc.*, 1958, **26**, 66.
[74] Symons, *Quart. Rev.*, 1959, **13**, 99.
[75] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338, 346.