Modified ionic states in crystals. By Dr C. P. SNOW, Christ's College, and Mr F. I. G. RAWLINS, Trinity College.

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1. *Ionic states in compounds of rare earths.*

Two distinct lines of research have already given considerable information about the ions of the rare earths. In the first place, Hund, in 1925, calculated the magnetic moments of compounds of the rare earths on the assumptions (i) that the ions were to a first approximation "free" (i.e. with as little influence upon each other as in the gaseous state), and (ii) that the spectral terms of the ions obeyed the normal laws of atom-building. The magnetic susceptibility is obtained from the formula $p = 2 \times 4{\cdot}97\,\{J(J+1)\}^{\frac{1}{2}}$, where J is the quantum number of the ion with Russell-Saunders coupling, and the numerical coefficient equal to 2 is the Landé splitting factor. Correspondence between the calculated and theoretical values is excellent, except for samarium and europium.

In the second place, the series of empirical investigations by many workers extending over a number of years has revealed a unique property of compounds of the rare earths—the spectra of their solutions, and even better of their crystals show, at room temperatures, narrow bands in the visible and ultra-violet regions of the spectrum. At low temperatures, as has been demonstrated by Freed and Spedding (*Phys. Rev.*, 34, p. 945 (1929)), these bands attain the order of fineness of normal spectral lines, and for any one rare earth persist unchanged in a series of compounds. For example, $GdCl_3 . 6H_2O$ shows sharp lines identical with those of $GdBr_3 . 6H_2O$. These lines are clearly produced by the rare-earth ion—although the nature of the electronic transitions has remained obscure, and we have been compelled to consider it later in this paper. From both the magnetic and spectroscopic observations there is no doubt that the metallic ions exist "so nearly free as far as orientation is concerned that the calculations for the gaseous phase may be utilized" (Van Vleck). The reason of this isolation is very convincingly explained when we consider the nature of the electrons which are responsible both for the paramagnetism of the substances and their characteristic spectra. In the rare earths, a shell of quantum number 4 is being built up inside a 5-shell of 8 electrons, and it is the electrons of this incomplete *inner* shell which are magnetically and spectroscopically active. Since they are shielded from the effects of neighbouring ions by the shell outside,

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the incomplete shell develops its characteristic properties. The wave-functions of these $4f$ electrons do not overlap electrons of other atoms to any appreciable extent. In fact compounds of the rare earths provide a very close approach to the free ionic state.

2. *Paramagnetism of compounds of transitional elements.*

In compounds of all other elements, the ionic condition seems to be very different. The only relevant information which can be supplied about the ionic state will again be provided by magnetic and spectroscopic investigations, for the deviation from the "free" ionic state obviously means in fact the interaction of incomplete electronic groups upon one another. This interaction will reveal itself most clearly in measurements of paramagnetism and in spectral transitions, both of which, as we have stressed before, are due to incomplete shells.

The transitional elements of the first group provide a series of compounds in which the metallic ion has an incomplete $3d$ group. These compounds differ from those of the rare earths in that the $3d$ groups are the outermost electronic shell, and there is no shielding of the kind furnished by the 5-shell of the rare earths.

Hund's treatment was found to break down entirely when applied to these compounds: the magnetic susceptibility calculated upon the basis of the free ionic state gave no sort of agreement with the observed values. The most reasonable construction to put upon this failure was that the metallic ions were exerting a profound influence upon each other. Empirical formulae were found by Bose to express the actual experimental susceptibility, and these gave an adequate approximation to the observed facts. He used the expression for the moment $p = 4{\cdot}97g\{S(S+1)\}^{\frac{1}{2}}$, where S is the resultant spin moment associated with the multiplicity $r = 2S + 1$. In 1929 Stoner outlined an explanation of this phenomenon. Instead of the orbital angular momentum L and the spin momentum S combining to form a resultant J for the individual ion, the L of a given ion is regarded as interacting with the L's of its neighbours in some unspecified manner which destroys them all. Stoner's illuminating suggestion has later been amplified and justified mathematically by Van Vleck. In the cases of some of the transitional elements, the L-S coupling for the ion is conceived as being broken without the consequent mutual quenching of the L's: that is the formula becomes $p = 4{\cdot}97g\{S(S+1) + L(L+1)\}^{\frac{1}{2}}$, and this is found to fit. Although some of the details of the magnetic investigations are not yet satisfactorily rounded off, nevertheless Stoner and Van Vleck have gone a long way towards a description of the paramagnetic behaviour of the ions of transitional elements.

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3. *Types of bands in spectra of compounds of transitional elements.*

Although the magnetic side is thus established, there has yet been no complementary spectroscopic evidence. At first sight it would seem that none should be expected, for in compounds of transitional elements we are dealing with a highly ionised state of the metal atom. In iron, for instance, we are concerned with Fe^{3+}, and it is known that this ion in its spark spectrum gives no strong line of longer wave-length than some 1300 Å. If the spectra of compounds of the transitional elements were due to such ions as this, then of course there should be no bands in any observable region of the spectrum. It is however well known that compounds of the transitional elements actually possess marked strong bands in the visible (that is, these substances are often coloured) and ultra-violet. Some time ago (*Nature*, 125, p. 349 (1930)) we suggested that the origin of these bands must lie in *molecular bindings* associated with the central ion, usually in co-ordination bonds supplied by the H_2O molecules, etc., which are a common feature of most of these transitional compounds.

The considerations which led to these conclusions are very obvious: (i) the physical properties of the bands themselves are not in the least like those of ionic lines, even allowing for the broadening to be expected from L interaction and thermal effects. The bands are usually hundreds of Ångströms broad, and both in crystal and solution have the structureless character of typical unresolved molecular bands; (ii) they vary drastically from compound to compound containing the same ion; thus $CuSO_4.5H_2O$ has a well-defined band in the red, whereas $CuSO_4$ (anhydrous) is transparent throughout the visible. The bands found in $CuSO_4.5H_2O$ and in many Cu^{2+} salts must therefore be attributed to the co-ordination electrons of the water molecules; (iii) we have been able recently to photograph the visible spectrum of a perfect crystal of anhydrous $FeCl_3$ which shows bands at about 5000 Å. and at 6200 Å. If these were directly due to transitions within the Fe^{3+} ion, then they should be observed in the spectra of all ferric compounds. Actually, careful search has revealed that the bands in ferric compounds vary very greatly from compound to compound, and that most of them do not show the bands of $FeCl_3$ at all. It follows automatically (*a*) that the bands in ferric compounds must be attributed to a "molecular" origin as already defined, and (*b*) that the bands in $FeCl_3$ (anhydrous) itself must be produced by some species of binding between the iron and its surrounding chlorines. As a subsidiary result, it appears that the crystal is not completely ionic.

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Thus the nature of the broad bands in transitional compounds may be taken as qualitatively settled. At present it is difficult to do more than speculate why they should occur so markedly in transitional compounds; presumably the cause is connected with the effect of the co-ordination electrons upon the incomplete 3*d* group. If these bands constituted the whole spectrum of transitional compounds, spectroscopic observations would have nothing to add to the magnetic information.

We have however to mention two fundamental considerations. The first is that in the spectrum of some transitional elements there are bands which cannot be explained by the suggestion above. The second is that the rare-earth spectra are unquestionably ionic, although the remark made upon spark spectra with reference to Fe^{3+} would apply as strongly to rare-earth ions as to the ions of the first transitional group. The ordinary spark spectrum of Pr^{3+} could have none of its normal lines corresponding to such small energy transitions as are actually observed in the visible spectra of its salts. It is necessary to go deeper than the first naïve view to explain these phenomena, although they are clearly connected with the ions themselves.

4. *Experimental evidence for ionic lines in compounds of transitional elements.*

Reference has been made in the last section to bands in compounds of transitional elements which cannot be taken to be of "molecular", as distinct from ionic, origin. We have made a spectroscopic investigation of a number of chromium salts in the crystalline form, and in aqueous solution. A chart illustrating the kind of experimental result for some typical substances is given below.

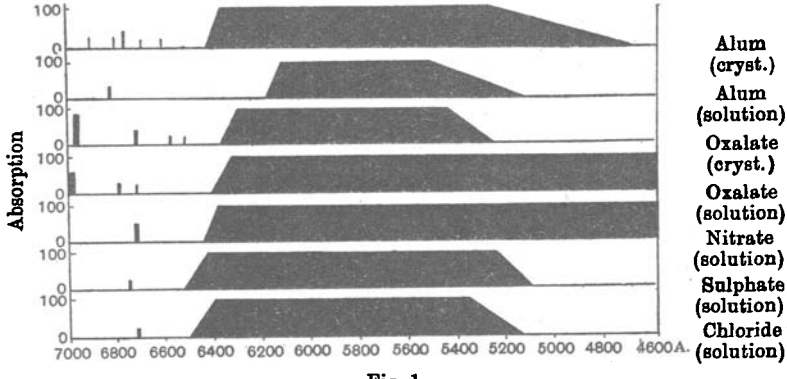


Fig. 1.

A general statement can be made upon the nature of the bands of any of the compounds considered. First of all, there is a strong

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band of variable position and intensity, situated in the green region; this band varies from compound to compound (even for substances so closely akin as the green and violet sulphates there is a shift of a hundred Ångströms). The band is very similar to the broad band in chromates and dichromates. In certain compounds it shows signs of structure towards the edge of shorter wavelength. The structure is of the same nature as that observed in chromyl chloride. The bands of the latter substance form a perfectly typical molecular spectrum with a well-marked vibrational structure.

There is thus every reason for believing the broad green band of the chromium salts to arise from the electrons of the co-ordination bonds in precisely the way suggested in the last section. There is however a system of bands in the spectrum of all the chromium salts which we have been able to obtain which are totally unlike the typical broad bands of crystals or solutions. For all these compounds there is a series of bands shown in the chart between 7000 Å. and 6500 Å. At normal temperatures, many of these bands, particularly those of the alum $K_2Cr_2(SO_4)_4 . 24H_2O$ are only a few Ångströms wide, that is of the order of fineness observed in the more diffuse lines of neodymium compounds. At the temperature of liquid air a perceptible sharpening is found, and the sharpest bands become more and more of the degree of fineness of the Nd lines. [The effect of low temperatures in introducing detail into the spectra of crystals is produced presumably by a lessening of the thermal agitation, and accordingly decreasing the variable Stark field acting upon a given ion. Some support is given to this view by the large shifts which can be brought about in broad crystal bands by cooling to low temperatures. The shift is precisely of the order—but of opposite sign—which is observed when the crystal is dissolved in a polar solvent, that is, subjected to a variable Stark field.]

The nature of these bands precludes any reasonable probability of their being due to molecular transitions. Both arrangement and width point at once to an atomic origin. It may be noticed that the position of the bands is fairly constant through a number of chromium salts with the exception of potassium chromium oxalate, which has a strong band at 7000 Å. not observed in the others. There is strong reason to think that these systems of bands are caused by ionic (or quasi-ionic, that is, due to an ion modified by the fields of its neighbours) transitions.

It remains to consider whether there is any spectroscopic justification for the existence of ionic transitions of such low energy content. We may take the normal state of Cr^{3+} as ${}^4F_{\frac{3}{2}}$, although of course in the crystal the L value could be subjected to a great change. Transitions of the ordinary kind ${}^4F—{}^4G$ or ${}^4F—{}^4D$ are of quite the wrong order of energy, and the lines resulting from them

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would fall in the Schumann region. The only possibility remaining is the inter-combination $^4F—^2G$. Saha (*Nature*, 125, p. 163 (1930)) has calculated the energy of this transition to be of the order 18,000 wave-numbers, which does not fit the red bands very well.

H. E. White (*Phys. Rev.*, 33, p. 673 (1929)) has however analysed the Cr^{3+} spectrum in the vapour of chromium, and obtained lines at 15,371, 15,138, 14,813 ... cm.$^{-1}$ due to $^4F—^2G$. These are very close to the red bands in Cr^{3+} salts at 14,000—15,500 cm.$^{-1}$ Deutschbein (*Zeits. f. Phys.*, 77, p. 489 (1932)), whose paper we have received while completing our own, has attempted to find an exact correlation between the $^4F—^2G$ lines in the vapour and bands in the crystal. The correspondence is not complete enough to prove the case finally.

In the next section it will be shown how the intensity of these bands of different transitional elements obeys the ordinary spectroscopic laws of combination series. Meanwhile, assuming that this transition is the true explanation of this system for chromium, it can add some details to our observations in special cases.

In the first place, such transitions of $3d$ electrons will clearly be affected by the L interaction invoked by Stoner to explain the magnetic properties of transitional elements. In this way we should expect, and do in fact get, the same line altering slightly in position and character from compound to compound according to the extent of the L interaction. The bands in chromium salts alter considerably in position. Thus the well-marked and sharp 6700 band in the alum is displaced by 30 A.U. in the nitrate and sulphate. The maximum shift in the corresponding case of the rare earths would be of the order of 1 A.U. The extent of the L interaction will be influenced to some extent by the shielding provided by the co-ordinated water, or other groups. For example, in anhydrous $CrCl_3$, where there is no shielding by co-ordination groups, the red bands are so diffuse as to be indistinguishable. In the alum on the other hand, with its large degree of co-ordination, the bands are remarkably sharp, and the L interaction is clearly minimised. An interesting confirmation of this view is provided by some measurements of magnetic susceptibility very kindly undertaken for us by Dr W. L. Webster. The alum had considerably the largest susceptibility of the compounds investigated. That is, the interaction has not completely destroyed the L contribution to the susceptibility. This is in perfect agreement with the results of the spectroscopic observations. Sharp bands, high susceptibility, point equally to the existence of considerable shielding, that is, persistence of the L term.

It is our intention to deal later with other cases in which spectroscopic and magnetic features may be expected to bring

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detail to our knowledge of these ions and the type of their co-ordination. The unique bands found in potassium chromium oxalate are so far only to be explained qualitatively by the different environment of the Cr ion. In the oxalate, Cr^{3+} is surrounded by three oxalate groups, and is part of the *negative* ion. Apparently this increases the probability of transition, leading to the band at 7000 Å.

5. *Multiplet intervals and intensity of inter-combination series.*

The suggestion that these bands in chromium may be attributed to an inter-combination transition of the type ^4F—^2G made first by Saha (*loc. cit.*) and taken up by ourselves has considerable support from the observations already described, but, in view of the behaviour of the oxalate and of more general considerations of intensity, further proof is necessary before the assignment can be regarded as definitely settled.

For the ions in most of the transitional elements there appears a possibility of these inter-combinations. As a matter of experimental fact they would seem to be observed in Cr and possibly in Mn and Co (see later). It remains to be seen whether this fact is in agreement with the theoretical intensities for inter-combinations in such ions as these. The condition for observable intensity for a transition ^4X—^2Y or ^3X—^1Y or any inter-combination in general is that the multiplet width of the lowest term shall be large relative to the distance between the terms X and Y.

It is now necessary to calculate the multiplet widths of the ions of transitional elements. The spectroscopic analysis of deep terms is not usually complete enough to allow us to proceed from direct measurement, and so we have to use the method described by Van Vleck. The multiplet intervals are given by

$$W_J = \tfrac{1}{2}AJ(J+1),$$

where A is proportional to $\frac{1}{2}(Z-\sigma)^4/S$, Z is the number of electrons in the ion and σ is the appropriate shielding constant. The results of multiplet separations for the various transition elements give a minimum for Fe^{3+} (which is an S term and consequently has no multiplet separation), a maximum for Cu^{2+} (which is a doublet term and therefore cannot take part in inter-combinations), and proportional values for electronic numbers lower than Fe^{3+} as follows: Ti^{3+} 4·5, V^{3+} 4·2, Cr^{3+} Mn^{4+} 4·0, Mn^{3+} Cr^{2+} 1·6—Fe^{3+} 0. Since all inter-combination lines are expected to be very weak, it is resonable that they should not occur for Mn^{3+}, Cr^{2+}. They are impossible for Fe^{3+} and Cu^{2+}.

From our considerations, which depend upon the rather undeveloped theory of the spectra of many electron atoms, we should

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expect inter-combinations for Ti^{3+}, Ti^{2+}, Cr^{3+}, Mn^{4+}, Co^{3+}, Ni^{2+}. Ti^{3+} and Ni^{2+} are ${}^3F$ terms and the others ${}^4F$. ${}^3F$ transitions, if they occur at all, will be ${}^3F—{}^1G$.

There is some evidence for the occurrence of inter-combination lines both in Mn^{4+} and in Co^{4+}. In both cases, the inter-combination lines appear to coincide with the molecular bands, but there are well-marked discontinuous bands in the spectra of compounds containing these ions which can be most satisfactorily explained by considering them as the inter-combination transitions (see A. M. Taylor on $KMnO_4$, where the Mn, on chemical evidence, can be regarded as Mn^{4+} surrounded by O^{--} (*Trans. Faraday Soc.*, 25, p. 860 (1929), and Hill and Howell for Co, *Phil. Mag.*, 48, p. 833 (1924)). For Ni^{2+} and Ti^{2+} the evidence is not so clear. All Ti^{2+} salts absorb so strongly in the visible that it is difficult to detect bands both weak and narrow as these inter-combination spectra must be. For Ni^{2+} we have some experimental data which suggest that inter-combination lines may possibly be present. This last result however cannot at the moment be taken as definite.

On the whole, the idea of intensity of inter-combination lines as determined by multiplet intervals probably, but not quite certainly, accounts for the facts in the transition elements. It is just conceivable that the ${}^4F—{}^2G$ transition is specially favoured, though such a selection rule is improbable.

6. *Intensity rules for the rare earths.*

Complete justification for the view which attributes these ionic lines to inter-combinations is provided by the spectra of compounds of the rare earths. All the difficulties which have been raised apply equally to the rare-earth ionic transitions. For instance, as we said

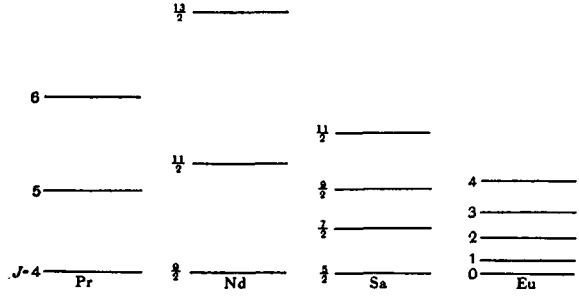


Fig. 2.

before, Pr^{3+} is a ${}^3H$ term, and its normal spectrum will be combinations of the ${}^3H—{}^3I$ type. In the same way, Nd^{3+} is a ${}^4I$ term, and its transitions are ${}^4I—{}^4H$, or ${}^4I—{}^4J$. Such transitions are, of

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course, quite different in energy content from those which are actually observed, and we are compelled to assume that the ionic lines of rare-earth compounds are only to be explained on the basis of inter-combination series. A very beautiful confirmation of this is given by a comparison of the intensities of these spectra of some rare earths based upon their multiplet intervals, along the lines suggested in the last section. Let us take the four ions Pr, Nd, Sa, Eu. The spectra of these are all well known. Pr and Nd absorb very strongly and give sharp lines. Sa and Eu give undoubted ionic lines of a much weaker order of intensity. The reason for these differences in intensity of the inter-combination series is immediately obvious when we calculate the multiplet intervals. The Pr^{3+}, Nd^{3+}, whose spectra consist of strong lines, have the wide multiplet intervals. Sa^{3+} and Eu^{3+} have narrow multiplet intervals and weak lines. This relation of multiplet interval to intensity of spectral line can be followed throughout the rare earths, and constitutes the best proof both of the suggested origin of these lines and of the application of the multiplet rules.

Summary.

After a review of the magnetic and spectroscopic properties of compounds of the rare earth and of transitional elements of the first group, the types of bands in spectra of the latter are considered in detail. Reasons are advanced for the view that these are of "molecular" origin in ferric salts, but that the spectra of some transitional compounds contain lines which cannot be regarded in this way. Such lines are shown to be ionic, or quasi-ionic, and accord well with the suggestion of inter-combination transitions such as $^4F—^2G$.

The theoretical intensity conditions, as a function of multiplet intervals, are in agreement with the observed appearance of inter-combination transitions in Cr, and possibly also in Mn and Co. Similar considerations apply to the rare-earth spectra. As an example we have shown that the strong absorption in Pr and Nd compounds, and the much weaker lines found in Sa and Eu, are in perfect agreement with the theoretical prediction of inter-combinations.

We have great pleasure in expressing our thanks to Professor A. Hutchinson, F.R.S., for enabling the experimental work to be initiated in his department. Dr E. C. Stoner has helped us in magnetic questions, and to him we are much indebted. Finally, we have to acknowledge our obligations to the Commissioners of the Exhibition of 1851 for a Senior Studentship (C. P. S.), and to the Government Grants Committee of the Royal Society for the purchase of apparatus (F. I. G. R.).

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