Optical and Photochemical Properties of some Halides and their Complexes

A Thesis presented for the degree of Doctor of Philosophy of the University of Leicester

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January 1965

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#### January 1965.

The studies described in this thesis have been placed under three headings: some properties of silver-iodide complexes  $(Ag_mI_n^{-(n-m)})$ , centres found in silver halides, and a discussion of confined electron centres including the F-centre in alkali halides. The introduction includes a discussion of some properties of the solid state and the principles of the experimental methods used - details of which are given in chapter two.

Studies on the silver-iodide complexes are reported in section 3.1. In dilute solutions of silver and alkali iodides in organic solvents, absorption bands occur at c.230 mp and c.310 mp, and are attributable to the species  $AgI_2$  and  $Ag_4I_6$ respectively. The diffuse reflectance of the solid complexes are also reported. Further, preliminary electron spin resonance studies of the gamma irradiated solid complexes are reported.

In section 3.2, it is demonstrated that the centres in irradiated silver halides which give rise to a conduction electron spin resonance cannot be silver particles. Gamma irradiation at low temperatures does not seem to give rise to simple paramagnetic colour centres as in the alkali halides. Cyanine dyed silver halides, illuminated at low temperature, show a single electron spin resonance, with a g-value slightly dependent on the halide. The results of Stasiw on chalcogen doped silver halides are discussed and some experimental studies are reported.

In section 3.3, magnetic resonance data on the F-centre (from the literature) is analysed to show the dependence of the density of the unpaired electron in orbitals of near neighbour cations on various parameters of the alkali halide. In particular this density is seen to decrease linearly with increasing halide (cavity) radius and increase with the covalent radius of the alkali metal. The importance of cavity size is stressed and implications for any theory of the F-centre are discussed. Some measurements of the absorption of iodide doped crystals are presented. 'The best laid schemes o'mice and men Gang aft agley...'

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R.Burns.

'Research is one tenth inspiration, nine tenths perspiration.'

Adapted from

R.W.Emerson.

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Chapter One

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Introduction.

1.1 General Introduction.

The halides have many interesting optical and photochemical properties. For example the silver halides are well known for their photosensitivity (Mitchell 1955,Kodak 1961). Even more ionic compounds, such as the alkali halides, exhibit interesting photochemical and optical properties (Compton and Schulman 1963, Dekker 1960 p366). Recently Forty (1963) has studied such properties in lead iodide.

Halides, then, offer a rich field for the investigator whether experimental or theoretical. Although the studies we report in this thesis have been mainly centred on the silver halides, both simple and complex, we have deemed it worthwhile to investigate other compounds which seem similar in some of their properties. Especially this course has been pursued when such studies might help our understanding of the properties of the halides.

In our studies we have used several experimental approaches. The theory of these approaches we have outlined in the later sections of this chapter. In section two we review some of the current ideas on the solid state and the effects of radiation on solids. In section three we discuss briefly the relevant theory of electron spin resonance. In section four we point out some of the principles of ultra-violet/visible spectrophotometry and of diffuse reflectance spectrometry.

The experimental methods we have used are described in chapter two. In section one of that chapter a brief description is given of the electron spin resonance equipment we have used and the experimental procedures involved. In section two we describe the experimental techniques used in the preparation of solutions. The diffuse reflectance technique is described in 2.23. In 2.4 we describe the method used to obtain spectra of single crystals including crystals irradiated and kept at low temperature. We have sometimes had to prepare single crystals: the methods used are collected together in section five. Section six gives the details of the preparation of the metal films we have used. Finally, some details of the irradiation procedures are given in section seven.

The photosensitivity of the silver halides has already been noted and this is the starting point of our studies. A number of questions naturally arise. What is the primary centre formed on exposure of the silver halide crystal to light? Why do certain treatments enhance the sensitivity to light? And so forth.

It has long been known that dipping an unsensitized photographic plate into a solution of silver nitrate sensitizes it, and then dipping it into a solution of an alkali halide desensitizes it (see Gernsheim,1953). Now complexes of the formula  $Ag_n X_m^{-(m-n)}$  are known, where X is a halogen and m can be greater or less than n. (See section 3.1 for bibliography). Possibly these are involved in this sensitization process. It therefore seems worthwhile to characterise these complexes by their ultraviolet/visible absorption spectra and then to see if such complexes can be observed on the surface of the silver halides, in powder form, by using diffuse reflectance spectrometry. Our studies along these lines are reported in the first section of chapter three. Next we could investigate the effect of radiation on these complexes especially by electron spin resonance, if applicable. Preliminary studies of such experiments are reported in 3.14.

Section two of chapter three deals with the centres found in pure or doped silver halide crystals. Irradiation of the silver halides with light or with ionising radiation leads to the formation of small spects of metallic silver in the crystal - this process being known as print-out. In section 3.2 we describe studies which have been made on crystals containing such particles. A similar effect seems to occur in cadmium sulphide - this is reported also in 3.2. Also in this section we discuss the studies of Stasiw's school on chalcogen doped silver halides, and report a few results that we have obtained. Sulphur sensitizes the silver halide with respect to the amount of light impinging on the crystal; the cyanine dyes do so with respect to the frequency of the light. Electron spin resonance measurements on illuminated silver halides so sensitized are discussed in 3.24.

In section three we turn mainly to the alkali halides to look at some of the fundamental characteristics of F-centres. For convenience, a number of other confined electron centres are also discussed in this last section.

Often in the past, silver halides and their properties have been regarded with a specialist attention. The approach of Gurney and Mott in 1938 stands in opposition to such a viewpoint - but even so, since then many workers have not looked further afield than the silver halides and photographic experience. In this thesis an attempt has been made to keep to the spirit of Gurney and Mott and regard the behaviour of the silver halides as just one particular example of the phenomena known as the physics and chemistry of the solid state.

The Solid State. Section 1.21.

In descriptions of the electronic and atomic structure of solids, two distinct approaches are made. For some purposes it is useful to consider a solid to comprise a perfect lattice on which, at each lattice point, is an appropriate ion, atom or group of these. This was the view of the early crystallographer. The X-ray crystallographer, however, knows that this cannot be true over too great a number of lattice spacings, but that the real crystal comprises a large number of mosaic blocks, each slightly disoriented with respect to its neighbours, and each supposed to have internally perfect structure.(James,1953).

The studies of a number of workers have shown that over quite small regions the crystal can be imperfect. For example, ions may be missing from their lattice sites and be in an interstitial position. In these regions a localised description seems most appropriate.

So far we have been thinking along atomic or structural lines and have not mentioned the electronic properties and structure of crystals. These,too, lend themselves to the two approaches and this is most clearly seen in the optical properties of crystals, i.e. their absorption and emission of radiant energy, corresponding to electronic energy changes. For some purposes the band picture of solids, the nonlocalised approach, is most used nowadays and we shall give a description of its most salient points. But localised descriptions have their value and may be more appropriate

in some cases than the band picture: the crystal field <sup>7</sup> spectra of the transition metal ions being a good example of recent interest.

We shall now proceed to a more detailed discussion of some of these points. Firstly, we shall find it useful to have available some details of localised structural imperfections in solids. Then we will discuss the band theory of solids. Finally some details of local electronic structure will be useful. At each point we shall see how the solid can interact to radiation, in many cases the radiation of interest will be in the visible or ultraviolet regions of the spectrum, but in some cases the effect of ionising radiation (X-rays,gamma rays, etc.) will be of interest. Imperfections in Solids:

The kinds of imperfections found in ionic solids have been listed in many standard works. For example those of Gurney and Mott(1940), Dekker(1960), van Bueren(1960) and Kröger(1964). We shall follow these authors, in general, and for further details and for many references to the original papers on this subject reference to these works may be made.

First let us consider the many kinds of point defects in ionic solids. We shall talk in terms of ions although it is believed that many of the solids to which these concepts are applied are to a large degree covalently bonded. In fig. 1.21 we see a two dimensional representation of the two main types of defects found in pure crystals. In the Schottky







Frenkel Defect

Figure 1.21

defect (1931,35) ions are missing from the crystal, leaving vacant lattice sites, whereas in the Frenkel(1926) defect the ion has moved from a lattice site into an interstitial position. The type of ion which moves into the interstitial position will clearly be determined usually by size. It is, however, possible for the larger ion to be the one which occupies the interstitial position in a binary crystal.(Gray 1957).

The Schottky defects lead us directly to the idea of charge compensation. Clearly the crystal will overall be electrically neutral. Thus the anion vacancies require an equivalent number of cation vacancies: this was the process initially considered by Schottky. There are other methods of charge compensation: impurity ions of the appropriate charge and number may be incorporated into the lattice or ions in the lattice - including impurity ions - may undergo a valency and, therefore, charge change. This case is especially associated with the transition metal ions. The vacancies may also trap electrons or holes and thus the crystal may achieve electrical neutrality: these states will be dealt with below under the title colour centres.

The introduction of appropriately charged impurity ions can lead to the 'artificial' production of vacancies. Doping potassium chloride with cadmium chloride leads to the formation of potassium vacancies; doping with potassium sulphide leads to the formation of chloride vacancies.

Immediately, we can think of equilibria occurring in the crystal and this leads to mass action equations describing these equilibria. First the charge compensation: suppose we incorporate n divalent cations  $M^{++}$  in a lattice of monovalent ions, then for charge neutrality:

### $n_{cv} = n + n_{av}$

where  $n_{cv}$  is the number of cation vacancies and  $n_{av}$  that of anion vacancies. Now in the pure crystal there will be a thermal equilibrium of vacancies of cations and anions:

### $n_{cv}/n_{av} = K_v$

These two equilibria will react on one another. Kröger and his collaborators have applied this approach to a number of substances, in particular cadmium sulphide (see Kröger 1964). We must also note at this point ionic diffusion in solids: the presence of defects is expected to enhance such phenomena. In the case of Frenkel defects the interstitial ion should readily diffuse - this is found for interstitial silver ions in the silver halides, by radioactive tracer and electrical conduction measurements. For Schottky defects the vacancy may move through the lattice leading, in effect, to ionic motion. Since the vacancies are charged (by default!) we can expect ones of opposite charge to be bound together to form a dipole. Then they will not contribute to ionic diffusion or electrical conduction, although they will contribute to dielectric relaxation.

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A slipped crystal.

Figure 1.22.







Figure 1.23

In addition to the point defects that we have considered there are line defects. In figures 1.22 and 1.23 we illustrate some of these. In the translational slip two halves of the crystal have slipped relative to one another; in the edge dislocation there is a missing row of lattice points; finally, the screw dislocation is shown. The jog occurs when the new row of atoms is added to the half layer: at some point the row may stop - the edge dislocation then drops down one lattice distance: this is the jog. The importance of line defects is their importance in solid state reactions. A simple example is provided by decoration. If an alkali halide crystal is deformed e.g. by compression, and then heated to a high temperature in the vapour of the alkali metal and finally cooled slowly, the metal precipitates out along the dislocation lines, where it may be observed by microscopy (Siedentopf 1905). Other metals may be precipitated out in the alkali halides (Urbach, 1930, Mitchell, 1957a). Silver halide dislocations can be decorated by silver, by photolysis (Mitchell). In fact the line defect acts as a nucleation centre for these precipitation reactions. It can also act as a source or trap for point defects. Surface defects follow the same general patternmas internal defects and will not be discussed in detail.

At this point we may conveniently mention the experimental methods of studying ionic defects in solids. The presence of point defects is shown by ionic diffusion in the crystal, this may be followed by radioactive tracer methods

or under the influence of electric fields, by electrical conductivity (see Dekker, 1960pp 168, 176). Vacancy pairs will not be detected in these ways, but can be detected by dielectric relaxation studies (Volger, 1959). Schottky defects could in principle be detected by density measurements, although these are in general not sensitive enough at room temperature there are about 10<sup>6</sup> vacancies per c.c. in sodium chloride. Thermal expansion studies have been used to show that silver chloride contains mainly Frenkel defects even near its melting point ( see below). Spectroscopic methods may be used: the defect may perturb the energy levels of nearby species. As an example we may mention the & and Abands found in the alkali halides, and which we discuss below. Magnetic resonance may also be used: Mahendroo and Nolle (1962) have studied vacancy diffusion by this method in sodium chloride and fluoride. Finally, we should note that electrons and holes may be trapped by defects, which will be discussed further below.

#### Section 1.22. The Electronic Theory of Solids.

The first attempt at a quantum theory of the states of electrons in solids was made by Sommerfeld(1927). Basically he thought of the surfaces of a metal as the boundaries of a potential box, which confined the electron in space. Then various energy states were allowed for each electron and each state would be filled by the electrons according to the Pauli Principle, i.e. the electrons would fill the states according to Fermi-Dirac statistics. Although this theory is useful for the interpretation for such simple phenomena as work functions, it fails to account for the behaviour of all solids and in fact merely modified many of the formulae of the classical Lorentz-Drude theory. For most purposes, the band theory is found to be the most useful for the interpretation of the electronic properties of solids.

In the case of electrons in a potential box, the energy of an electron is given by  $\mathbf{E} = \frac{\pi^2 \mathbf{k}}{2m}$ , where  $\mathbf{k} = 2\pi/\lambda = p/\hbar$ . k is the magnitude of the wave vector, k,  $\lambda$  is the wavelength, and p the momentum of the electron. In the Sommerfeld theory the box has dimensions of the solid and since an integral number of waves must fit the box, i.e.  $n\lambda = L$ , the length of the box, many closely spaced levels result. In the case of a model of a lattice of ions a different result obtains. The ionic lattice will produce a periodic potential and the study of Schrödinger's

equation for such a potential shows that:-

1. There exist allowed energy bands, separated by gaps or forbidden regions.

2. The functions  $E(\underline{k})$  are periodic in  $\underline{k}$ . (For details see Brillouin, 1953, Wilson, 1953, Reitz, 1950 or Jones, 1960).

The periodic potential of the electron will satisfy V(x) = V(x+a), where x is the electron coordinate and a the lattice spacing, considering, for simplicity, just one dimension. The wave equation is:

$$\frac{d\Psi}{dx^2} + \frac{2m}{n^2} \left[ \mathbf{E} - \mathbf{V}(\mathbf{x}) \right] \boldsymbol{\psi} = 0$$

It can be shown that there exist solutions of this of the form  $\psi(x) = e^{\pm ikx} u_k(x)$ , where  $u_k(x) = u_k(x+a)$ , that is,  $u_k$  has the same periodicity as the lattice. This principle is known as Bloch's or Floquet's theorem. Kronig and Penney(1930) applied this theorem for the case of a simple potential model. They assumed the potential energy of the electron has the form of a periodic array of square wells:-V(x)

$$\circ$$
  $1 = - 1$   $1 = - 1$   $2 = - 1$   $2 = - 1$   $2 = - 1$   $2 = - 1$ 

The period of the potential is (a+b). Thus we have two wave equations:  $\frac{d^2 \psi}{dx^2} + \frac{2m}{h^2} = 0$  for 0 < x < a

and  $\frac{d^2 \Psi}{dx^2} + \frac{2m}{n^2} (E - V_0) \Psi = 0$  for  $-b \langle x \langle 0 \rangle$ 







These have the solutions:

$$u_1 = Ae^{i(\alpha - k)x} + Be^{-i(\alpha + k)x}$$
$$u_2 = Ce^{(\beta - ik)x} + De^{-(\beta + ik)x}$$

where  $a_{\pm}^2 = 2mE/\hbar^2$  and  $\beta^2 = 2m(V_0 - E)/\hbar^2$ . These solutions and their derivatives must be continuous at the boundaries. This leads to equations for the constants in these solutions. Then for simplification the barriers are made infinite and b zero in such a manner that  $\boldsymbol{V}_{O}\boldsymbol{b}$  is finite. Then the satisfactory solutions are  $P \underline{\sin da} + \cos da = \cos kd.$ such that where  $P = mV_0 ba/\hbar^2$ , i.e. it is a measure of the binding energy. Plotting the left hand side of this equation against da (fig. 1.24) we see that only certain values of da are allowed since  $\cos kd = \pm 1$ , and these values are represented by heavy strokes. Since  $\ll$  is proportional to E, we conclude: 1. The energy spectrum of the electrons consists of a number of bands separated by forbidden 2. The widths of the bands increases regions. 3. The width of a given band decreases with E. with increasing P, i.e. increasing binding energy. This is also shown in figure 1.24. Finally it is possible to plot energy against wave number or reduced wave vector - which is limited to  $-\pi \langle k \langle \pi_a \rangle$ , this has been done in fig.1.25. Finally it is possible to show that the number of energy levels in a band is 2N + 1, where N is the number of unit cells in the lattice( details of this are given by Wilson).







Figure 1.27

Whilst dealing with the one dimensional case, we may mention studies of the motion of an electron in a crystal according to the band theory. First the velocity of a moving electron. The velocity of a particle according to quantum mechanics is the group velocity of the associated wave (Mandl,1957,p34):  $v = \frac{d\omega}{dk}$ ,  $\omega = 2\pi f$ .

since  $\mathbf{E} = \mathbf{h}\boldsymbol{\omega}$ , we have  $\mathbf{v} = \frac{1}{h} (\frac{d\mathbf{E}}{d\mathbf{k}})$ .

For free electrons this gives v = p/m, but for electrons in a band this no longer holds, as E is not generally proportional to  $k^2$ . Figure 1.26 gives an example of how v may vary with k. At the top of the band, and at the bottom, dE/dk is zero and here v = 0.

Another remarkable fact is noticed on considering the application of an electric field, F, to the crystal. For one electron in the band we have, in time dt, an increase in the electron's energy dE = eFv.dt

=  $(eF/\hbar)(dE/dk)dt$ .

Differentiation with respect to time gives the acceleration  $a = (eF/k^2)d^2E/dk^2$ .

Comparing this to the free electron we see that(the free electron has a = eF/m) the electron behaves with effective mass,  $m^* = \hbar^2/(d^2E/dk^2)$ .

The band theory gives an immediate explanation of the fact that substances can be classified as insulators, semiconductors, or(metallic)conductors. The three cases are represented in figure 1.27. At ordinary temperatures the insulator has a filled <u>valence</u> band and the forbidden gap is about 10 eV. For metals the upper or conduction band is only partly filled and contains many free electrons. In the semiconductor, the basic structure is as for the insulator, but the gap is only about one electron volt so that electrons may be excited thermally at, say, room temperature from the valence band into the conduction band. Thus electrons occur in the conduction band and holes in the valence band and these will give rise to conduction. Increasing the temperature will mean more electrons in the upper band and more holes in the valence band and hence the resistance will decrease.

At this point we may examine the absorption of ultraviolet radiation by the alkali halides, which are insulators. These have a band gap of about 8.5 eV, which corresponds to ultraviolet radiation of about 69 Kcm<sup>-1</sup>. In fact most absorb at energies well below this. The usual explanation of this fact is that there exist exciton levels in the crystal, as in figure 1.27. An exciton, or electron in such a level bound to a hole in the valence band, can then exist, and the absorption of radiation can lead to the formation of such a state. It is often stated that these levels are bands, i.e. that they are not localised. Experimental support for this idea, is now thought to be ambiguous (Philip and Taft, 1957).

So far we have looked at a perfect lattice, but impurities and defects may exist in the crystal, and we should ask how these will affect the band structure of the crystal. This problem has been considered by Slater (1949). Basically, in the defect region new levels appear: in the energy gap: for example, for an impurity providing a coulomb force, hydrogenic levels appear. These levels will be available to trap out electrons from a band thus localising the electron.

In the previous sections we have largely been discussing a one dimensional model of a crystal. The ideas, however, may be generalised to three dimensions. The discontinuities which give rise to allowed and forbidden energy regions now occur in k space and are represented by surfaces. One important result of this is that although there are discontinuities in the energy, the energy surfaces can cut one another and the bands may overlap, i.e. no forbidden gap may occur. The discontinuity surfaces in k space are said to separate off Brillouin zones. For a simple cubic lattice the first zone is a cube. The effective mass will now be a second order tensor:  $(m^*)^{-1} = (h^2)^{-1} \sqrt{r} \cdot E(\underline{k})$ 

The theories so far mentioned may be investigated and some extent corroborated by experimental methods such as soft X-ray spectroscopy: for further details the books by Wilson and Dekker may be consulted.

In the past decade a number of new techniques have been developed in the theory of bands. Such techniques have been applied, for example, in the theory of conduction electron spin resonance. We shall not attempt to review these rather esoteric theories here;a ddtailed account of these techniques has been given by Blount(1962).

### Section 1.23 Imperfect Crystals.

We have already mentioned how defects and impurities may give rise to local energy levels lying in the forbidden region. Often these will trap out electrons or holes and as a result the ultraviolet/visible spectrum of the crystal will change. Some of the earliest examples studied were the point defects in the alkali halides. An anion vacancy (Schottky defect) may trap an electron - the result is an 'F' centre. Crystals containing an appreciable number of such centres are intensely coloured: hence it is natural to group such electron or hole containing, impurity or defect centres under the general title 'colour centres'.

The first extensive studies of these were carried out at Göttingen from about 1930 onwards by Pohl and his collaborators. A number of general reviews exist: Seitz (1946,1954) has been mainly concerned with centres in the alkali halides, as have Compton and Schulman (1963), Doyle and Symons( 1960) are mainly concerned with their chemical significance. The term colour centre is not usually applied to photoconductors such as cadmium sulphide, although essentially the same kind of centres do exist in these compounds - perhaps because conduction is the most considered property here, and so trap and recombination centre are more illustrative terms.

Irradiation of an alkali halide, kept at 77°K, with high energy rays (gamma, X or electrons) changes the optical absorption of these substances considerably. This



is true whether the crystal is pure or contains impurities. For instance, in potassium chloride, normally optically clear from below 200mp to above 40p, irradiation produces a whole set of new bands (figure 1.28). Changes can be brought about in these by bleaching, i.e. strongly illuminating the crystal at the wavelength of one of these absorptions, and also by heat treatment. These new absorptions are believed due to centres which have trapped the electrons and holes produced in the crystal by the radiation. The simplest centre is an electron trapped at an anion vacancy and this is identified, as implied above, with the F-band. Of the various V bands, no simple model seems possible, although Seitz (1954) originally suggested that the  $V_1$  band was due to a hole trapped at a cation vacancy. Simple optical studies do not tell us much about a centre. More information, it is true, may be obtained by using polarised light absorption and bleaching of the various bands. Further evidence can be obtained from luminescence and photo-electric measurements. When electron spin resonance is applicable, it yields the structure of the centre most directly. Now the  $V_1$  centre model proposed by Seitz should show an electron spin resonance absorption, but studies have indicated no such simple centre - the centre giving rise to the  $V_1$  band seems to be non paramagnetic. Castner et. al. (1957, 1958) and Delbecq et. al. (1959) have studied a centre which has an absorption close to the  $V_1$ centre - the  ${\tt V}_k$  centre. The structure of this centre is
quite different to that proposed by Seitz for the  $V_1$ centre. It can be described as a halogen molecule ion  $(X_2^-)$ oriented along a (110) axis of the crystal. It has been suggested by Kanzig and Woodruff (1958) that the  $V_1$  centre is merely a halogen molecule at a simple anion lattice site, and this is consistent with many of the experimental studies of it. Other more complicated structures exist and give rise to other V bands. This tendency for 'complexes' rather than simple centres is not surprising in view of the strong covalent bonding tendency of the halogen atom, in fact the existence of halogen molecule ions is postulated in irradiated aqueous solutions of chlorides (Grossweiner and Matheson,1955).

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In addition to the simple F centre, more complicated centres exist having trapped electrons. Low temperature bleaching of the F band in an additively coloured alkali halide crystal leads to the formation of a broader band at lower energy, which is believed due to two electrons trapped at a halide vacancy - the F' centre. At room temperature such bleaching results in the formation of a number of new bands, the M,N and R bands. It seems clear that these must be electron excess centre bands. These bands may also be produced by prolonged room temperature irradiation of the alkali halides. A number of complicated models have been proposed by various authors (Sitz,1954, Knox,1959, and Pick,1960), some being shown





KNOX



PICK



in figure 1.29. All these models are based on a common idea - they are aggregates of F centres and halide vacancies Recently Seidel (1963) has studied the electron spin and electron nuclear double resonance of the excited state of the M centre. We have already mentioned the difficulty of assigning an absorption to a given centre or model of a centre merely on the basis of optical absorption studies. This is especially so in the case of these aggregate centres: much of the experimental 'evidence' seems controversial. Thus the experiments of Seidel are very welcome. We shall not pursue the devious paths of the experimental evidence relating to these centres any further, since they have been fully plotted and charted by Compton and Schulman (1963).

A stage further in aggregation is reached when alkali halides are additively coloured with metal and then cooled slowly to room temperature (Siedentopf, 1905). Under these conditions colloidal metal is precipitated out in the crystal. The colloidal centres absorb light at a frequency characteristic of their size: the crystals will be red if the particles are small(0 - 20 mµ) through to blue for large particles( 40 - 80 mµ). These figures are from the calculations of Savostianova (1930) for sodium in sodium chloride, and using the classical theory of Mie(1908). Doyle (1958) and Hampe (1958) ascribe the absorption of light by the particles to plasma resonance of the conduction



electrons in the colloidal metal, (see also Jensen, 1963). Prior to the formation of the larger colloidal particles, which show Tyndall scattering, smaller centres, absorbing at about 550 mµ in sodium chloride, are formed. Some of argument exists as to their nature: whether they are 'atomically disperse' (Shatalov, 1959) or colloidal (Doyle 1960). It seems that the presence of a hydroxyl ion impurity in the alkali halide is necessary for their formation by  $\gamma$ - irradiation (Etzel, 1960). We should mention here that the spin resonance of the conduction electrons in the colloidal particles has been observed by Ingram and Doyle (1959) and by Kim, Kaplan and Bray (1960).

Before leaving the colour centres in pure alkali halides, we should mention the  $\alpha$  and  $\beta$  bands. These were found by Delbecq et. al.(1951,1952) near the absorption edge of potassium iodide (figure 1.210). They are believed to be perturbed exciton bands, the  $\beta$  band being due to an exciton in the neighbourhood of a halide vacancy, the  $\alpha$  band to an exciton near an F centre. We might mention here that photo-electric studies have indicated that excitons can interact with halide vacancies to give F centres and free holes( Apker and Taft,1950,51a,b,52, and Hebb 1951 and Philip and Taft,1956,1957).

The last type of centre found in the alkali halides and that we wish to mention here is the impurity centre. An impurity ion can perturb the usual colour centre found

in the pure alkali halide. Perhaps some of the past studies on the nominally pure alkali halides have, unwittingly, been studies of these effects! An example of such, is the A centre - an F centre in potassium chloride with a near neighbour sodium ion (Kojima et.al. 1961). We shall not dwell further on such effects. But the impurity itself, both before and after irradiation may give rise to a characteristic absorption in the spectrum.

The first such centre that we should mention is the U-centre: a hydride ion substituted for a halide ion. This can be converted to a number of other centres by irradiation.(Compton and Schulman,1963, have given many references to the literature on this subject).

A number of oxygen containing centres are known. Hydroxyl ion is a common impurity in crystals of alkali halides (Rolfe,1958,Otterson,1960, and Kerkhoff,1960). An  $0_2^+$  centre has been suggested by Ewles and Barmby(1956).  $0_2^-$  has been studied by e.s.r.(electron spin resonance) by Kanzig and Cohen(1959) and optically by Rolfe et. al. (1961).

Centres associated with a number of impurity cations have been studied. Introduction of the alkaline earth cations leads to new bands in an additively coloured crystal which has been subjected to various treatments. Similarly, X-irradiated crystals show such bands - Z bands.

There seems to be some contradictory evidence in the literature and no detailed picture can be given for the structure of these centres, although it seems clear that they are electron excess centres. Compton and Schulman (1963) have given a short discussion of the experimental evidence available.

Some impurity centres due to heavy metal cations have been studied. Divalent lead may be incorporated into the alkali halides and this leads to a characteristic absorption. This may be bleached by X-irradiation, which leads to colloidal lead formation, (Schulman et. al.1950).

A number of transition metal imputities have been incorporated into the alkali metal halides and centres formed by the trapping of electrons by the transition metal ions have been studied (Hayes et.al. 1958). Manganous ions in potassium chloride show interesting properties especially in the presence of divalent lead. Illumination into the absorption of the lead ions gives rise to luminescence of the manganous ion. This is termed sensitised luminescence(Klick and Schulman,1957, and Dexter,1953).

We shall now conclude this discussion of the colour centres in alkali halides with a short discussion of the centres associated with the monovalent ions cuprous, argentous and thallous. These ions can be incorporated substitutionally for the cations. Studies of the oscillator



a \_ KCl:Ag crystal at 77<sup>0</sup>K following X-irradiation at 77<sup>0</sup>K.

b - the same crystal after warming to 223<sup>0</sup>K
 for two minutes followed by cooling.

Figure 1.211

strengths and temperature dependence of the absorptions of the crystals so produced, indicate that they are atomic energy level transitions of the ions and of pairs of the ions. These centres show a strong luminescence and this has been extensively studied - especially that of the thallium centre. ( See Compton and Schulman, 1963 for extensive references on this subject). New centres are produced by X-or gamma-irradiation of the crystals - some of the silver centres have been definitely identified. The new optical absorptions produced have been examined by Etzel and Schuman (1954) and van der Vorst (1958). Recently Delbecq. et. al. (1963) have shown by combined optical and e.s.r. studies that at low temperature silver ions act as electron traps. Thus the irradiation produces silver atoms in the crystal. On warming the crystal a luminescence is observed at about 208°K. On cooling the crystal after luminescence has ceased, the resonance due to the silver atoms is found to have decreased slightly, the resonance due to the Cl<sub>2</sub> originally present ( these studies were made on sodium and potassium chlorides) has disappeared and a new resonance due to Ag<sup>++</sup> ions is now observed. By careful correlation of the optical absorptions and the e.s.r. and by bleaching experiments using polarised light, they were able to assign the various absorptions found in the crystal, as in figure 1.211.





Two interesting facts arise from these experiments. First, the  $Ag^{0}$  centre resonance indicates the delocalisation of the 5s electron onto the surrounding octahedron of chloride ions. Hence we have a  $d^{10}$ s transition metal complex. From the absorption bands Symons (1964) has concluded that the eg level of the octahedral complex lies below the t<sub>1u</sub> and a<sub>1g</sub> levels. This conclusion is contrary to the arbitrary assignments of energy levels in octahedral complexes which are often made and it may generally apply to such complexes. Secondly, at room temperature the  $Ag^{2+}$ centre is stable and thus the net photochemical process is

 $2 \text{ Ag}^+ = \text{Ag}^0 + \text{Ag}^{2+}$ 

The possibility arises that this process can occur in silver chloride and is in fact the basis of the latent image formation in the photographic process.

The studies we have discussed can conveniently be gathered together in a band energy level diagram for potassium chloride. This has been done in figure 1.212.

We shall now discuss some of the optical, electronic and defect properties of the silver halides. Many of the studies of the properties of the silver halides have been carried out with a view to elucidating the nature of the photographic process. The first point we should note is that their point defect properties are quite different from those of the alkali halides, although the chloride and bromide possess the sodium chloride structure.

We should mention that although the fluoride has the same structure as these salts, it is quite different in that it is solublelin water and in fact is deliquescent. Perhaps this latter fact and the resultant difficulty of handling it explain why so few studies of its properties have been carried out. We shall follow the general usage and in talking of silver halides imply the chloride, bromide and iodide, which though possessing a different structure from the other two salts resembles them in many of its properties.

Schottky defects, which predominate in the alkali halides, do not seem to occur to any great extent in the silver halides, which possess instead many Frenkel defects: i.e. interstitial silver ions, (see Seitz, 1951, Nicklow and Young, 1963, and Lawn, 1963). This difference is probably connected with the known more ionic character of the alkali halides. Nuclear magnetic resonance studies by Kanda (1955) and X-ray studies by Waidelich (1961) indicate that the silver halides have a considerable homopolar character. Resulting from the presence of Frenkel defects, a great freedom for diffusion through the lattice is found for the silver ion. This can be shown by radioactive tracer measurements and by the resultant large ionic conductivity (Friauf, 1962). The electronic band structure of these compounds

has been subjected to some close scrutiny in recent years.

29 n At although the experimental data is still relatively sparse. Brown (1962) has given a discussion of the data available and its probable interpretation. The conduction band structure is believed simple, i.e. with a minimum at k=0. from magnetoresistance measurements (Tippins and Brown, 1963) and cyclotron resonance studies (Ascarelli and Brown, 1962). The optical absorption of the silver halides has been studied by, amongst others, Okamoto(1956), Moser and Urbach (1956), Brown, Masumi and Tippins(1961), and Cardona (1963). Brown and co-workers found it possible to interpret their results on the basis of the above band structure. The silver and alkali halides show very similar structure in their ultra-violet absorption, and the bands first occurring in both are ascribed to excitons. In both cases absorption occurs at energies below the band gap. This gap is quite small for the silver halides - about 5eV. Ultra violet illumination of the silver halides at low temperature leads to a luminescence (see Mitchell, 1957). Various models have been proposed for this process, but Brada and Mardix (1960) claim that pure vacuum grown crystals show no such luminescence and that an oxygenty impurity in the samples of previous. workers caused the observed luminescence.

Absorption of blue light in the silver halides, leads to the formation of centres which sensitise the crystal to chemical reduction. This is, of course, the basis of the

photographic process. There is still some controversy over the mechanism by which such centres - latent image centresform in the microcrystals of the photographic emulsion. Reference may be made for the details of this controversy to the articles by Berg(1962), Mitchell(1957 and 1962), Hamilton and Brady(1962) and Kröger(1964). However, it seems clear that the Gurney-Mott theory (1938) forms the basis of modern discussion. The essential idea of these authors is that the light absorption produces photo-electrons. These are then trapped at sensitivity specks - which they postulated to be, in the case of sulphur sensitised emulsions, silver sulphide. This centre of negative charge attracts Ag<sup>+</sup> interstitials, which readily diffuse through the lattice to it, and are then 'neutralised' to form Ag<sup>0</sup>. By a cycle of such events, more silver is formed. It now seems doubtful whether silver sulphide would act as an the b electron trap: its importance is understood when two points due to Mitchell(1957) are noted. First, he was able to demonstrate that continued exposure to light results in print out of colloidal silver along dislocation lines in the silver halide crystal. This seems to imply that points such as kinks or jogs act as formation points for the latent image. Secondly he pointed out that Gurney and Mott had neglected to consider the photo-holes which must be produced at the same time as the electrons. Clearly an efficient hole trapping site must be present or they will

recombine with the electrons. This is the role assigned to the silver sulphide in the Mitchell theory.

Perhaps at this point we should mention the rather unsatisfactory methods of studying latent image formation, Most work in the past has been based on photographic evidence, i.e. studies of the development of the latent image or of the developed latent image. In fact, most of the evidence produced for its structure and other properties has been obtained by its destruction. We shall not attempt to review experimental methods here: Berg (1962) gives a clear discussion and many references.

On the other hand most of the knowledge of electronic and defect properties of the silver halides has been obtained from measurements on large single crystals. This knowledge is used in the interpretation of the experiments on latent image formation. Mitchell (1957) has used such evidence as the basis of a detailed theory of latent image formation. In particular, we may mention his use of ionic conductivity data to deduce the number of interstitial silver ions in a photographic emulsion grain. His deductions now seem incorrect in the light of the results of Hamilton and Brady (1962). We shall not attempt a detailed criticism of Mitchell's theory here (see the articles quoted and Urbach, 1960).

Before closing this section, mention should be made of the work of Palma et al.(1960,1963). These workers

following earlier experiments by Tucker(1958), have shown by electron spin resonance that cuprous ions in silver chloride act as hole traps on illumination, i.e. form Cu<sup>++</sup>. These ions are known to intensify the print out of silver in silver chloride (Clark and Mitchell,1956). This seems to be evidence in favour of Mitchell's theory, but the claims of these workers to have demonstrated that first holes are trapped and then electrons, does not seem valid, since they did not perform any rate experiments.

## The Principles of Electron Spin Resonance, Section 1.3.

In this section we shall consider the factors which may contribute to the energy of a paramagnetic substance placed in a magnetic field. We shall do this without too much detail, since extensive and clear discussions are given elsewhere: Bleaney and Stevens, 1953, Bowers and Owen, 1955, Bagguley and Owen, 1957, Griffith, 1961, Slichter, 1963, Pake, 1962. We shall only briefly mention such topics as line shape and spin lattice relaxation.

Many substances are paramagnetic. The classical explanation of this phenomenon on a microscopic basis was given by Langevin, who supposed such a substance to possess many microscopic magnetic dipoles, which tended to orient in the presence of an external magnetic field. He was thus able to derive Curie's law:

## $\chi = C/(T - \Theta),$

X is the susceptibility, C the Curie constant, T the absolute temperature, and  $\Theta$  a constant.

Quantum theory has enabled us to understand the basis of this in great detail. Some substances possess unpaired electrons and it is these electrons which can be identified with Langevin's dipoled. Each electron possesses a spin, associated with which there is a magnetic moment. Often, however, the electron will be in a state which possesses orbital momentum and this may couple with the spin to produce a different magnetic moment. If we take, for example, a transition metal ion

such as Ti<sup>3+</sup>, then in the free state its odd d electron will have its orbital and spin moments coupled. But in a crystal the surrounding ions will compete with the nucleus: their coulombic field will also in part determine the state of the system. It is immediately apparent that if we can measure the apparent moment of the electron, then we will have some information about the field provided by the ions - the so-called crystal field. But this information needs interpretation. Similar considerations will apply to odd electrons trapped in solids.

So far our picture is simple, but other effects are present. Firstly there is an isotropic hyperfine interaction when the electron has a finite probability density at the nucleus. This, of course, implies some s-state character of the eigenstate of the electron, although this can arise also from polarisation of other electron orbits. And further interactions occur, leading to a fairly complex picture. The natural description of this is in terms of energies and their associated quantum mechanical operators (see Dirac,1958 or Mandl,1957). This will be done after a short description of the resonance phenomenon. The resonance phenomenon.

If we place a sample containing ions, molecules or defect sites containing one or more unpaired electrons, in an external static magnetic field, then the electrons may exist in various spin states of different energies.



Figure 1.301

Application of radiation of the correct frequency and in an appropriate manner may then cause transitions between the energy levels. This process may be viewed semiclassically. On applying the external static field, H, the angular momentum vector (in general largely comprising the spin) will precess around the field axis with angular velocity,  $\omega = g(\xi/2mc)$  H, where g is the spectroscopic splitting factor (Kittel, 1949). If a circularly polarised magnetic field is applied such that it rotates about H in synchronisation with the spin angular momentum and thus its magnetisation vector, a constant couple acts on this vector and may cause the spin to'flip' over and change its projection on H. In the quantum view, the projections of angular momentum J ( which is integral or half integral) on H are limited to half-integral or integral values:  $M = J, J - 1, \dots, J - J, - J$ . Such a transition will occur between states of differing energy g/H - the selection rule for this magnetic dipolar transition being  $\Delta M = \pm 1$ . This will occur when the incident radiation has the frequency  $\lambda = g\beta H/h$ , which is equal to the precession frequency.

Usually, experiments are carried out at frequencies of 300 Mc/s to 30,000 Mc/s. For 300 Mc/s ultra high frequency radio techniques are used, and these have advantages for some purposes over the microwave techniques necessary at higher frequency, Three factors affecting



Figure 1.303

sensitivity may be mentioned here: at higher magnetic fields the energy levels are further apart and hence the lower level is more heavily populated, but a higher radio-frequency is needed and the electronic techniques become more difficult and the resonant cavities become smaller so that less sample may be used. X-band (10,000 Mc/s) is the most widely used this frequency, the field is then about 3,000 gauss, and this is about the optimum for sensitivity in most cases.

So far we have seen that in, for example, a state with  $S=\frac{1}{2}$ , L = 0,  $J = \frac{1}{2}$ , one resonance would occur: we represent this in figure 1.301. Thus in the experiment the field is swept through the resonance and the energy is absorbed when the energy splitting equals h, a being the frequency of the radiation. Other absorptions are, however, found. The first we will mention is the fine structure effect. Consider an ion with S = 3/2. In a crystal an axial electric field may exist and this could split the four levels of different  $M_{g}$ , into pairs of doublets  $M_s = \frac{+1}{2}, \frac{+3}{2}$  - it is known that no further splitting can occur (Kramer's theorem, which states that in an odd electron system, in the absence of a magnetic field, the degeneracy is even). An energy level diagram can be drawn as in figure 1.302. Three absorptions, at different fields, now occur. The initial divergence of the levels is uniform in our diagram, implying the same axis for the



Figure 1.304

magnetic and the electric field, otherwise the divergence will not be uniform. The central lines are more intense, since they are due to transitions for which the projection of the magnetic moment on the radio frequency magnetic field is greatest.

If the electron responsible for the resonance is associated with a nucleus possessing a magnetic moment, further 'Hyperfine' structure may be observed in the spectrum obtained by sweeping the field. The nuclear moment orientation will be quantised: for nuclear spin I we have 2I + 1 orientations or  $M_T$  values. Each provides a different field for the electron so 2I + 1 absorptions are seen. In fact there are two parts of this effect. The first is an anisotropic effect, the nucleus simply acting as a magnetic dipole, this will average to zero for samples containing species in many different orientations. Secondly, there is an isotropic interaction due to the contact or Fermi interaction of the electron with the nucleus - this only occurs for electrons in orbitals having some s character. If the field, H, is large relative to the nuclear field, then the 2I+1 lines are equally spaced and of equal intensity ( the selection rule  $m_T = 0$  applies). For fields of the order of the hyperfine splitting, the lines are not equally spaced states with differing mare mixed - so that 'forbidden' transitions are seen.

A further effect which gives rise to forbidden lines is found in the case of nuclei possessing quadrupole moments and at which there is an electric field gradient. The quadrupole moment will tend to precess around the electric field axis, thus when <u>H</u> and grad <u>E</u> ( the gradient of the electric field ) are not parallel the various nuclear states are again mixed. This effect, which unfortunately is often too small to be observed, may allow a measure of the quadrupole moment or the field. gradient.

Suppose we have the electrons associated with some atomic nucleus in a crystal placed in an external magnetic field. Then we can write down the Hamiltonian or energy operator for the system. It contains a number of terms:-1). The coulombic interaction of the electrons with the nucleus and with themselves:

$$\sum_{k} \left( \frac{p_{k}^{2}}{2m} - \frac{Z\varepsilon^{2}}{T_{k}} \right) - \sum_{j>k} \frac{\varepsilon^{2}}{T_{jk}}$$

In the case of molecules two or more nuclei may be involved and in some cases, such as F-centres many nuclei are involved.

2). The magnetic interaction between the electron spins and orbits:

 $\sum \left\{ a_{jk} e_{j} \cdot s_{k} + J_{jk} e_{j} \cdot e_{k} + c_{jk} s_{j} \cdot s_{k} \right\}$ 

This is given here in the simple cosine law for two vectors

as given by Van Vleck (1932). Other forms are possible: for example, dipoles interact classically with an energy  $r^{-3}(1 - 3\cos^2\theta)$ , and so Pryce (1950) uses a spin-spin interaction of the form:

$$\sum 4\beta^{2} \left[ \frac{\underline{s_{j}} \underline{s_{k}}}{\underline{r_{jk}}} - \frac{3(\underline{f_{jk}} \underline{s_{j}})(\underline{f_{jk}} \underline{s_{k}})}{\underline{r_{jk}}} \right]$$

3). The interaction with the external magnetic field:

$$\sum_{\substack{k \in h \\ 4\pi me}} (\underline{l} + 2\underline{s})_{k} \cdot \underline{H} = \beta (\underline{l} + 2\underline{s}) \cdot \underline{H}$$

For accurate work the factor 2 before  $\underline{s}$  should be 2.0023 (the gyromagnetic ratio).

4). The interaction (if any) with the magnetic nuclei and the electronic orbital and spin magnetism:

$$2 \gamma \beta \beta_{N} \sum_{k} \left[ \frac{\left( \frac{l_{R} - \underline{s}_{R}}{T_{R}^{3}} + \frac{3(\underline{r}_{R} \cdot \underline{s}_{R})(\underline{r}_{L_{R}} \cdot \underline{I}_{R})}{T_{R}^{3}} + \frac{8\pi}{3} \delta(f_{R}) \underline{s}_{R} \cdot \underline{I}_{R} \right] \right]$$

This is obtained from the Dirac theory of the electron (Fermi, 1930). The first two terms in the brackets comprise the usual dipolar interaction, which averages to zero in a powdered solid or in a liquid. The last term is the contact, isotropic term which only exists for electrons having s character.

5). The electrostatic interaction between the electrons and nucleus not included in (1), in effect the quadrupole interaction (see Bleaney and Stevens, 1953, for details).

$$V_{Q} = \frac{\varepsilon^{2}Q}{2I(\mathbf{I} + 1)} \sum_{j} \left\{ \frac{I(\mathbf{I} + 1)}{\tau_{j}^{3}} - \frac{3(\tau_{j} \cdot \underline{I})^{2}}{\tau_{j}^{5}} \right\}$$

6). The interaction of the nuclear magnetic moment with the external field:

## - YBN H.I

We have ignored, so far, the importance of neighbouring groups. These may give rise to an electric field - the crystal field  $V_x = V(x_j y_j z_j)$ . This was first treated by Bethe (1929) and Van Vleck (1932). Its importance will, of course, depend on its order of magnitude compared to the other terms. Three cases are usually discussed:l.Where some covalent bonding to the neighbouring groups occurs and the nucleus-electron interaction is larger than the crystal field which is larger than the electronelectron interaction.

2.Where the coulomb interactions are greater than the crystal field which is greater than the spin-orbit coupling.

3.Where the crystal field is only greater than the nuclear interactions.

Since this theory has been well reviewed in recent times (e.g. Ballhausen, 1962) we shall not go into great detail.

The coulombic forces between the nucleus and electrons and between the electrons are treated by the standard methods such as the self-consistent field method to obtain the energies of the various terms, e.g.  ${}^{4}$ F of a  $3d^{3}$  transition ion. Now perturbation theory is applied.

The actual calculation will depend on the order of magnitude of the various terms. For the iron group transition metal ions, the crystal field is the next largest term - of order  $10^4$  cm<sup>-1</sup> The spin-orbit term is of order  $10^2$  cm<sup>-1</sup>, and the spin-spin term of order lcm<sup>-1</sup> Finally, the Zeeman term  $\beta \underline{H} \cdot (\underline{L} + 2\underline{S})$  is of order lcm<sup>-1</sup>, and the nuclear terms are much smaller - the hyperfine splitting is of order  $10^{-2}$  cm<sup>-1</sup> and the nuclear Zeeman term  $\beta \underline{H} \cdot \underline{I}$  of order  $10^{-3}$  cm<sup>-1</sup> We should note that the perturbation theory appropriate to degenerate states should be applied.

For the crystal field, the method is as follows. Assuming the potential satisfies Laplace's equation, it can be expanded in spherical harmonics:

$$V = \sum_{mn} A_n^m r^n Y_n^m(\Theta, \phi).$$

The harmonics present will depend on the 'crystal'symmetry, and the expansions for simple symmetries are quite short. For example, for octahedral symmetry:

$$\mathbf{V} = \mathbf{D}_{4}\mathbf{r}^{4} \left\{ \mathbf{Y}_{4}^{0}(0, \mathbf{\phi}) - \sqrt{\frac{10}{7}} \left[ \mathbf{Y}_{4}^{3}(0, \mathbf{\phi}) + \mathbf{Y}_{4}^{-3}(0, \mathbf{\phi}) \right] \right\}$$

In cartesian coordinates these harmonics become simple polynomials. Thus the octahedral potential becomes:

$$\mathbf{V} = \mathbf{C}_{4} \mathbf{L} \mathbf{x}^{4} + \mathbf{y}^{4} + \mathbf{z}^{4} - (3/5)\mathbf{r}^{4} \mathbf{J}.$$

Now the secular equation is set up: its elements are integrals or matrix elements of the form  $\langle m | \sum_{j} - \epsilon V(x_{j}, y_{j}, z_{j}) | m \rangle$ 

This will, therefore, involve the finding of matrix elements of polynomials in x,y, and z, which is simplified by the operator equivalent method of Stevens (1952). It can be shown that the matrix elements of terms in x,y,z are proportional to those in which  $L_x, L_y, L_z$  replace x,y,z. But since the components of angular momentum do not commute, it is necessary to replace terms such as xy by  $\frac{1}{2}(L_xL_y + L_yL_x)$  and similarly for other products. The proportionality constants are obtained by evaluating a simple case. This procedure is aided by the tables of operator equivalents which have been given by Stevens.

The next stage in the perturbation treatment is of great importance. It leads to the so-called Spin Hamiltonian due to Pryce (1950), and Abragam and Pryce(1951), which is the meeting point of theory and experiment. The terms in the Hamiltonian above can be re-written in a more convenient form. This was done by Abragam and Pryce and is fully discussed by Bleaney and Stevens (1953). The result is of the form:

$$\frac{4}{4} = V_{+} (\lambda - \frac{1}{2}\rho)(\underline{L} \cdot \underline{S}) - \rho(\underline{L} \cdot \underline{S})^{2} + \beta \underline{H} \cdot (\underline{L} + 2\underline{S})$$

$$+ p[(\underline{L} \cdot \underline{I}) + \{\underline{S} L (L + 1) - k\} \underline{S} \cdot \underline{I} - \frac{3}{2} \underline{S} (\underline{L} \cdot \underline{S}) \underline{L} \cdot \underline{I}) - \frac{3}{2} \underline{S} (\underline{L} \cdot \underline{I}) \underline{C} \cdot \underline{S}) ]$$

$$+ q' \{ (\underline{L} \cdot \underline{I})^{2} + \frac{1}{2} (\underline{L} \cdot \underline{I}) \} - \gamma \beta_{N} (\underline{H} \cdot \underline{I})$$

V denotes any crystal field not yet considered.

Now the perturbation calculation may be carried out. In fact it is usual to do this in two stages. First,

following Pryce (1950) no representation is chosen for  $\underline{S}$  or  $\underline{I}$ , so that an expression containing these is obtained. (This method is applied where the ground state is an orbital singlet). This is the so called spin Hamiltonian. This general case can, then, be applied to any situation being studied experimentally with relative ease. The final stages of the perturbation - from this Spin Hamiltonian to the energy levels - being carried out by the experimenter. A simple case will be studied as an illustration, taking the perturbation:

$$\mathbf{A}' = \beta \underline{H} \cdot (\underline{L} + 2\underline{S}) \cdot + \lambda \underline{L} \cdot \underline{S} + A \underline{I} \cdot \underline{S}$$

|0) represents the ground orbital state,  $|n\rangle$ , n = 1,2,3...the excited states. The ground orbital state is nondegenerate, so applying first order perturbation theory we want  $\langle 0|A'|0 \rangle = \langle 0|\beta H.(\underline{L}+\underline{95}) + \lambda \underline{LS} + A\underline{1S}|0 \rangle$ Since they contain no orbital operators the terms  $\langle 0|\beta \underline{H}.2\underline{S}|0 \rangle$  and  $\langle 0|A\underline{I}.\underline{S}|0 \rangle$ 

give  $2\beta \underline{\mathbb{H}} \cdot \underline{\mathbb{S}} + A\underline{\mathbb{I}} \cdot \underline{\mathbb{S}}$ Now the 'orbital' term  $\langle 0|\beta \underline{\mathbb{H}} \underline{\mathbb{L}} \cdot \lambda \underline{\mathbb{S}}|0 \rangle$  in cartesian form is  $\sum_{xyz} (\beta \underline{\mathbb{H}}_i + \lambda \underline{\mathbb{S}}_i) \langle 0|L_i|0 \rangle$ , which vanishes as the last term is zero -  $L_i$  either destroys  $|0 \rangle (L_z)$  or shifts it to an excited state  $(L_x)$ . Proceeding to second order we require  $-\sum_{x \in [0, ||\mathbf{N}||^2} \frac{|\mathbf{N}|^2}{|\mathbf{N}|^2}$ 

Since  $\langle 0 | n \rangle$  is zero, terms not involving orbital operators vanish. The orbital terms become

$$-\sum_{\substack{n\neq 0}} \left| \sum_{\substack{xyz}} (\beta H_i + \lambda S_i) \langle 0 | L_i | n \rangle \right|^2$$

The matrix elements  $\langle o | L_i | n \rangle$  have to be calculated in a particular case, but we can note that the result will be quadratic in the components of <u>H</u> and <u>S</u> and of the form

$$-\beta^2 \Delta_{ij} H_i H_j + \beta f_{ij} H_i S_j + d_{ij} S_i S_j$$

Collecting terms:  $A_s = \beta(2\delta_{ij} - f_{ij}) H_i S_j + A \underline{I} \cdot \underline{S} + \beta \underline{\Lambda}_{ij} H_i H_j + d_{ij} S_i S_j$ Which may be written

$$\mathcal{H}_{s} = \beta \underline{\mathbb{H}} \cdot \underline{g} \cdot \underline{S} + A \underline{I} \cdot \underline{S} - \beta^{2} \underline{\mathbb{H}} \cdot A \cdot \underline{\mathbb{H}} + \underline{S} \cdot D \cdot \underline{S}$$

 $g = 2\delta - f$ ,  $\Lambda$  and D are tensors. For the general perturbations and assuming spin-spin and electron nuclear interactions need be taken only to first order, the Spin Hamiltonian is

$$\mathcal{J}_{s} = \beta \underline{H} \cdot g \cdot \underline{S} + \underline{S} \cdot \underline{T} \cdot \underline{I} + \underline{S} \cdot \underline{D} \cdot \underline{S} + \underline{I} \cdot \underline{P} \cdot \underline{I} - Y \beta_{\mathsf{N}} \underline{H} \cdot \underline{I} - \beta^{2} \underline{H} \cdot \underline{\Lambda} \cdot \underline{H}$$

The spin Hamiltonian will reflect the symmetry of the paramagnetic species. Often this will possess axial symmetry and then we can write  $g_x = g_y = g_L$  and  $g_z = g_{\parallel}$ .

Thus for a tetragonal or trigonal crystal field around a paramagnetic ion:

$$\begin{aligned} H_{s} &= \beta \left[ g_{\parallel} H_{z} s_{z} + g_{I} (H_{x} s_{x} + H_{y} s_{y}) \right] + A I_{z} s_{z} + B (I_{x} s_{x} + I_{y} + s_{y}) \\ &+ D s_{z}^{2} + P I_{z}^{2} - \gamma \beta_{N} H \cdot I + \beta^{2} H \cdot \Lambda \cdot H \end{aligned}$$

The first term represents a physical behaviour which can be pictured in two ways. Either the electron can be thought of as free, but precessing around a field  $(g_{\mu}H_{\chi},g_{\mu}H_{\chi},g_{\mu}H_{\chi},g_{\mu}H_{\chi})$ or as having an anisotropic moment  $(g_{\mu}S_{\chi},g_{\mu}S_{\chi},g_{\chi}S_{\chi})$ . Similarly, the terms in I.S and the quadrupole term  $PI_{Z}^{2}$ are anisotropic. The last term may be neglected as an added constant, not dependent on <u>I</u> or <u>S</u>.

At this point we may mention two theorems. Kramers (1930)(see also Griffith,1961) showed that in the absence of a magnetic field, if a system contained an odd number of electrons, it is evenly degenerate. Jahn and Teller (1937) showed that, apart from linear species, a complex having a degenerate ground state will distort in such a way that the degeneracy is removed, since it can so reduce its energy. Bleaney and Stevens (1953) have discussed the general features of the Spin Hamiltonian of transition ions having an orbitally degenerate ground state, on the basis of these two theorems. Longuet-Higgins and Carrington (1960) have given a detailed account of the application of these theorems to the case of  $Ti^{+3}$ . For further details reference may be made to these two reviews.

Two points arise which are of interest. The higher states having orbital momentum can mix in with a ground orbital singlet level an so give rise to a 'g shift'. This fact is already implicit in the theory we have described, but is shown very clearly in the review by Longuet-Higgins and Carrington. The second is the anomalous



hyperfine structure: thus a large isotropic hyperfine structure is found for  $Mn^{+2}$  (3d<sup>5</sup>,<sup>6</sup>S). This is interpreted as a configurational interaction of terms such as 3d<sup>5</sup>3s4s arising from the term  $\sum_{ij}^{i} r_{ij}$  in the Hamiltonian.

Such an effect has often been found.

A further effect is the hyperfine interaction from surrounding ions (Stevens, 1953). The electron may be in an orbital which is best described as a molecular orbital having some orbital content from the surrounding ions, i.e. the electron is delocalised onto the ligands. Then, if the surrounding ions possess a hyperfine interaction, this may split the observed line into a number of components. A recent example is the electron spin resonance of silver atoms trapped in potassium chloride. The silver has two isotopes each of spin half, so we expect two hyperfine components for each, separated by about 600G. In fact the surrounding six chloride: ions give rise to a further splitting, and nineteen lines are expected instead of each silver hyperfine component, (figure 1.305).

The importance of the Spin Hamiltonian is that it enables the experimental results to be reported in shorthand form, even though its application to a particular case may be difficult. Unfortunately, authors often state that they have fitted their results to a Spin Hamiltonian, without giving even an outline of the calculation they have carried out. In some cases explicit






formulae for the energy levels derived from a Spin Hamiltonian have been given (e.g. Bleaney,1951). Even for the simple case of an isotropic nuclear interaction quite complex formulae may result. For the Spin Hamiltonian

# $\mathcal{J} = \beta \underline{H} \cdot \underline{g} \cdot \underline{S} + A \underline{I} \cdot \underline{S} - \gamma \beta_{v} \underline{H} \cdot \underline{I}$

the last term may be neglected, usually, and if the first term is much greater than the second (e.g. a hyperfine splitting of thirty gauss and a field of three thousand) the perturbation treatment is simple. Absorption lines are found A/2 gauss each side of the field given by  $g_{\beta}H = h \partial$ , as in figure 1.306. For larger hyperfine splittings it is necessary to carry out the perturbation for both terms simultaneously. Formula for the energy levels in this case have been given by Breit and Rabi (1932, see also Ramsgy,1956) and by Hanna and Altmann (1962).

In the simplest cases the parameters in the Spin Hamiltonian can be deduced from the spectrum obtained from a powdered or glassy sample. The spectra to be obtained in such cases and their interpretation have been discussed by various authors (e.g.Kneubthl,1960). Figure 1.307 shows some of the line shapes to be expected. More complex cases can sometimes be analysed by the use of a second spectrum at a different microwave freqency. Hyperfine effects will be much the same at both frequencies whereas g value effects depend on the field and will change. Single crystal spectra are often used. The analysis and interpretation of the data so obtained is quite complex. Several methods exist e.g. those of Geusic and Carlton Brown(1958), and Weil and Anderson (1958). Schonland gives a simplified method (1959).

So far we have been following the theory for isolated ions or molecules, but have not mentioned a large class of paramagnetic substances: the conductors and semiconductors. In these substances the paramagnetism may be associated with the free electrons in conduction bands. The theory in this case becomes difficult: the magnetic field applied to the specimens can have a large effect on the energy of the bands and perturbation theory may not be applicable. We shall not delve into the theory to any extent, but will mention some salient points. Yafet(1963) has written a review of this subject, which contains many formulae, but which is most useful for its references to the original papers and for results.

As with the 'isolated' ion case, the total magnetic moment is the sum of an orbital part and a spin part:

$$\mu = - \beta(\underline{L} + 2\underline{S}).$$

Now from the band theory, for electrons at the band edge:

# ħL = X x π

where  $\mathbf{T}$  is a momentum operator and  $\mathbf{X}$  a periodic coordinate operator, which is inversely proportional to the band gap.



 $T_{\rm D}$  = diffusion time  $T_{\rm Z}$  = spin - lattice relaxation time Figure 1.309



W = probability for spontaneous change.

So for a small gap, a very large L may result and hence very large g values: for indium antimonide Bemski (1960) found  $g \div 50$ . For the metals in which resonance has been observed, g values close to the free spin value have been obtained. A further point of interest is the line shape. Unusual line shapes are found when the samples used are thicker than the skin depth of the material at the microwave frequency being used. Two factors give rise to this. First, the microwave amplitude and phase will be different at different depths in the material. Secondly, spins can diffuse out of the oscillating field. The theory was first treated by Dyson (1955). Asymmetric line shapes are expected, as in figure 1.308, depending on the time it takes for the spin to diffuse out of the field. This fact gives, of course, a method of recognising the resonance due to conduction electrons.

At this point we are approaching experiment and real absorptions closely, so that we may briefly stop to consider some factors affecting line shapes and widths. A simple analysis will help us. Consider the simple system represented in the diagram, 1.309. Consider the equilibrium in the absence of the oscillating field. The rate of change of the spins can be written:-

$$\frac{dN_{-}}{dt} = N_{-}W_{\uparrow} - N_{+}W_{\downarrow} = 0$$

At the steady state  $W_{\downarrow}/W_{\downarrow} = N_{+}/N_{-} = \exp(-E/kT)$ 

Application of the appropriate oscillating field will tend to disturb this equilibrium, the transition probability  $V_{\uparrow} = V_{\downarrow}$  in this case (see Pake,1962), hence  $N_{+}$  will tend to equal N\_. Should this occur the system is said to be saturated: no more microwave energy is absorbed and so no resonance is observed. Normally, however, the spontaneous change occurs, whereby the spin system exchanges energy with the lattice vibrations. Thus, by this spinlattice relaxation, saturation is prevented. There is a characteristic time associated with this as may be seen from our simple rate equation. If the system is disturbed the return to equilibrium is given by:

$$\frac{\mathrm{dn}}{\mathrm{dt}} = \mathrm{N}(\mathrm{W}_{1} - \mathrm{W}_{2}) - \mathrm{n}(\mathrm{W}_{3} + \mathrm{W}_{2}).$$

Where  $N = N_{+} + N_{-}$  and  $n = N_{+} - N_{-}$ . Putting  $n_{0} = N(W_{\downarrow} - W_{\uparrow})/(W_{\downarrow} + W_{\uparrow})$  and  $T_{1}^{-1} = W_{\downarrow} + W_{\uparrow}$ 

we have  $\frac{dn}{dt} = \frac{n_0 - n}{T_1}$ .

Solving  $n = n_0(1 - e^{-t/T_1})$ Thus we see that  $T_1$  is a characteristic time for the return of the system to equilibrium: it is known as the spin-lattice relaxation time.

We have mentioned previously in this section, how a rotating field synchronous with the spins could tip them over. This view can readily be put on a quantitative basis which was first done by Bloch(1946).

By analogy with our simple picture above, we expect the magnetisation of the sample along the direction of the static field to be described by the equation:

$$\frac{\mathrm{d}M}{\mathrm{d}t}\mathrm{z} = \frac{\mathrm{M}_{\mathrm{O}} - \mathrm{M}_{\mathrm{Z}}}{\mathrm{T}_{\mathrm{I}}} \cdot$$

In fact there is another factor in  $M_Z$  owing to the fact that the oscillating radio frequency magnetic field produces a varying magnetisation. This can be derived using Heisenberg's equation of Motion (Mandl,1957,p100)

$$ih \frac{dA}{dt} = [A_t, A]$$

Now for angular moment  $I_z$  in the field H, the Hamiltonian operator  $\mathcal{A} = -\mathcal{J} \operatorname{\tilde{h}HI}_z$ , hence

$$\frac{dI}{dt} = \frac{i}{t} [\mathcal{A}, I_{x}]$$

$$= -\gamma H_{0} i [I_{2}, I_{x}]$$

$$= \gamma H_{0} i [I_{2}, I_{x}]$$

$$I_{y} = -\gamma H_{0} I_{x}, \quad \dot{I}_{z} = 0$$

$$\frac{dI}{dt} = I \times \gamma H$$

In vector form

Similarly

dt

Remembering  $\underline{M} = \gamma \underline{h} \underline{I}$ , we can now write

$$\frac{\mathrm{d}\mathbf{M}}{\mathrm{d}\mathbf{t}^{\mathrm{Z}}} = \frac{\mathbf{M}_{\mathrm{O}} - \mathbf{M}_{\mathrm{Z}}}{\mathbf{T}_{\mathrm{I}}} - \mathbf{i} \left( \mathbf{M} \times \mathbf{H} \right)_{\mathrm{Z}}$$

In addition transverse relaxation equations are intro- $\frac{dM}{dt}x, y = \gamma(\underline{M} \times \underline{H}_1) - \frac{\underline{M}x}{T_2}, y$ 

 $H_{I}$  is the oscillating field.  $T_{J}$  is the transverse relaxation







time, which conserves energy in the static field. It is often associated with spin-spin energy exchange.

For small  $H_1$ , solutions of the Bloch equations can be obtained (Pake,1962,p 28). An important fact becomes apparent: the magnetisation can be regarded as constant in a rotating reference frame. Normally the resonance experiment, in effect, measures the magnetisation along Ox. Hence  $M_x(t) = (\chi' \cos \omega t + \chi'' \sin \omega t) H_{\chi 0}$ , where  $M = \chi H$ and  $H_x(t) = H_{\chi 0} \cos \omega t$ . So that there are two parts of the magnetisation. One - the dispersion - is in phase with the magnetic field; the other - the absorption - is out of phase with the magnetic field. (See figures 1.310, 1.311). Furthermore, it is possible to show that for small  $H_1$ 

$$\Delta \omega_{\frac{1}{2}} = 1/T_2$$

Usually resonance is observed in absorption.

We now mention some factors which affect the intensity of a line. The population difference between the upper and lower states can be increased by lowering the sample temperature. This does not apply in the case of conduction electrons, where cooling aids pairing, the electrons following Fermi-Dirac rather than Bose statistics. Thus another method of distinguishing the resonance of conduction electrons is apparent. Comparison of the unknown signal against the signal of a standard free radical sample, e.g. charred dextrose, at say room temperature and

and a lower temperature, e.g. 77°K, tells us if the unknown sample shows a conduction electron signal. If it does, its signal will decrease on cooling with reference to the standard: in fact the standard increases in intensity and the conduction signal decreases slightly.

The cooling of the sample may be absolutely necessary if the spin lattice relaxation time of the sample being studied is short. Then the excited state is short lived and its energy becomes 'smeared out' according to the Uncertainty Principle:  $\Delta E. \Delta t = \%$ Cooling will extend the life of the excited state by

'Smearing'of the energy levels can arise also from exchange interactions of neighbouring paramagnetic centres - thus it is often necessary to grow magnetically dilute crystals. In the case of centres produced by radiation damage, this is no problem - so few centres are produced usually.

removing the higher energy lattice vibrations (phonons).

We have not discussed here such matters as line shape theories, and transition probabilities. The books by Pake and by Slichter.discuss these matters.

We should not leave the subject of e.s.r. without mentioning the electron nuclear double resonance (ENDOR) technique of Feher (1956). Sometimes in solid state work the e.s.r. signal is very broad and lacking in information, therefore, on the centre. A typical example



Figure 1.312

is the F-centre resonance in alkali halides. The ions surrounding the anion vacancy give rise to hyperfine splittings which overlap and so produce an unresolved line width of the order 50 gauss, at half height. Kip, Kittel, Levy and Portis (1953) by comparing the signal from <sup>59</sup>KOl and <sup>41</sup>KCl were able to deduce the hyperfine splitting from the near neighbour potassium ions. Feher's method allows the direct determination of this quantity to great accuracy and, furthermore, allows determination of the corresponding quantity for other shells of ions. The method can be understood from the diagram of the energy levels for a system with  $I = \frac{1}{2}$ ,  $S = \frac{1}{2}$  (figure 1.312). The electron resonance  $(h \partial_e)$  is saturated and then a radio frequency field applied and the frequency slowly swept. When the energy of the applied r.f. is equal to the difference between the hyperfine levels, it will'flip' the nuclear spins and so de-saturate the e.s.r. signal which will then be observed. This will occur when

$$h v_n = \frac{1}{2} A + g_n \beta_n H.$$

Where A is the appropriate hyperfine splitting and H the static magnetic field.

#### Radiation and Matter. Section 1.4.

#### 1.41. Electronic Absorption Spectra.

When a substance absorbs light in the visible or ultra-violet regions of the spectrum, a change usually occurs in the energy of the electronic system of the substance. Often we think in terms of single electrons being promoted in an orbital energy level scheme of a molecule or from a lower to a higher band in a solid, in both cases such that the energy change in the system.  $\Delta E = h \partial$ , where  $\partial$  is the frequency of the light absorbed. The extent to which a system will absorb such radiant energy is determined by selection rules and measured in the first instance by an extinction coefficient. Beer's law (1852) states  $\ln I_0/I = \epsilon cd$ , where I is the transmitted and I<sub>o</sub> the incident intensity of radiation, c the concentration (usually in mole/litre) of absorbing substance in the path of length d( usually in cm.), and e the extinction coefficient. If a molecule of cross sectional area a  $\stackrel{O2}{A}$  absorbs a quantum of light incident upon it, with a probability p, then it can be shown (Braude, 1950) that  $\boldsymbol{\epsilon}_{\max} = 10^{4} pa$ ,  $\boldsymbol{\epsilon}_{\max}$  being the extinction coefficient at the band maximum. In fact solvent effects, for example, may broaden the band, so that the extinction coefficient at the band maximum is not a good measure of the strength of the absorption, rather the integrated extinction coefficient is a good measure. The strength of a band may be

indicated by talking of its oscillator strength, f, which in the classical theory of vibrations is the number of oscillators of mass, m (electronic) and charge  $\boldsymbol{\varepsilon}$  giving rise to the band. In the case of smooth symmetrical bands it can be obtained to a good approximation by measuring the maximum extinction coefficient and the band width at half height,  $\Delta \boldsymbol{k}$  (cm<sup>-1</sup>) :

$$f = 2.2 \times 10^{-9} \epsilon_{max} \Delta$$

Using the quantum theory, Mulliken (1939), has shown

$$f = 1.085 \times 10^{-5} q^2$$

 $\mathbf{\hat{v}}$  is measured in cm<sup>-1</sup> and Q is the electronic transition moment in  $\mathbf{\hat{A}}$ . The latter measures the mean displacement of electronic charge in the transition:

$$Q = \int \phi_n(\mathbf{Z}_i \mathbf{r}_i) \phi_m \cdot d\mathbf{r}$$

 $\phi_n, \phi_m$  are the ground and excited state wave functions and  $r_i$  the displacement of the i th electron.

Often, selection rules are used, which merely categorise transitions as forbidden (very small Q) or allowed (large Q). Simple considerations may allow the prediction of the intensity of a band - specially we should notice the very intense bands ( $\epsilon > 10^{4}$ ) which are termed charge transfer bands. In these electronic charge moves from one atom to another. A special case is that of charge transfer to solvent exhibited, for example, by the halide

ions in solution (e.g. Smith and Symons, 1958).

Whereas in the simple molecule, the excited state will return to the ground state either by a radiation transition (fluorescence) or non-radiative process, in the case of solids with localised centres, no return to the ground state may occur. For instance, irradiation into the F-band excites the F-centre into its excited state and luminescence, i.e. re-emission from this state after the surrounding lattice has relaxed, can be observed in the infra-red region (Botden, van Doorn, and Haven, 1954). On the other hand, the excited electron may enter the conduction band and be recapture by another F-centre - thus an F'-centre is formed.

#### 1.42 The Principles of Diffuse Reflectance.

Although the absorption spectrum of a substance is usually and preferably determined by measurement of the absorption of a homogeneous sample, either a liquid, solution or single crystal, there are times when this method is not practicable. This is especially true in the case of solids of which single crystals are grown with difficulty, and in the case of absorbed species. In both these cases, the required information can be derived from a study of the light reflected diffusely from a flat surface of the highly powdered sample.

Two types of apparatus are used to extract this information. In one, light falls perpendicularly on the surface and that scattered within some solid angle is collected by a toroidal mirror and focussed onto a detector such as a photo-cell. In the other, light falls on the surface, often at an angle, and all the light scattered is collected by a surrounding spherical reflector, and eventually finds its way out of the sphere onto a detector (after multiple reflection within the sphere).

In recent times the diffuse reflectance method has been studied by a number of workers. Kortum and co-workers (1963) use a theory due to Kubelka and Munk(1931,1948). This theory considers the reflection using a model of small optical inhomogeneities in a layer of uniform reflecting material, but it neglects particle size and

59 refractive index effects, and is therefore clearly not valid. For this reason Poole and Itzel (1963) have rejected this theory and used one recently developed by Melamed (1963), which uses more realistic model of a stack of homogeneous uniform spheres. However, they had to fit their results to the theory, which contained adjustable parameters. Using these theories both Poole and Itzel and Kortüm derive extinction coefficients for the bands they observe. Kortüm verified the Kubelka-Munk theory by comparing the absorption of a rare earth glass to the spectrum derived from the diffuse reflectance of a powder of the glass. It is interesting to note that Melamed used the same method to test his theory.

Simple consideration suggests two factors affecting the diffuse reflectance at any given wavelength: the particle size and the 'regular' reflection, i.e. the true reflection arising from the correctly oriented surfaces of the crystallites in the powder. Kortum suggested that the latter may be eliminated by use of polarised light or by dilution of the sample with the reference material (1:1000). The latter fact had been obtained empirically by Griffiths, Lott and Symons(1959). In the usual apparatus, the reflectance of the sample is compared with that of a reference surface of material which is known not to absorb in the region studied. Magnesium oxide and lithium fluoride are often used. If the sample is diluted with the reference substance then the particle size effect should be compensated for, to a large extent. Thus we conclude that the method of Griffiths,Lott and Symons, i.e. simply plotting apparent optical density against frequency, is adequate for the recording of diffuse reflectance spectra - certainly so if the extinction coefficients are not required. The other authors seem to have used a theory which is applicable to the absolute diffuse reflectance from a surface. They do not seem to have realised that their experiments were comparing two surfaces - and that many effects would then cancel out.

Chapter Two

Experimental Methods





Figure 2.12

#### Electron Spin Resonance Methods, Section 2.1

E.s.r. spectra were taken on a Varian V4500 spectrometer or on a machine built by Mr.J.A.Brivati (1962). Both instruments are operated at X-band (10,000 Mc/s) and employ 100 Kc/s modulation and phase sensitive detection. g values were determined by measurement: (1) of the field. using proton resonance, the frequency of which was either locked to a crystal (departmental machine) or checked against a crystal oscillator (Varian). In both cases the accuracy was better than one part in one hundred thousand. (2) of the microwave frequency using a Philips wavemeter. with an accuracy better than one part in ten thousand, which could be improved in the case of the Varian instrument by use of a calibration chart. Alternatively, the g value of a standard sample (charred dextrose) could be measured at the same frequency as the unknown. In all cases a check measurement (at an arbitrary frequency) of the g value of charred dextrose was made each time either instrument was used. For reference purposes a block diagram of the instruments is given in figure 2.11.

Low temperature measurements, i.e. at 77<sup>o</sup>K, were made in two ways. In the departmental machine, the whole cavity is cooled by a surrounding bath containing the coolant (liquid nitrogen), the bath being thermally insulated by expanded polystyrene (figure 2.12). Dry nitrogen must be passed through the cavity to prevent



condensation of moisture and liquid oxygen therein. In the case of the Varian, a cold finger dewar was placed in the resonant cavity, through which dry air passed (figure 2.13). This dewar was made with a cold finger of quartz, since glass would dampen the resonant cavity and is known to contain traces of Mn<sup>++</sup> ions which show a strong signal. This method of cooling the cavity has some advantages. It enables the sample to be illuminated through the end slots of the cavity - a further reason for using the quartz cold finger, since it is transparent to ultra-violet light. It enables alternate measurements to be made readily at any temperature. It has the disadvantages that the resonant cavity is slightly damped by the 'glass-ware', and the amount of sample is limited by the smallness of the inner of the dewar. Further, the liquid nitrogen boiling off disturbs the sample, thereby detuning the cavity slightly and thus producing noise. In searching for a resonance and, when one is found, in order to obtain the best spectrum possible, several points must be noted. No resonance will be seen if the sample is saturating, so always we have checked that the power is not toogreat by reducing it in a check run. The signal can be broadened by the use of too much 100 Kc/s modulation - and this point has always been checked. Finally, when searching for a signal as wide a sweep of the field and as slow a sweep as possible was made.

The Preparation of Solutions of Complexes for Spectrophotometry, Section 2.2.

Materials were prepared as follows:

Solvents: Dimethyl formamide and acetonitribe of spectro-

grade quality (Eastman-Kodak) were used. The acetone used was MacFarlan's B.P.C. grade. Laboratory chemical grade dichloromethane from May and Baker was used. The iso-propanol used was B.D.H. Special for Spectroscopy. The dimethoxy ethane used was Kodak Spectrograde which had been refluxed over calcium hydride for several hours from which it was finally distilled. This procedure removes peroxides and dries it.

Solids: Silver iodide was prepared by precipitation from

an aqueous solution of B.D.H. silver nitrate (99.5% assay) by addition of an equivalent quantity of potassium iodide (M & B, 99.5% assay). The precipitate was filtered washed and dried at 110<sup>0</sup>C. Silver perchlorate was B.D.H. laboratory reagent. N-hexyl ammonium iodide was recrystallised from petroleum ether. <u>Solutions</u> were made up by direct weighing of 10 to 100 mg. of solute into 25 ml flasks and making up to 25 ml of solution.



Figure 2.31

### Diffuse Reflectance, Section 2.31.

For this useful technique, the Unicam S.P.500 manual single beam spectrophotometer was used. This instrument was fitted with a modified S.P.540 Diffuse Reflectance Accessory as in figure 2.31. The modified apparatus has the reflecting cone as shown, whereas the standard equipment has a ground glass screen, shown by the dotted line, onto which the diffusely reflected rays are brought to a focus. The standard apparatus uses a photocell, but we have used a photomultiplier, SZG 500, as described by Griffiths et al. (1959). The conical reflector deflects the light rays in the direction of the detector, and the use of this is found to enable spectra to be recorded well into the ultraviolet. A ground quartz screen was first tried in place of the ground glass screen, but improved sensitivity was obtained by the use of the reflector. As a result of these modifications it has been possible to make measurements down to approximately 210 mp. Lithium fluoride was used for the reference reflective surface and as a diluent for the sample being measured. The sample was ground up in an agate vibratory ball mill for several minutes, well mixed with lithium fluoride (about one in ten upwards of sample to lithium fluoride) and then spread in the sample tray. A good surface was obtained by pushing down on the powder with a stainless steel cylinder, then giving it a twist and lifting it off.

<u>Preparation of Complexes for Diffuse Reflectance. 2.32.</u> Samples of the solid silver iodide complexes were prepared in two ways. Firstly the method of Marsh and Rhymes (1913) was used. In this method appropriate quantities of the silver and potassium iodides were dissolved in acetone, and this solution then evaporated by drawing dry air through it. Secondly, X-ray studies have shown that the solids may be prepared by melting together the two halides in the appropriate molar ratio(Hirsch,1964). This method was also used, and was especially applied in the case of  $Ag_2I.Clo_{h}$ .

## Spectrophotometry, Section 2.4.

2.41 General All spectra were recorded on a Unicam S.P.700 spectrophotometer. This is a double beam recording instrument covering a range from about 54 Kcm<sup>-1</sup> to the near infra-red region.

2.42 Solutions. Solution spectra were recorded using mainly fixed path length fused silica cells of path length 0.01 and 0.05 cm. A corresponding solvent filled cell was placed in the reference beam of the spectrophotometer, In some cases, e.g. solutions in acetone, smaller path lengths were required and then a demountable cell (Research and Industrial Instruments Co., type UV11) was used. Teflon washers gave path lengths of 7 and 25  $\mu$ . The spectrum of the solvent had to be subtracted by hand, since only one



cell was possessed. In all cases spectra were measured using solutions of maximum optical density 1.0, unless otherwise stated.

### 2.43 Single crystals.

Single crystals were mounted on a brass or copper plate in which a hole had been cut. Often this hole was quite small, e.g. about 3/32 ins. in diameter. In order to balance the instrument, a plate with a similar hole was placed in the reference beam. For room temperature measurements crystals were mounted on such a plate using silicone grease, and the plate then placed in the cell holder of the instrument.

Low temperature measurements are often desirable as then bands may sharpen up and become resolved. Crystals can be cooled for this purpose in several ways: the crystal may be placed in the cooling liquid (figure 2.41), in a cell surrounded by coolant and containing a suitable gas (figure 2.42) or may be suspended in vacuo from the bottom of the inner of a dewar. The first method suffers from the interference due to bubbles of gas boiling off around the crystal and is not generally practised. It and the second method also suffer from the difficulty of constructing vacuum tight window which can be cooled down. (However, an apparatus using the second method has been described - see Broude,1957, and Wolf,1959.) For these reasons we chose the last method. The apparatus in







figures 2.43 and 2.44 was constructed in the departmental workshops.

In the case of some crystals we wished to Firradiate at liquid nitrogen temperature and then to take the absorption spectrum at the same temperature without letting the crystal warm up. Attempts were made at transfering the crystal from a dewar to the low temperature crystal holder, but difficulty from frosting up of the crystal occurred. A new crystal holder was therefore designed for this purpose. Since the irradiation would 'colour'the windows if they were exposed to it, the holder was designed to have the windows placed on it after irradiation. The gamma cell used, possessed only a small  $(5\frac{1}{2}$ "x  $3\frac{1}{2}$ ") compartment, so that a compact apparatus was required - for this reason a glass apparatus was designed. The apparatus used is shown in figure 2.45. In the apparatus the crystal is held throughout all the operations in vacuo and at low temperature. The tap keys A and B are open-ended, the ends being ground flat to take quartz windows which are fixed on with a hard vacuum wax. B has a duplicate key B', which is a simple cone connected to the vacuum system. Turning spigots are fitted to the sides of the keys A and B, between the ends and the points where they enter the barrel. Tap  $T_1$  has a recessed bar fitted to the key, instead of the usual handle, this enables the key to be turned and removed when necessary

and yet shortens the overall length of the tap. A plastic (perspex) wrench was made, which made the turning of the key more easy.

The mode of operation of the apparatus is as follows. All the tap keys are removed and greased. The windows are fixed to A and B with hard wax. The crystal is mounted on its holder. The keys are replaced in the taps, B' in its barrel, i.e. the apparatus is attached to the vacuum line.  $T_2$  is turned off, and  $T_1$  on in order to evacuate the dewar through B'. After evacuation, T<sub>1</sub> is turned off, thus separating the dewar from the vacuum line and from the windows. The dewar is now removed from the vacuum line and filled with coolant. The key A and its associated window are removed from the apparatus and then the latter is placed in the gamma cell, the coolant being replenished as necessary throughout the irradiation. After the irradiation A and B are inserted in their barrels and the space between the windows and  $T_1$  evacuated, through p and then  $T_2$  and  $T_2'$  are turned off. Then  $T_1$  is turned on so that a light path now exists through the windows and the crystal. The absorption spectrum of the crystal can now be taken.




### Preparation of Crystals, Section 2.5.

The crystals used were prepared in various ways: from solution, and from the melt. The cadmium sulphide crystals used were obtained from A.E.I.Ltd. or from G.E.C. and these had been grown by a vapour phase method.

Growth from solution is the simplest method from the point of view of apparatus. Sophisticated methods, however, are necessary when large crystals are required. Many details of the methods used have been described by Buckley (1951), Lawson and Nielson (1958), Smakula (1959) and others. We must emphasize that there are only general principles to be followed and recipes. Crystal growing is very much an art and not a science.

## Growth from Solution.

In this method a saturated solution is slowly made supersaturated. Sometimes a seed crystal may be added. Slow evaporation at room or some other temperature is sometimes effective. Another method is to cool a hot saturated solution slowly. We have used this method for some crystals, by placing a hot solution in a stoppered flask into a large dewar (about 5 litres) containing hot water, which is then closed with an insulating stopper and left to cool. This takes several days.

For some crystals this supersaturation process can be achieved by precipitation using another solvent. This is readily carried out in the tubes shown in figure 2.51.

Suppose we have a liquid L which is lighter than solvent S with which it is miscible, and that we can dissolve the substance X in S but not in L. Then we pour into B L and then pour a little S into A followed by the saturated solution of X in S. Three layers then exist in B. On leaving for a few weeks they diffuse into one another and X is precipitated to form, if we are lucky, a single crystal. In a variant, L and S are solutions of a chemical which react to form an insoluble substance. In this way we have produced a crystal of  $CaHPO_{l_1}$  from  $CaCl_2$  and  $Na_2HPO_{l_1}$  in ageous solutions.

#### Growth from the melt.

Although growth from solution has its merits, it is slow and impurities cannot always be added, or may not be excluded. For large crystals with various impurities, growth from the melt is often used. Two methods may be mentioned. In the Kyropoulos or Czochralski method a seed crystal is formed or attached to a cooled holder which allows the seed to just dip into a bath of the melt. This is then slowly withdrawn from the melt: a single crystal forms as the melt being withdrawn cools. In the Bridgman method, a crucible containing the melt is gradually lowered through a hot furnace into a cooler region. Usually the crucible containing the melt has a slightly pointed base. A single crystal forms throughout the crucible if the rate of lowering is slow enough. We have

Figure 2.52



used a simplified Bridgman method (figure 2.52). A small heater was wound from nichrome wire on a stainless steel former covered with fire cement, then the whole covered with fire cement and fire brick. This was supplied from a five amp Variac transformer, which was adjusted to give the correct temperature (as measured by a thermocouple pyrometer). A silica or glass tube carrying the substance was slowly lowered through this heater, by means of a float falling in an aspirator, out of which water slowly dripped. This method gave a very slow rate of lowering ( up to an inch in several hours). Crystals of alkali and silver halides large enough for optical work could be grown in this manner.

# 2.5 Appendix. Handling of silver halides.

Silver halides being light sensitive were handled, when necessary in light from a Kodak red safety light. Whereas the alkali halides can be cleaved to give plates suitable for measuring their absorption spectra, the silver halides have a soft tough character, and it was found that plates could be obtained by sawing the crystal with a fine saw, and then polishing the surfaces first on a ground glass surface covered with sodium thiosulphate solution and then on a cloth soaked in the same solution.

## 2.5 Appendix B.

Single crystals of silver halides containing silver selenide and telluride were required. Since these substances are not available commercially it seemed, they were prepared according to the method given in Partington's Textbook of Inorganic Chemistry. A small quantity of the element (e.g. selenium), of the order a few grams, was heated with a good excess of silver nitrate solution and the mixture kept boiling for several hours. After this time there was no sign of further reaction - no brown fumes were being evolved. The liquid was poured off the solid product, which was washed several times by decantation with hot water. The product was then filtered and washed on the filter and finally dried in a desiccator over calcium chloride. In both cases the theoretical yield was obtained.

 $4 \text{ Ag}^+ + 3\text{Te} + 3\text{H}_20 = 2\text{Ag}_2\text{Te} + \text{Te}0\overline{3}^- + 6\text{H}^+$ 

Metal Films, Section 2.6.

Metal films of aluminium, copper, silver and gold were kindly prepared by Mr. D.Gibbons (Physics department). The metal (Johnson-Matthey pure) was suspended on a tungsten filament over which was placed a quartz plate. After evacuation of the apparatus (pressure less than  $10^{-5}$  mm of Hg.), the filament was brought to white heat, whence the metal evaporated onto the plate. Films of the order of skin depth were produced ( estimated from opacity and from the amount of metal used). The skin depth we refer to here is that at microwave frequencies of 10 KMc/s, and was calculated by the formula

 $d = 1/\sqrt{\pi f \mu \sigma}$  (see Wilson, 1953).

Results:

Metal	d A	
Cu	700	
Ag	700	
Au	90 <b>0</b>	
Ca	1500	

A cadmium film was made using a glass vacuum line and distilling the metal several times and finally onto a plate, using a gas torch.

FINAL FILM CL -

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Radiation Methods, Section 2.7.

The following radiation sources were used:-

- 1.Visible light. A 500 watt projector using a tungsten filament lamp, and glass condensing lenses.
- 2.Ultra-violet. A high pressure mercury arc, unfiltered using a quartz lens - this gave radiation at 365 mµ. approximately.
- 3.Gamma rays. A Canadian Atomic Energy Gamma Cell 200. This contained a <sup>60</sup>Co source of 1900 Curies initially, but which had fallen to about 1200 curies by the last experiments. The makers estimated a radiation dose rate of 0.326 Mrad per hour.

Chapter Three

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Results and Discussion.

### Section 3.1, The Ultraviolet Absorption of Silver

## Iodide Complexes.

<u>1. Introductory.</u> Griffiths and Symons (1960) reported the ultraviolet absorption spectra, in several solvents, of the iodide complexes of zinc, cadmium and mercury of the formula type  $MI_n^{-(2-n)}$ . These spectra are largely solvent independent, unlike the charge transfer to solvent (C.T.T.S) spectra associated with the simple halide ions. The band position of the absorption spectrum of these complexes was found to decrease in energy (1) in order Zinc, cadmium, mercury for a given n, and (2) with increasing n for a given cation. Solvent interactions with the complexes were tentatively introduced in order to explain some of the results.

The existence of similar silver complexes has already been mentioned in the general introduction. Fromherz and Menschick (1929) studied the absorption spectra of solutions of silver halides dissolved in solutions of the alkali halides. Their spectrum of, for example, the iodide shows a band at 252 mp, log  $\epsilon = 4.16$ which is assigned to AgI<sub>2</sub>, and also some shoulders which were not assigned. King et al. (1952) found that de Beer's law was not obeyed in ageous solutions of these complexes and concluded that polymeric units of no definite size were involved. No other spectroscopic studies of these complexes seem to have been made, but other techniques



have been applied to their study.

Leden (1956), Lieser (1957,1960) and Krahtovil (1957) have made extensive studies of the aqueous solutions of mixed silver and alkali halides using solubility, radioactive tracer and electrochemical methods. These and other workers have measured the equilibrium constants for such reactions as  $Ag I + I^{-} = AgI_{2}^{-}$ ,  $+ I^{-} = AgI_{3}^{-}$ , and for the formation of polymeric species such as  $Ag_2I_6^{-4}$ and  $Ag_{L_{6}}I_{6}^{-2}$ . Of particular note, for our purposes, is the work of Mackor (1951): e.m.f. studies of the iodide complexes in water acetone mixtures, indicated that, in the main, two complexes were formed -  $AgI_2^-$  and  $Ag_{l_1}I_6^-$ . This was confirmed by ultra-centrifuge molecular weight determinations. Dallinga and Mackor studied the structures by the X-ray diffraction of the solutions. This method, which is analogous to gas phase electron diffraction, involves an initial guess about the structure, thus the structure of  $AgI_2^-$  is almost certainly bent, whereas the structure of  $Ag_{4}I_{\overline{6}}^{\overline{5}}$  may be that shown in figure 3.11. No other structural studies seem to have been carried out on the species in solution - early Raman studies were unsuccessful, (Braune and Engelbrecht, 1930). On the other hand, X-ray structure studies have been made of the solid alkali metal complex salts (1949,1952,1954).



Figure 3.12



Figure 3.13



Figure 3.14

Absorption of acetone solutions of potassium and silver iodide.

7 pr Pathlength



Figure 3.15

Figure 3.16





In addition to the anionic silver-iodide species, cationic ones are known to exist and solid complexes have been isolated (Hellwig, 1900, Lieser, 1960, and Leden, 1956). Fromherz and Menschick (1929) studied the ultraviolet absorption of solutions of silver iodide dissolved in aqueous silver perchlorate. A band at 245 mp was ascribed to Ag<sub>2</sub>I<sup>+</sup>. We may summarise their results: Shoulders Solutions of Bands 270, 310 KI + AgI 228 (I<sup>-</sup>) 252 245•5 AgI + AgClO<sub>L</sub> 270

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#### 2. Results and Discussion.

We have studied the spectra of silver iodide dissolved in solutions of potassium iodide in various organic solvents, and in a solution of n-hexyl ammonium iodide in dichloromethane. In figures 2, etc., we have shown some of the spectra which we obtained. In figure 3.12 we see the changes which occur as we add potassium iodide to a solution of silver ions (as perchlorate), the presence of equilibria is shown by the isobestic points I. In the case of the cationic species, formed by dissolving silver iodide in a solution of silver perchlorate, Only in the case of acetone as solvent, could absorption bands be found with certainty, as is shown in figure 3.17. The reason for this is probably one related to solubility and equilibria - the silver perchlorate is not readily soluble

# Table:

Ions in various Solvents.				
Solvent:	Iodide present as:	Absorption Maximum: m <b>µ</b>	Ascribed to:	
Water	KI	227	I_	
Meth <b>yl</b> cyanide	KI	229	AgI	
		246	I_	
		311	$Ag_{4}I_{6}^{=}$	
Dimethoxy- ethane	KI	232.6	AgI <sub>2</sub>	
Dichloro- methane	tetra n-hexyl ammonium iodide	227	AgI_2	
		242	I_	
Acetone	KI	228	AgI2	
		256	I_	
		310	$Ag_{4}I_{6}^{=}$	
		317	Ag3I4	
Dimethyl- formamide	К <b>І</b>	, 310	Ag <sub>3</sub> I <sub>4</sub>	

The Absorption of Solutions of Silver and Iodide

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N.B. Silver ions were always added as the perchlorate.

in the organic solvents we have used, and a concentrated solution is necessary, since the formation constant of the cationic species is very low.

Since the species present in acetone have been studied in detail by Mackor, we shall discuss our results for this system. On adding a solution of silver perchlorate in acetone to a solution of potassium iodide a change of absorption is noted (figure 3.15). First the iodide band decreases in favour of a band at 230 mµ, then when the molar ratio Ag:I exceeds 1:2 a band at 310 mp grows. Comparing with the results of Mackor, we thus assign the band at 230 mp to the species  $AgI_2^-$  and the band at 310 mp to  $Ag_{L}I_{6}^{=}$ . The band at 230 mµ may be compared to that at 243 mp found in solutions of cadmium iodide and assigned to CdI<sub>2</sub> molecules in solution. The shift to lower energy on going from silver to cadmium might be expected from their relative electronegativities, providing we assume that these bands arise from a process involving transfer of charge (electron) from iodide to metal. Jørgensen (1961) has suggested that these bands arise from the charge transfer process **M**iodide -> 5s (Ag).

In addition to  $\operatorname{AgI}_2^-$  other simple monomeric species are expected to exist. We can write equations for their formation:  $\operatorname{AgI}_2^- + \mathbf{I}^- = \operatorname{AgI}_3^-$ ,  $\operatorname{AgI}_3^- + \mathbf{I}^- = \operatorname{AgI}_4^{-3}$ . We expect that these will be present in concentrated solutions, especially when there is a high ratio of iodide to silver ions. There is some spectral evidence for these.

The band found at 245 mm by Fromherz and Menschick might be due to the tri-iodide complex and a shoulder which we have found at 270 mm may be due to  $AgI_4^{-3}$ . Similar trends on increasing the number of iodide ions were found in the corresponding complexes of the group IIB cations(Griffiths and Symons,1960).

In concentrated solutions of potassium iodide ( in, for example, acetone) silver iodide dissolves up to a mole ratio corresponding to  $Ag_3I_4^-$ . The band we have found at 310 mp was obtained under quite different conditions. Firstly, the solutions were relatively dilute in iodide, secondly, the molar ratio was less than 2:3. Finally, the measurements were made under similar conditions to the e.m.f. measurements of Mackor (1951), from which he was able to establish the presence of the ion  $Ag_4I_6^-$ .

It is, however, possible to obtain a band at 317 mpt by nearly saturating acetone with potassium iodide and then with silver iodide ( the mole ratio of these is then 2:3). This band is presumably due to  $Ag_3I_4$ . The band in dimethyl formamide may be similarly ascribed, since Chateau (1963) claims that e.m.f. measurements show this ion to be preferentially formed in this solvent.

The species  $Ag_2I^+$  and  $Ag_3I_2^+$  exist in aqueous solutions of silver salts into which silver iodide has been dissolved. Lieser (1960) found the latter to be more stable than the former from solubility studies. Thus the band found by Fromherz and Menschick may be due to this ion. We have

found bands in the case of solutions of silver iodide in silver perchlorate in acetone, figure 3.17. From the table of absorptions, it is apparent, as was suggested in the introduction, that the solvent has little effect on the absorption spectra of the complexes, in contrast to the iodide spectrum, which possesses a marked solvent dependence (see for example Smith and Symons, 1958). Solvent interactions, however, are believed to occur especially for AgI<sub>2</sub>. Dallinga and Mackor (1956) found this ion to be bent in acetone solution. In the case of the zinc and cadmium iodides a possible interpretation of the spectra involved solvent interactions, whilst evidence from Raman work indicated linear  ${\tt MI}_2$  molecules although this evidence was not decisive. The presence of solvent interactions in the present case suggests this interpretation may be correct.

The structure of  $Ag_{4}I_{6}^{=}$  according to Dallinga and Mackor may be derived from a deformed **q**-AgI lattice. Cardona (1963) has recently studied in some detail the absorption at low temperatures of thin films of silver iodide. Exciton bands at 420 mµ and 320 mµ were found. It seems possible that the latter can be related to the 310 mµ band of  $Ag_{4}I_{6}^{-}$ . This seems in accord with recent general views put forward by Jørgensen (1961). Further, the 420 mµ band in silver iodide does not seem to arise as was suggested by Seitz (1951), from a forbidden silver

ionktransition, which becomes allowed in the lattice. It is unlikely that such an intense band would arise from a previously forbidden band, and in any case such a transition should arise in the complex. It appears, then, to be a property of the crystal as a whole. Cardona, indeed, interprets it in terms of the known band properties of similar semiconductors; bands arise from transitions between the valence band at the point k = 0, to exciton levels.





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# 3.13, Diffuse Reflectance Spectra of Complexes.

We have used the diffuse reflectance technique to study the absorption spectra of several of the solid complexes, which may be obtained. In figures 3.18, etc., we record the spectra of  $K_2AgI_3$ ,  $KAgI_2$  and  $K_2Ag_{\downarrow}I_6$ . These solids were prepared by the method of Marsh and Rhymes (1913). Figure 3.111 shows the spectrum we obtained for silver iodide, and 3.112 that for silver iodide precipitated in excess potassium iodide solution. No apparent difference is seen: thus we are not able by this technique to distinguish any complexes which may be formed on the surface of the silver iodide, by this treatment. This is probably due to the large extinction of the silver iodide in the region of the characteristic absorption of the complexes.

Some comment seems necessary on the difference between the solid and solution spectra. It is notable that the silver seems to be tetrahedrally coodinated in the solids which have been investigated by X-ray methods (see Brink,1953, etc.,). This seems to be borne out by the spectra, all of which possess a broad maximum at about 300 mp. In solution, however, the ionic units are separated and very real differences appear in their structure - as is now apparent from their spectra.

Figure 3.113 shows the spectrum of the anionic complex(Ag<sub>2</sub>I) ClO. Curve I is the spectrum obtained before



Figure Al





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melting the mixture of silver perchlorate and iodide. Curve II is that found after melting the mixture (followed) by grinding for diffuse reflectance). The difference between these two curves is clear indication of the formation of a compound. The curve III was obtained after further grinding of the solid - the spectrum indicates decomposition resulting from this treatment. Two absorption peaks do seem distinguishable at about 250 mµ and 280 mµ.

#### 3.13 Appendix.

In order to test the validity of our diffuse reflectance technique, we have studied the spectra of a few substances where single crystal spectra have been obtained. In figure Al we show the spectrum of potassium iodide, which shows peaks at 215 mp and 225 mp. The spectra of evaporated films show a peak at about 220 mp. The difference between the two results, may be ascribed to strains introduced through grinding or to surface states - the diffuse reflectance method emphasizes the latter, since multiple reflection within each crystallite of the powder may be supposed to occur. In figure A2 we show the spectrum we obtained for cadmium iodide, this resolves all the gas and solid state bands previously found and ascribed to bulk and surface species by Griffiths et al.



### 3.14, Photochemistry of the Complexes.

The photochemical interest of silver-iodide complexes has already been remarked. We have carried out some preliminary studies.  $K_2AgI_3$  and  $KAgI_2$ , prepared from solution, were gamma irradiated for ten to twenty hours at liquid nitrogen temperature and then placed at  $77^{\circ}K$ in the cavity of the Varian e.s.r. spectrometer. A reproducible spectrum was not obtained in the second case, but in the first, the signal shown in figure 3.114 was obtained. Such a complicated spectrum cannot be interpreted without further studies. A preliminary attempt was made to study the sample at Q-band (wavelength 0.8 cm.), but no signal was obtained - probably owing to sensitivity reasons. Further studies will have to be carried out either at Qband or using a single crystal, before anything can be said about this spectrum.
#### 'Colour'Centres in the Silver Halides. Section 3.2.

#### 3.21 Introduction.

We have already mentioned that the silver halides though possessing the rocksalt structure, have many properties, especially with regard to defects, which are quite different from those of the the alkali halides. This difference becomes more apparent when we consider their behaviour with regard to colour centre formation. Since few anion vacancies are present in a crystal of, for example, silver bromide, we do not expect F-centres to be readily formed in it. Since the Frenkel defects present imply the presence of cation vacancies, presumably the v-centres found in the alkali halides have analogies in the silver halides.

At this point we should remember a fundamental difference between these two sets of compounds: namely the freedom with which the cationic silver can diffuse through the lattice. Thus suppose we form by  $\chi$ -irradiation an electron excess centre in a silver halide, then at room temperature a silver ion may diffuse up to the centre and so form silver - thus the start of the latent image of photographic theory has taken place. Thus we must keep the crystal at low temperature (less than about 140°K), if we wish to study the primary centre.

There seem to be few reports of evidence for elementary centres, such as **F** and V centres, in the silver halides. Melklyar(1954,etc.) claims to find an

F-centre absorption in silver bromide: a band at 410 mp at 90°C which shifts, on raising the temperature, to lower energy. This work is, however, disputed in the Russian literature(Grenishin,1954) and does not seem to be accepted by Western authors. Since this band occurs in an unirradiated pure crystal, and increased in intensity on raising the temperature even above the melting point of the crystal, Meiklyar's interpretation seems erroneous.

Recently Hennig (1963) has reported an e.s.r. signal from silver bromide which had been heated in a bromine atmosphere. He interpreted the signal as that due to a hole trapped at a cation vacancy, i.e. a centre with a similar structure to Seitz's model for the  $V_1$  centre in alkali halides. Crystals so treated did not possess an absorption spectrum which could be attributed to such a centre but e.s.r. is expected to be more sensitive in this case. Two difficulties do arise on close consideration of this work. Firstly, a seven line e.s.r. spectrum is observed instead of the nineteen line spectrum to be expected from an anisotropic interaction from six equivalent bromide nuclei. By some involved reasoning the author attempts to explain the occurrence of the seven lines, but does not present any explanation for the non-existence of the usual  $Br_{2^{\bullet}}$  spectrum. A further point requires explanation: why the bromine atoms, implicitly present, do not bond to the neighbouring bromide ions to form Bn as in solution

<sup>89</sup> and in the alkali halides. This might be explicable on the basis of the greater homopolar character of the silver bromide, compared to the alkali bromides. Finally, recent studies of Sliker (1963) on silver chloride put doubt on this work - silver chloride could not be 'coloured' by heating in a chlorine atmosphere, and crystals so treated did not show an e.s.r. signal. Clearly the evidence for the centre in silver bromide is dubious and requires further investigation.

The one type of centre which has certainly been found to occur in the silver halides as well as the alkali halides, is the colloidal metal centre. Optical irradiation of the silver halides in the first exciton band results in the formation of a broad band at lower wavelengths. (Brown and Wainfain, 1957, see also Gurney and Mott, 1940, and Seitz, 1951 for earlier studies). Neither the peak position nor the halfwidth of this band vary appreciably on cooling. Long irradiation generates particles of the order of 10 mp diameter (Haynes and Shockley 1951), which give rise to Tyndall scattering and which can be observed by X-ray diffraction ( Burgers and Krooy, 1948). The absorption due to small particles can be preferentially bleached by monochromatic light ( Wainfain, 1957). Furthermore the longer wavelength part of the broad band is less stable than the short wavelength part. Heating to 150°C for ten minutes, shifts the peak from 580 mµ to 500.

Ingram and Smith (1961) have observed an electron spin resonance signal in silver bromide powder which had been irradiated with 2537 Å light. A single line about seven gauss wide at g = 2 was observed. Little change of signal intensity was observed on cooling the sample a behaviour, as we have previously noted, typical of the signal from conduction electrons. Following previous studies of colloidal lithium similarly produced (Doyle, Ingram and Smith, 1959), the authors conclude that the signal is due to colloidal silver particles. A later communication ( Ingram et al., 1963) indicates that there are difficulties associated with this interpretation: the signal strength implies that there are enough conduction electrons present to make the sample metallic and this is not indicated by the appearance of the sample. 3.22 Results of Studies of Pure Silver Halides. We have carried out further investigations of pure silver halides. Firstly we have attempted to produce electron excess and hole excess centres by  $\langle$ - irradiation of pure single crystals (supplied by Kodak) at various temperatures ( 77°K, -80°C and room temperature). Irradiations were carried out for varying periods of time: 5 minutes, 10, minutes, 30 minutes, one, three, six and thirty hours. In no case was any electron spin resonance signal observed in the sample - the sample being kept at 77°K after irradiation and during measurement.

In order to interpret this negative result, we should consider the centres which might be formed. In the crystal we have already Frenkel defects, interstitial silver ions and silver ion vacancies. The latter should readily act as hole traps, and by analogy with the alkali halides we expect  $Br_2^-$  ions to be formed or, following Hennig's work, a hole trapped at the vacancy and shared equally by the surrounding six bromide ions. The electrons perhaps would be trapped at interstitial ions, but then the silver atom so formed would be to large to fit into the interstitial site, so perhaps this would only occur at kink sites or similar positions. Another possibility arises from the work of Delbecq. et al.(1963) on silver chloride doped potassium chloride, in which irradiation produced an effective disproportionation:

 $2 \text{ Ag}^+ = \text{ Ag}^\circ + \text{ Ag}^{+2}$ .

It is possible that this process could occur in the pure silver halide.

All these centres should give rise to an electron spin resonance signal. Such a signal would be observed providing the centre did not saturate or relax too rapidly. From studies of such centres in other compounds we may conclude that the latter is unlikely, and the former was always tested for by reduction of power at the resonant cavity. We therefore strongly doubt the existence of such centres in our samples. We must point

out the difficulty of reconciling our results with those of Hennig. It seems they throw further doubt on the interpretation by Hennig of his e.s.r. signal. It is possible that the centre he studied was in fact some kind of impurity centre. The sensitivity of e.s.r. coupled with the difficulty of preparing very pure silver halides make this quite likely.

At room temperature we expect prolonged irradiation to yield colloidal silver particles in the solid. Following Ingram et al. (1961) we should expect to see the e.s.r. of the conduction electrons in the particles. Samples of nominally pure silver halides were found, after illumination with a high pressure mercury arc, sometimes to possess an electron resonance signal and sometimes not. Samples of silver halides were also studied which had been precipitated in strong illumination from aqueous solutions of analar alkali halides and recrystallised silver nitrate. These samples showed an electron resonance signal. Colloidal silver can also be precipitated in the silver halides by melting them in an open tube. Samples of nominally pure silver halides so treated again showed varying results - some possessing an electron resonance signal and some not. Further g-value determinations were made on the samples which showed a signal, with the following results:

 AgCl
 AgBr

 g =
 2.003
 2.009

 AH =
 7.5 Gauss
 5.9 Gauss.

These results immediately throw doubt on the original interpretation of Ingram et al., since the g-value of the resonance of the conduction electrons in silver will be independent of the original source of the silver.

Since the electronic resonance due to conduction electrons has been seen in few metals, it seemed worth checking to see if it could be observed in bulk group IB metals. In fact thin films ( approximately of skin depth thickness at microwave frequencies) did not show any resonance at room temperature or at 77°K. A simple calculation indicated that, assuming one conduction electron per atom, a strong signal should have been observed. It seems likely that, as with the transition metals so far studied, no signal is observed in these metals probably due to an unfavourable relaxation time. Colloidal solutions of gold and of silver in water were prepared. Again these showed no signal. Finally, colloidal gold in potassium chloride did not show a signal. We conclude that the centre found by Ingram et al. and in some of our samples cannot be ascribed to colloidal silver. The basis of the interpretation of Ingram et al. was analogy of their results with previous studies of colloidal lithium in ultraviolet irradiated lithium hydride. It must be pointed out that in the latter case the interpretation

was backed by the work of Kip, and Feher who found such a resonance in bulk lithium and in colloidally dispersed metal (1954). The silver halide case has, as we have shown no analogy here.

Since the centre is present when colloidal silver is present, it may be associated with the colloidal silver. Further, the temperature dependence of its e.s.r. intensity is characteristic of conduction electrons. so that the 'centre' may be a low lying impurity band in the silver halide, produced by irradiation or by heat treatment. This band may be connected with the presence of colloidal silver particles and may be localised in the silver halide in regions surrounding the silver particles. We should note in passing that the resonance signals obtained were always symmetrical, indicating that the conduction electrons were in a region less than skin depth(at microwave frequencies) in dimensions. We should also mention the work of Abe (1957) who found a central line at g= 2, of width 52G. in the e.s.r of a single crystal of manganese doped silver chloride - this was in addition to the usual six line spectrum of  $Mn^{+2}$ . We have looked at a powder spectrum of such a material - some of our samples seemed to contain manganese as an impurity, which on melting was converted to Mn<sup>+2</sup> which then showed an/electron spin resonance signal. It seems quite likely that the central line of Abe was similar to that found in

the work of Ingram et al. and that mentioned above. Appendix.A.

We note here some similar results on cadmium sulphide. This substance has some similar properties to the silver halides: it is slightly more homopolar and has a smaller band gap, it is photoconducting (is believed to contain Frenkel defects, but has a hexagonal structure. Wright (1962) found an electron spin resonance signal in cadmium sulphide heated to about 800°C in vacuo for about one hour. This he ascribed to interstitial singly charged sulphide - a centre often postulated to occur in cadmium sulphide. A similar centre seems to arise on prolonged gamma irradiation of cadmium sulphide at room temperature. We have repeated Wright's experiments. A very broad line (90 gauss between points of maximum slope) at g= 2.01 was found at room temperature, which on cooling to 77°K did not alter appreciably in width or intensity. Thus the resonance may be associated with conduction electrons.

These conduction electrons could presumably occur in colloidal cadmium metal - the heating process might simply be a distillation off of sulphur from the cadmium sulphide. The ultraviolet - visible absorption spectrum of a crystal so treated did not clearly indicate the presence of colloidal particles. Further, a thin film of cadmium metal did not show electron spin resonance either at room temperature or at 77°K. It is therefore

necessary to invoke some other explanation of the resonance signal. Some sort of impurity centre seems likely since the cadmium sulphide used by Wright and in the present studies was not specially purified and, indeed, showed the spectrum characteristic of manganous ions. <u>Appendix B</u>.

During the irradiation at low temperature of single crystals of silver bromide and iodide, a colour change was noted in the case of the bromide - a greenish colour formed after many hours irradiation. Preliminary studies have been made of the effect of gamma irradiation on the absorption spectrum of silver chloride, the irradiation and the spectrum being carried out at 77°K. Further experiments involving greater periods of irradiation and thinner crystals could not be carried out owing to breakage of the apparatus. Irradiation of a crystal of silver chloride about 2mm. thick, for one hour produced a slight increase in the optical density in the region of the tail of the fundamental absorption, 20 - 26 Kcm<sup>-1</sup>. Clearly, further experiments should be carried out.

#### 3.23, Some Properties of Group VI Anion doped

#### Silver Halides.

The addition of group six anions  $(0^{-}, S^{-}, Se^{-}, Te^{-},$ hereafter called Ch<sup>=</sup> - chalcogenide), to the silver halides, should have interesting results. In the case of alkali halides, doping with such anions leads to an increased number of halide vacancies. As a result, Fcentre formation on X-irradiation occurs more rapidly than in the pure crystal (Burstein and Henvis, 1952). By analogy, addition of such ions to the silver halides might lead to the formation of anion vacancies. Alternativly charge compensation: might occur by the formation of more Frenkel defects (interstitial  $Ag^+$ ) or even by a valence change mechanism:  $S^{=} = e + S^{-}$ ,  $e + Ag^{+} = Ag^{0}$ . Of course, we have assumed that there are no other impurities present which act as electron traps. In any case an interesting crystal should result. It should be pointed out here that studies of such crystals do not necessarily throw light on the mechanism of the photographic process: of sulphur sensitisation: the latter is, rather, a surface phenomenon, (Mtchell, 1957)

During the past twenty years, many studies of such doped crystals have been carried out by O.Stasiw and his collaborators. Stasiw has recently reviewed this work (1960). These workers grow doped crystals of the halide by melting together the halide and 0.02 to 0.04 mol.%. of



impurity, followed by slow cooling to solidification point. Then the crystals are quenched immediately to about 100°K, or this treatment is given after reheating the crystal to about 400°C for about an hour. The crystal shows a new absorption, and the this absorption possesses structure. Its position is dependent both on the halide and on the impurity. Stasiw (1960) attributes this absorption to the presence of chalcogen ions substituted in the lattice for halide ions. Examples of the absorptions obtained are shown opposite. The structure of the absorption requires explanation and so, too, does the necessity to quench the crystal. Volke (1954) suggests that on leaving the crystal at room temperature silver chalcogenide precipitates out, being relatively insoluble at room temperature in the halide.

Stasiw (1960) interprets the absorption process as ejection of an electron by the impurity ion into the conduction band. The structure arises from the possible energy levels of the remaining Ch<sup>-</sup> ion. The spectral terms of Ch<sup>-</sup> are, in the usual notation,  ${}^{2}P_{\frac{1}{2}}$  and  ${}^{2}P_{\frac{3}{2}}$ and these are split by spin orbit coupling. It is not possible, however, to explain the results so simply. Firstly the splittings are in peverse order in the series S to Te to the atomic spin orbit splitting, secondly more than two bands are observed in some cases. The  ${}^{2}P_{\frac{3}{2}}$ level can be further split by an electric field into

states with different  $M_{J}$  values and this idea is invoked to explain the splitting. Such a field might arise from a charged defect near the Ch<sup>-</sup> ion, or from a Jahn-Teller distortion. Stasiw (1960) and Ebert (1960) suggest the latter (Ch<sup>-</sup> is degenerate). However, they seem to have neglected the Franck-Condon principle: Ch<sup>-</sup>, which is orbitally non-degenerate ( ${}^{1}S_{0}$ ) would have no such distortion and such a distortion could arise, therefore, only after the absorption process. Indeed, associated defects might well be frozen in by the quenching process.

Illumination of the doped crystals at room temperature leads too new absorption band, which is very broad, at about 700 mu. Scheidler (1961) attributes this to colloid entres. On the other hand, illumination at low temperatures leads to other absorptions. Scheidler (1961) has interpreted these in terms of well known defects. Further experiments are required to establish his models as valid, and we shall not discuss this topic any further.

Nuclear magnetic resonance (of the bromine) has been studied in crystals of AgBr:Ag<sub>2</sub>S by Seifert (1960). The linewidth at various temperatures could be explained by the presence of interstitial silver ions near the bromide ions. The presence of the sulphide seems to be required only in order to increase the number of interstitial ions. But no study of the dependence of the broadening on the concentration of sulphide seems to have been carried out. If such a dependence were found then one might have evidence

for the sulphide introduction resulting in interstitials rather than bromide vacancies.

Finally, we should mention the e.s.r. studies of Ebert (1960,1961) on these systems. The Ch ion postulated in the absorption spectral studies, possesses an unpaired electron and might therefore show an electron spin resonance. In fact a signal was observed at 90°K by Ebert, in crystals which had been quenched to about 173°K and illuminated at that temperature. A single line was observed in all cases, with a g value greater than free spin value and linewidth of the order of 60 - 70 G. A plot of g-shift against estimated spin-orbit coupling constants, gave a straight line. This agrees with the interpretation of the resonance as due to Ch. Studies seem to have been made on polycrystalline specimens, and only a weak line or indication of a signal could be obtained in the case of a single crystal. The reason for this was thought to be the low solubility of the impurities in the crystal.

A surprising feature is the lack of hyperfine structure in the spectra observed. Surrounding chalcogenide ions would be silver ions, and one might expect these to share the unpaired electron to some extent and thus give rise to hyperfine structure. As in the case of the F-centre this may just broaden the line - indeed this may be an explanation for the large line width observed. The

selenium has an isotope with a nuclear moment in a few percent natural abundance. This should also produce an hyperfine splitting, but which may be lost in the width of the line. Studies of a single crystal would be especially useful in this respect, since then the anisotropic hyperfine interaction could be detected.

#### Ebert's Results:

Crystal	g-value	line width.		
$AgBr + Ag_2S$	2.017 <u>+</u> 0.005	70 <u>+</u> 5 gauss		
+ Ag <sub>2</sub> Se	2.12 <u>+</u> 0.015	70 <u>+</u> 10		
+ Ag <sub>2</sub> Te	2.21 <u>+</u> 0.03	107 <u>+</u> 15		
$AgC1 + Ag_2S$	2.014 <u>+</u> 0.005	46 <u>+</u> 7		
+ Ag <sub>2</sub> Se	2.082 <u>+</u> 0.015	60 <u>+</u> 10		

#### Our Work:

We have attempted to repeat Ebert's work and extend it by growing a silver bromide crystal doped with silver selenide, in the apparatus previously described. We were unable to find any resonance under the same conditions. This is surprising since our apparatus ( the Varian spectrometer) had a sensitivity orders of magnitude greater than that of Ebert, which was a low frequency 10 cm. wavelength type. Our method of preparation of silver selenide was different and perhaps interfering impurities were present in our case - or necessary impurities in Ebert's.



We have already discussed how the presence of Se<sup>=</sup> could lead to the formation of anion vacancies, which on irradiation could trap electrons to form an F-centre. We have, therefore, gamma irradiated such a crystal at liquid nitrogen temperature for times up to several hours and then looked for an e.s.r. signal with the crystal kept at low temperature. Again no reproducible signal was observed. However the irradiated crystal on warming to room temperature emitted a red luminescent flash. This indicates that some kind of unstable centre is formed in the crystal by irradiation. This may be paramagnetic and not observed for some reason such as unfavourable relaxation ion times. It seems profitable to study such a crystal by its absorption and luminescent spectra.

In conclusion, although our results have not borne out the work of Ebert, further studies including measurements of absorption spectra are required before any definite conclusions can be drawn.

#### Appendix:

Irradiation of the crystal discussed above might lead to 'damage'of the selenide centre. For this reason the silver selenide used in the doping, was also irradiated. At room temperature a weak signal occurred at X-band when an e.s.r. signal was sought. Q-band measurements showed the signal, but it was too weak for quantitative study. The X-band spectrum is shown in the figure 3.23A.

3.24, Electron Spin Resonance Studies Of Cyanine Dyed

Silver Halides.

<u>Introduction</u>: The photosensitivity of silver halides to blue light can be extended into the red region of the visible spectrum by coating the surface of the crystals with organic dyestuffs. Especially well known for their sensitizing power are the cyanine dyes. Examples of these are: 1. Diethyl thiadicarbocyanine bromide.

 $\begin{bmatrix} S \\ N \end{bmatrix} = CH - CH = CH - CH = CH - C \begin{bmatrix} S \\ N \end{bmatrix} \begin{bmatrix} 1 \\ N \end{bmatrix} = B_T$ 

2. Diethyl-2'-cyanine bromide

Chiler AND Br

The fundamental question of the mode of action of these dyes is not yet fully understood. One theory suggests that they react with the halogen of the crystal, another that they merely absorb the radiant energy and transmit it to the crystal by some kind of exciton process. West et al. (1961) recently reported an e.s.r. signal from silver bromide dyed with various cyanine dyes and illuminated at 77°K.

<u>Results</u>: We have repeated some of West's work and have extended them to other silver halides. If illumination causes a reaction between the silver halide and the dye, then we may see a change in g-value in going from chloride to bromide to iodide, whilst keeping the same dye. In fact little shift is seen:-

Dye I. on silver;-

chloride bromide iodide g = 2.0071 2.0050 2.0060 Thus no conclusions may be drawn. In addition we note the following. The signals were always very weak, but improved on evacuation of the sample tube - as found by West et al. The strongest signal was obtained in the case of the dyed silver iodide. Since dyes similar to these have been reported to show e.s.r. signals, and since the signals observed in our case were very weak it is

questionable whether the observed signals can be associated with the adsorbed dyes.

#### Confined Electron Centres, Section 3.3.

If an electron is contained within a box, i.e.some small definite volume, by suitable potential barriers at the walls, then its energy may assume only certain discrete values. Transitions between these energy levels will give rise to characteristic spectra. The actual values of the energy levels and their spacing will depend on the size of the box. Hence, if we take a given type of box, then the absorption spectrum will be characteristic of the box size. This simple approach seems to be useful in a number of cases, in particular in explaining the spectra of F-centres and of the  $I^-$  ion in polar surroundings,e.g. in solution.

#### 3.31 The F-centre.

In the case of the F-centre the box may be thought of as the space within the surrounding shell of twelve anions - in the case of the 6:6 coordinate alkali halidesbut within this box there are six cations. Despite the latter complication the size of the box still seems to characterise the spectrum: Ivey found the frequency of the F-absorption band maximum simply depended on the lattice parameter, thus:

# $\lambda = 703 a^{1.84}$

 $\lambda$  = the wavelength at maximum absorption and d the lattice parameter (see Ivey,1947). Strictly speaking we should really compute the potential energy of the electron by

summing over all the surrounding ions to get a 'Madelung' potential, and we should remember that the lattice will distort around the F-centre. This is to some extent the approach adopted by Gourary and Adrian (1957), although they used group theory to expand the potential in a series of Kubic Harmonics. This expansion then was used together with similar wave functions in a variational treatment of the F-centre.

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In connection with the theories of the F and similar centres, it is of interest to know the distribution of the electron within the 'box' and around it. In fact e.s.r. and, especially, electron nuclear double resonance (ENDOR) measurements do give us information about the distribution of the electron. If we consider the electron in the F-centre case, then when it is near the near neighbour cation, it can be considered to be in an s orbital on the cation. The same will apply to the halide ion, although in this case this orbital is not low lying and thus we do not expect the electron to be in the vicinity of this ion. Thus the electron will have a contact or Fermi interaction with the nucleus of the cation, should that nucleus possess a magnetic moment. This will lead to isotropic hyperfine splitting of the electron spin resonance. Unfortunately, this splitting is not usually resolved in the case of F-centres: the many splittings which occur produce many lines which overlap and add to give a broad

line of width about fifty gauss. However, each nucleus will show a magnetic resonance absorption and this will be split by the electronic magnetic moment. In effect, this splitting is observed in the ENDOR experiment. The coupling constant, measuring the interaction between the nucleus and the electron, will naturally be the same whether we measure it by e.s.r. or ENDOR, If the coupling constant A is known for the atom - as is usually the case for the alkali metals - then to a good approximation we can measure the amount of electron on the ion in the crystal by measuring the coupling constant in the crystal:

Percent electron on  $M^+ = A_M^+ / A_{atomic}^+$ 

The case of the anion cannot be analysed in such simple terms. An electron on the halide ion could be described as being in an (n+1) s orbit. We might, then, nafvely compare it with the alkali metal having an outer electron in this orhit, thus:

Ahalide = Aalkali x Phalide Palkali .

Where **p** is the nuclear magnetic moment and the A's are atomic values. We have carried out estimations along these lines and include them in the table. Such values are much smaller than those for one electron in a p orbital on the halogen (also tabulated). In fact, such values lead to an impossible electron density on the halogen. The reason is that we have forgotten core polarisation: the presence

of an unpaired electron will affect all the s orbitals of the ionic core. This leads to large hyperfine splittings for each s orbital, some positive and some negative, the final splitting being the difference between a number of large terms. In fact, since we do not expect very large amounts of electron on the halide, we can conclude that the quite large hyperfine splittings observed to arise from the halogen nucleus are in fact core polarisation effects. Our conclusion is that we cannot make reliable estimates of the electron density on the surrounding halides. Intuitively it seems small, and comparison of the observed hyperfine interaction with that for an electron in a p orbit on the halogen, implies that our view is correct.

The ions can be divided into a number of shells surrounding the F-centre, each ion in a given shell will be identical from the 'viewpoint' of the centre, and will give an identical coupling constant. From the data in the literature we have computed the percentage of electron on the first shell, by multiplying the coupling constant ratio by the number of ions in the shell, and similarly for other shells. In table 3.31 we give the results of our calculations for a number of F-centres. In the figures 3.31, etc., we have plotted the percentage electron on the first shell against various parameters of the elements.



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		Table I	
	Some	Atomic Constants.	
Nucleus.	Moment.	H.F.S (p orbit)	Estimated H.F.S
	(n.m.)	(Mc/s)	= $\mu_{x} \times A_{M} \mu_{\mu} \mu_{\mu} \mu_{\mu}$
19 F	2.629	47,900	1060
<sup>35</sup> C1	0.822	4,662	478
$^{81}$ Br	2.110	21738	15 <b>9</b> 0
127 <sub>I</sub>	2.809	_	3550
		H.F.S. (s orbit)	
$7_{Li}$	3.256	40 <b>2</b>	
23 <sub>Na</sub>	2.218	886	
39 <sub>K</sub>	0.3915	231	
85 <sub>Rb</sub>	1.353	1012	
137 <sub>Cs</sub>	3.48	4400	

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Source: Kusch and Hughes (1959)

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## Table II.

Observed	Hyperfi	ne Spi	littings a	and Calcula	ted Elec	ctron
Density	on the S	hells	of Ions	Surrounding	the F-c	entre.
Substance	Shell	<u>Ion</u>	Observed	H.F.S. TO	<u>K P%</u>	<u>Ref</u>
LiF	1	Li	39.06	Mc/s 1.	3 58.3	a
	2	F	105.9		2.7	
	3	Li	0.5		1.0	
NaF	l	Na	105.6	1.	3 71.4	а
	2	F	61.6		1.5	
	3	Na	1.28		1.1	
KF	1	К	34 <b>.3</b>	90	89.2	ъ
	2	F	35•5		0.9	
LiCl	1	Li	19.1	1.	3 28.6	a
	2	Cl	11.2		2.9	
	3	Li	2.1		4.2	
NaCl	l	Na	61.5 62.4	1. 90	3 41.7 42.3	a b
	2	Cl	12.5	90/1.	3 3.2	a,b
	3	Na	0.34	90	0.3	Ъ
KCl	1	K	20.6 20.77 21.03	1.) 90 300	3 53.4 54.0 54.6	a b b
	2	Cl	6.9	1.	3 1.8	а
	3	K	0.3		1.0	
RbCl	1	Rb	98.2	90	58.2	с
	2	Cl	5.8		1.5	

			Table II (cont	inued	).	. ۲. ۴	L
Substance	<u>Shell</u>	<u>Ion</u>	Observed H.F.S.	<u>T<sup>o</sup>k</u>	<u>P%</u>	Ref.	
KBr	l	K	18.8 Mc/s	300	48.9	ъ	
	2	Br	43.5		2.4		
RbBr	l	Rb	87.8	90	52.0	с	
	2	Br	36.9		2.0		
KI	l	K	15.0	20	39.0	Ъ	
	2	I	49.5		_		
NaH	1	Na	c75	90	50	đ	
The number	of ion She	 s in 11	the shells are:- Number of ions				
	l		6				
	2		12				
	3		8				
The data a 7 <sub>Li</sub> 23 <sub>Na</sub> 3	bove re 9 <sub>K</sub> 85 <sub>Rb</sub>	fer t 19 <sub>F</sub> 3	o the following n <sup>5</sup> Cl <sup>81</sup> Br <sup>127</sup> I.	uclei	:		
References	: a -	Holto	n and Blum (1962)				
	b –	Sėide	1 (1961)				
	с –	Wolf	and Sei <b>del (1</b> 963)				
	d -	Doyle	and Williams <b>(</b> 19	61).			
Ionic radi	i for t	he pl	ots were from Gou	rary	and Ad	rian(19	60)
and covale	nt radi	i fro	m Sidgwick (1950)	•			

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It can be seen that the electron is in the anion vacancy or on the first shell of cations. In the following discussion we shall follow the change of electron density on the first shell of cations as we change the cation and keep the anion the same - and also for the reverse procedure. Because of the lack of reliability of our estimates of 'atomic' hyperfine splittings for the halides, we have not felt it worthwhile to carry out comparisons of the various derived percentages of electron on the anion shell.

Since we can largely apportion the electron to the cavity or to the first shell of cations, we could expect the electron to be described by a wave function of the form:  $p'_F = a p'_{cavity} + b p'_{M^+(s)}$ The second wave function represents the contribution of the s orbitals of the metal ions. For a given cavity size the proportion of electron in the s orbital might depend on a number of factors. First one might expect that the electron affinity of the cation will be of importance. The plot of percentage electron on the first shell of cations, P, however, falls with increasing ionisation potential of the metal. Hence whatever effect this quantity has, it is outweighed by other properties.

The plot of the percentage P against the atomic number of the cation, figure 3.302, is linear initially and increases.with atomic number. This could be interpreted

in a number of ways, however, the next figure, 3.303, shows that the percentage P increases linearly with the covalent radii of the alkali metals. This seems to indicate that it is the increasing radius of the available s orbit which is important. Indeed the more this reaches into the cavity, the more one would expect it to contribute to the F-centre wave function.

The plot of the percentage P against the ionic radius of the halide, for a given cation, falls linearly with increasing anion radius. This clearly indicates the importance of the cavity size. The larger the cavity, the lower the kinetic energy of the electron within the cavity and hence the more the electron tends to reside in the cavity. In this connection it is useful to apply the plot to a determination of the hydride ion radius. From the tables we can see that the value of P for sodium hydride is approximately 50%. This value, read off on the plot for the sodium halides gives hydride a radius of about 1.45. It seems necessary, however to correct this since it implies a lattice near neighbour distance of 2.62 Å. This could imply unusual distortions around the F-centre. Alternatively we can correct the apparent radius by subtracting from it the difference between the true lattice parameter and 2.62 Å, to obtain 1.27 Å. This is the value obtained by subtracting the sodium radius from the near neighbour distance.

We should comment here on one aspect of Gourary and Adrian's theory. Most theories to date, including that of Gourary and Adrian, have neglected the overlap between the orbitals of **adjacent** ions, especially with regard to the first shell of cations. The importance of the cavity size has been seen to be very great and must be included before any second order effects such as ion-ion orbital overlap.

A-criticism might be made of our use of atomic coupling parameters to calculate the electron density on the near neighbour cations. Although some alteration of the hyperfine splitting of, say, sodium is expected when it is embedded in the ionic lattice, a similar alteration would apply to the ionic parameters such as radius - and in fact should be quite small.

A further point which requires mention is the temperature dependence of the observed hyperfine coupling constants. As the temperature rises the lattice will expand, and since the cavity will increase in size, one might expect the hyperfine couplings observed to be larger the higher the temperature. In fact the reverse is true. A possible explanation is that the lattice distortion around the F-centre, increases as the temperature rises the changes in electron density on the cations surrounding the cavity is only of the order of one percent.

The last point we shall discuss is the application





of our correlations to the data of Mieher (1962) on the lithium A centre in potassium chloride. These centres are believed to be F-centres in which the near neighbour cation shell has one lithium ion replacing a potassium ion. Since the sizes of the two cations are quite different, quite large distortions of the lattice occur around the vacancy. Using the plot of P against anion radius, i.e. apparent cavity radius, we can use the ENDOR results to calculate approximately the distortions of the lattice around the centre.

First the distance of the centre of the cavity to the lithium: Mieher found  $A_{Li} = 8.03 \text{ Mc/s}$  , which corresponds to 6 x 8.03 x 100/402 = 12% of electron on an hypothetical lithium shell. From figure 3.304 we find that this corresponds to an apparent anion radius of 1.98 Å. For the  $K_{\mathbf{x}}^{\mathbf{+}}$  ion ( the potassium ion opposite the lithium ion) the hyperfine coupling corresponds to 62% electron on the cation shell and to an apparent cavity radius of  $1.57^{\text{A}}$ . For the K<sub>B</sub> ( the four ions in a plane perpendicular to the lithium -  $K_{\alpha}$  axis) we calculate an apparent cavity radius of 1.54 Å. We have, of course, neglected to take into account the usual cavity distortions which occur around an F-centre. These are believed to be quite small (Gourary and Adrian, 1960) and will in any case affect the calculations similarly. In figure 3.305 we have drawn to scale the structure of this centre according to our calculations.


Figure 3.36

## 3.32 The Spectrum of The Iodide Ion.

The ultraviolet absorption of the iodide ion in solution has long been known to be solvent dependent (Franck and Scheibe,1928). Essentially the role of the solvent is to provide a cavity which will confine the excited state (Smith and Symons, 1958). Since different solvents will provide different sized cavities, the energy of the excited state and hence the energy of the absorption maximum will depend on the solvent. But the cavity size cannot be simply defined in solutions - even the coordination of the solvent molecules around the iodide is not known. For This reason there is interest in the spectrum of iodide in the solid state: where distances and coordinations are well known. Little work seems to have been carried out on the spectra of iodide impurities in crystals, but Ishii (1961) has measured the spectrum in potassium chloride. We have grown crystals of potassium sulphate and sodium tetra-fluoroborate both containing iodide as an impurity. The first crystal was grown by slow evaporation of an aqueous solution at room temperature, the second by slow precipitation of a solution in diglyme by addition (diffusion) of chloroform. In figure 3.306 we have plotted the energy of the maximum absorption of these crystals together with Ishii's result, against the sum of the cation and anion radii. The straight line obtained must, of course, be regarded with caution in the case of so few results.













3.33 Studies of Alkali Halides doped with Silver Ions. Following the work of Delbecq, et al. (1963) we have attempted to prepare from the melt crystals of potassium chloride, bromide and iodide, sodium bromide, rubidium bromide, and caesium chloride and powders of potassium fluoride and lithium fluoride. These samples were gammairradiated to effect conversion of the silver ions to Ag<sup>o</sup> and Ag<sup>+2</sup>. In the case of the potassium chloride, it was found that the results of Delbecq et al. were readily repeated, and the silver atoms proved to be stable in the crystal at room temperature. The other samples, however, gave no e.s.r. signals which could be readily attributed to silver species. The reason for this difference from the chloride remains an enigma. Absorption spectra of some of the crystals which had been gamma-irradiated at and kept at 77°K were taken and are reproduced in figures 3.307 to 3.319.

## Appendix A.

An attempt was made to prepare a crystal of potassium chloride containing Au<sup>+</sup>, by addition to potassium chloride and growth from the melt. Decomposition occurred to give a potassium chloride crystal, probably containing colloidal gold, which was coloured purple. Its spectrum is shown in figure 3.310.

<u>B.</u> Figure 3.311 shows the absorption spectrum of a single crystal, gamma irradiated and kept at  $77^{\circ}$ K, of tetra-

n - amyl ammonium iodide.

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