MAGNETISM AND INORGANIC CHEMISTRY

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THE magnetic properties of inorganic compounds have been studied for more than one hundred years, but the value of magnetic measurements in inorganic chemistry has increased remarkably during the last two decades. This development is largely the outcome of work on valency theory which now enables us to correlate more confidently the valency, bond type, and stereochemistry of an atom with its effective magnetic moment. Before discussing the modern views on this subject the fundamentals of magnetism will be summarised without experimental details. The application of magnetic susceptibility measurements to the above kinds of problem in inorganic chemistry will then be examined ; particular regard will be paid to the more recent work. Attention will be confined almost entirely to the results of measurements on paramagnetic compounds, because these provide more useful information than do studies on diamagnetic substances. Finally, some developments in crystalline field work and paramagnetic resonance will be reviewed.

Theoretical Principles

(a) **Fundamental Definitions.**—Theoretical aspects of this subject are dealt with at length in standard works ; [1-6] a summary of fundamentals will suffice for our purposes. Chemical substances may be classified on the basis of their behaviour when placed in a non-uniform magnetic field. Those substances which tend to move from a stronger to a weaker part of the field are called " diamagnetic ", whilst those which tend to move from a weaker to a stronger part of the field are usually called " paramagnetic ". (Further sub-divisions will emerge as discussion proceeds.) The extent to which a material becomes magnetised is measured by its magnetic moment per unit volume, usually known as intensity of magnetisation, I. Inside the material the total number of lines of force per unit area (the magnetic induction, B) is given by the expression $B = H + 4\pi I$, where H is the strength of the magnetic field *in vacuo*. On dividing throughout by H, we obtain $B/H = 1 + 4\pi I/H$. The ratio of the number of lines of force per unit area inside the material to the number of lines of force per unit area

[1] J. H. Van Vleck, " Theory of Magnetic and Electric Susceptibilities ", Oxford Univ. Press, London, 1932.

[2] E. C. Stoner, " Magnetism and Matter ", Methuen, London, 1934.

[3] S. S. Bhatnagar and K. N. Mathur, " Physical Principles and Applications of Magnetochemistry ", Macmillan, London, 1935.

[4] P. W. Selwood, " Magnetochemistry ", Interscience Publ., New York, 1943.

[5] L. F. Bates, " Modern Magnetism ", Cambridge Univ. Press, 2nd Edn., London, 1948.

[6] W. Klemm, " Magnetochemie ", Akademische Verlagsges., Leipzig, 1936.

in vacuo, *i.e.*, B/H, is called the "magnetic permeability * " (μ) of the material. The ratio I/H is known as the "volume susceptibility" of the material and is given the symbol k. This is what one usually measures in experimental determinations, but of greater interest is the gram-susceptibility χ, related to the volume susceptibility by the expression $\chi = k/\rho$, where ρ is the density of the substance. For chemical compounds the molar susceptibility χ_M is more important; this is obtained by multiplying χ by the molecular weight. Similarly the gram-atom χ_A and gram-ion χ_{A^+} susceptibilities are obtained by multiplying χ for an atom or ion by the atomic or ionic weight respectively.

For most chemical substances χ is independent of the field strength, but for ferromagnetic substances it first increases rapidly as H increases and then gradually decreases as saturation is approached. We shall not be concerned with ferromagnetism here except insofar as incipient ferromagnetism is observed in some paramagnetic compounds, *e.g.*, ferric fluoride.[7] Wherever χ is found to be dependent on field strength, magnetic moments become meaningless.

A convenient way of determining χ is by the use of Gouy's method.[8] The simple theory of this illustrates several general principles. A cylindrical column of the material, of cross-sectional area A and length l (usually in a suitable glass tube), is suspended from a sensitive balance so that one end is placed between the poles of an electro-magnet capable of producing a strong magnetic field H_1, generally of the order of 3000—10,000 oersteds. The length of the specimen must be such that H_2, the field strength at the other end, is negligible compared with H_1. The difference in pull on the balance δw with the magnet on and with the magnet off is then measured. If the volume susceptibilities of the surrounding medium (usually air) and the specimen are respectively k_2 and k_1, then the force F acting on the specimen owing to the magnetic field is given by $F = \delta w \times g = \frac{1}{2}(k_1 - k_2)(H_1^2 - H_2^2)A$. When H_2 is very small compared with H_1, this reduces to $\delta w \times g = \frac{1}{2}(k_1 - k_2)H_1^2 A$, whence

$$k_1 = k_2 + 2\delta w \times g/AH_1^2$$

Replacing k_1 by $\chi \times$ density, and taking v and W as the volume and mass of the specimen respectively, we get

$$\chi = (k_2 v + 2gv\, \delta w/AH_1^2)/W.$$

This equation contains the unknowns v, H_1, and A, which need not be measured (except in absolute determinations of χ) if one is prepared to calibrate the tube with a material of known susceptibility, *e.g.*, nickel chloride solution.[9] The expression reduces to $\chi = (a + b\delta w)/W$, where a and b are constants for any particular tube and field strength. δw is generally measured in milligrams. Values of χ vary from -3 to $-0\cdot1 \times 10^{-6}$ for diamagnetic substances and may be as high as $+100 \times 10^{-6}$ for para-

[7] H. Bizette and B. Tsai, *Compt. rend.*, 1939, **209**, 205.   [8] *Ibid.*, 1889, **109**, 935.

[9] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1939, **A**, **173**, 313.

* Not to be confused with the "magnetic moment", discussed presently, for which the same symbol is used.

magnetic substances like ferric salts. An excellent apparatus for measuring both dia- and para-magnetic susceptibilities by the Gouy method is described by Baddar, Hilal, and Sugden.[10]

(*b*) **Diamagnetism.**—An electron in an orbital produces a magnetic field equivalent to that of an electron moving in a circle. On application of an external magnetic field, a precession occurs (the Larmor precession) which gives rise to a magnetic field in the opposite direction to that of the imposed field. This results in diamagnetic susceptibilities being negative.

(i) *Atomic Diamagnetism.*—For an atom containing n extranuclear electrons it can be shown by a classical mechanical treatment that

$$\chi_A = -2 \cdot 832 \sum_n \overline{r^2} \times 10^{10},$$

where $\overline{r^2}$ is the mean of the squares of the radii of the projections of the orbits perpendicular to the field. Diamagnetism is characteristic of *all* atoms, though it is often swamped entirely by the much greater paramagnetism arising from spin or orbital motion. A quantum-mechanical treatment gives essentially the same result but the expression obtained enables one to calculate χ_A more readily. This involves the use of effective nuclear charge $Z_{\text{eff.}} \times e$ instead of $Z \times e$. Even so, for the apparently simple inert gases, only fair agreement has been obtained between experimental and calculated results.[11] It follows from the above formula that atomic diamagnetic susceptibilities (α) are independent of temperature, and (β) increase with increasing size of the atom.

(ii) *Ionic Diamagnetism.*—Theoretical calculation of this is carried out in the same way as for atoms, the effect of a negative charge being to increase the value as compared with that of the free atom. For most practical purposes it is obtained experimentally by assuming that in a solution or ionic lattice $\chi_M = \chi_{\text{Cation}} + \chi_{\text{Anion}}$. As with similar problems, the allocation of the total χ_M between cation and anion is somewhat arbitrary and variations of the order of $\pm 5\%$ (or more) are found between the values recommended by various workers.[4, 5, 12, 13] The diamagnetism of ions has been reviewed by Myers,[14] who emphasises that no simple method for obtaining ionic diamagnetic susceptibilities has yet been found.

(iii) *Molecular Diamagnetism.*—This is of special interest to the inorganic chemist since it must be corrected for in calculations of effective magnetic moments. The classical theory of diamagnetism is inapplicable to molecules, but for hydrogen the susceptibility has been calculated by using quantum mechanics ; good agreement between theory and experiment is observed.[15] For other molecules the calculation is not practicable and use is made of the expression $\chi_M = \sum_n n_A \chi_A + \lambda$, where n_A and χ_A are the

[10] *J.*, 1949, 132.   [11] P. W. Selwood, ref. 4, p. 34.

[12] V. C. Trew, *Trans. Faraday Soc.*, 1936, **32**, 1658 ; 1941, **37**, 476.

[13] W. Klemm, *Z. anorg. Chem.*, 1941, **246**, 347.

[14] W. R. Myers, *Rev. Mod. Physics*, 1952, **24**, 15.

[15] G. Steinsholt, *Phil Mag.*, 1947, **38**, 748, and refs. therein.

number and atomic susceptibilities of the different kinds of atom present and λ is the " constitutive correction ", correcting for all incalculable effects such as double bonds, stereochemical isomerism, etc.   In effect, all departures from additivity are embodied in λ.   Tables of commonly used values of χ_A and λ are available ; [16] they are usually known as Pascal's constants, after the first important worker in this field.   Molar susceptibilities calculated by using these are at best approximate, but since the diamagnetic correction is usually small compared with the paramagnetic susceptibility, the uncertainty of atom and ionic susceptibilities is not serious.   For mixtures of diamagnetic substances, additivity is generally assumed,[17] but when marked solvation occurs, as when a salt is dissolved in water, considerable deviations from additivity are observed.[14]   The disagreement between experimental and estimated diamagnetic susceptibilities of molecules has severely limited the value of magnetic measurements for the confirmation of structure of diamagnetic compounds.[18]   Gray and Cruickshank [19] put forward a method to overcome the lack of additivity of Pascal's constants which takes into account resonance structures, residual charges based on dipole moments, and the effect of bond formation, as well as more usual features.   In general, agreement between calculated and experimental susceptibilities is better by their method than if one uses Pascal's constants alone, but considerable disagreement is often observed.[20, 21]   Although frequently successful, the method is largely empirical and lacks a sound theoretical basis.   The distribution of charge using electric dipole moments is undoubtedly incorrect in many instances because no allowance is made for the importance of the lone-pair moment.[22]

(*c*) **Paramagnetism.**—The theory of paramagnetic and electric susceptibilities has been fully described by Van Vleck,[1] the essential principles being the same.   If a substance with a permanent magnetic moment μ is placed in a magnetic field with the molecular magnets free to orient themselves, they will be subjected to two opposing effects : (i) the magnetic field of strength H which tends to align all molecular magnets in the same direction, and (ii) the thermal effect of vibration, rotation, and translation (the kT effect), which tends to make the directions of the molecular magnets entirely random.   It can be shown that $\chi_M = N^2\mu^2/3RT$, where $N =$ Avagadro's number and $\mu =$ magnetic moment.   From this expression it follows that $\mu = \sqrt{3RT\chi_M}/N$.   In practice we are interested in the magnetic moment of a particular *atom* in a compound rather than that of the molecule as a whole, and hence we replace χ_M by the susceptibility of the atom χ_A with which we are concerned.   Therefore, to χ_M must be added a correction for the diamagnetic susceptibilities of all atoms present in the molecule including that of the paramagnetic atom itself, though this last correction is often

[16] P. W. Selwood, ref. 4, p. 52.   [17] *Idem*, ref. 4, p. 57.

[18] W. R. Angus, *Ann. Reports*, 1941, **38**, 27.

[19] *Trans. Faraday Soc.*, 1935, **31**, 1491.

[20] S. K. Siddhanta, *J. Indian Chem. Soc.*, 1947, **24**, 21.

[21] S. K. Siddhanta and P. Ray, *ibid.*, 1943, **20**, 359.

[22] C. A. Coulson, " Valence ", Oxford Univ. Press, London, 1952, p. 210.

ignored. On substituting $\chi_{M'} = (\chi_M + \text{diamagnetic correction})$ in the place of χ_M in the above expression we obtain the " effective magnetic moment ", $\mu_{\text{eff.}}$, of the paramagnetic atom, i.e., $\mu_{\text{eff.}} = 2\cdot839\sqrt{\chi_{M'} \times T}$. Since in nearly all work $\mu_{\text{eff.}}$ rather than μ is used, the subscript is often dropped. The effect of making the necessary diamagnetic correction is illustrated by Table 1. Magnetic moments are now expressed in Bohr magnetons (B.M.) ; this is the natural unit of magnetism and equals the magnetic moment of an electron assumed to be " spinning " on its own axis. It is given by the expression $eh/4\pi mc$ and has the numerical value $9\cdot273 \times 10^{-21}$ erg gauss^{-1}.

TABLE 1. *Effect of diamagnetic correction on the magnetic moment*

Compound	$\chi \times 10^{-6}$ at 20°	$\chi_M \times 10^{-6}$ at 20°	μ (B.M)	Diamag. corrn. $\times 10^{-6}$	$\chi_{M'} \times 10^{-6}$ at 20°	μ_{eff} (B.M.)
$[Ni(NH_3)_6]Cl_2$ . .	17·10	3962	3·06	133	4095	3·11
$[Ni(dipy)_3]I_2,6H_2O$.	4·16	3698	2·95	458	4156	3·13

The value of μ obtained from the above formula is a constant only when χ_M is proportional to $1/T$; this is true for a large number of magnetically dilute substances.* The compound then obeys Curie's law, but more generally the Curie–Weiss Law, $\chi_M \propto 1/(T + \theta)$, represents the variation of χ_M with absolute temperature. The value of θ is constant over a smaller or greater temperature range ; several factors contribute to its origin, particularly the effect of external fields on the molecular magnetism.[1, 4, 5] When θ is known, μ is usually calculated by using $(T + \theta)$ instead of T in the above formula. Paramagnetism is found mainly in the following classes of compound : (a) compounds of the transition elements (particularly the first series from Ti to Cu) owing to the presence of unpaired d electrons ; (b) compounds of the rare-earth and actinide series owing to the presence of $4f$ and $5f$ electrons respectively ; (c) a few compounds of the first period which contain unpaired p electrons, e.g., O_2, NO ; (d) a temperature-independent paramagnetism is shown by a few compounds which have no unpaired electrons, e.g., $KMnO_4$, K_2CrO_4.

Except in rare instances, e.g., (d) above, paramagnetism arises from the presence of unpaired electrons in an atom. Unpaired electrons have both spin angular momentum s and orbital angular momentum l ; a combination of these two gives rise to the magnetic moment but the way in which they are coupled is most important. The usual way in which coupling occurs in an atom containing more than one unpaired electron is according to the Russell–Saunders scheme. In this the spin moments (s) are first coupled to give a resultant spin momentum S ; if n is the number of unpaired electrons in an atom, then $S = n/2$. The various l values of the different

* A magnetically dilute compound, e.g., $[Ni(NH_3)_6][ClO_4]_2$, is one in which the number of paramagnetic atoms is small compared with the total number of atoms present. Hence the distance between paramagnetic atoms is large compared with their usual bond radii ; this ensures that the interaction between them is negligible.

electrons are then separately coupled to give a resultant orbital angular momentum L. The spectroscopic rules governing this are discussed by Herzberg ; [23] Hund's rules are of special importance.* The resultant S and L vectors are then coupled together but often less strongly than the way in which the various l and s vectors are coupled to one another. The significance of this looser coupling becomes evident in the moments of the compounds of the first transition series ; often the L component is almost entirely quenched, leaving only the S component contributing to the magnetic moment. The coupling of L and S gives the inner quantum number J from which the magnetic moment can be calculated ; J measures the resultant total angular momentum. J can have the possible values $(L + S), (L + S - 1) \ldots (L - S + 1), (L - S)$, positive values only being real. It can be shown that when $L > S$ the number of possible J values for a given value of L is $2S + 1$, and when $L < S$ the number of possible J values for a given value of S is $2L + 1$. In calculating the magnetic moment it is the value of J corresponding to the lowest energy (J_0) which is usually most important (see Rule 3 †). The energy separation between levels corresponding to successive J values, relative to the size of kT, determines the extent to which levels other than the lowest are occupied. In the ideal case when the multiplet intervals, which correspond to the adjacent values of J, are large compared with kT, only the lowest energy level (J_0) will be occupied. On application of a magnetic field, this level will be split into $2J_0 + 1$ energy levels, the separation between which is $g\beta H$, where H is the magnetic field, β is the Bohr magneton, and g is called the Landé splitting factor, which is given by the expression

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}$$

The magnetic moment (in B.M.) is then given by the expression $\mu_{\text{eff.}} = g\sqrt{J(J + 1)}$. It is noteworthy that for atoms in S states (i.e., when $L = 0$ and $J = S$), $g = 2$. If it is found experimentally that g lies between 0 and 2 both spin and orbital momenta are involved in the magnetic moment, but when $g = 2$ the magnetic moment arises from spin alone. This will be referred to again in discussing paramagnetic resonance. As an example, the Ce^{+++} ion has one unpaired electron, the term symbol for the ground state being $^2F_{5/2}$.† Here $s = \frac{1}{2}$, $l = 3$, and since the $4f$ shell is less than half full it follows that $j = l - s = 2\frac{1}{2}$. g can be shown to be 6/7, hence $\mu_{\text{eff.}}$ (calc.) $= 2\cdot54$; the experimental value is $2\cdot51$ B.M. For precise results allowance must be made for the temperature-independent contribution of the high-frequency elements of the magnetic moment of the diamagnetic part (the α correction) ; this is discussed by Van Vleck.

[23] " Atomic Spectra and Atomic Structure ", Dover Publ., New York, 1944, p. 128.
* Namely, (1) S has the highest value allowed by the Pauli principle ; (2) the value of L is the highest then allowed ; (3) $J_0 = L - S$ if the shell is less than half full and $J_0 = L + S$ if it is more than half full.

† In a term symbol the letter (here F) gives the value of L. The letters S, P, D, and F represent L values of 0, 1, 2, and 3, respectively. The prefix gives the spin multiplicity $(2S + 1)$, and the suffix the value of J.

Modification of the above formula is necessary when certain of the conditions, *e.g.*, wide multiplets, absence of field effects, etc., are not satisfied. It is most convenient to discuss the various kinds of magnetic moments observed in paramagnetic compounds under seven headings. We shall then use these as the basis for a survey of recent magnetochemistry of the elements of the Periodic Table.

Class I. Spin and orbital momenta free and $h\nu(J_0 \rightarrow J_1) \gg kT$. (Rare-earth type.) Here the separation between the ground state and the next higher level is large ($\sim 10^4$ cm.$^{-1}$) compared with $kT(\sim 200$ cm.$^{-1}$). The α correction being ignored, μ is given by $g\sqrt{J(J+1)}$. Curie's law is obeyed closely by this class of compound. With the exception of Sm(III) and Eu(III), this formula agrees well with the observed moments of the compounds of the rare earths.

Class II. Spin and orbital momenta free and $h\nu(J_0 \rightarrow J_1) \ll kT$. This is the opposite extreme to Class I; when these conditions obtain the moment is given by $\sqrt{4S(S+1) + L(L+1)}$. In this expression $L(L+1)$ gives the orbital and $4S(S+1)$ the spin contribution. In practice some quenching of the orbital momenta occurs but reference to Table 3 shows that in certain circumstances moments of the Fe^{++} and Co^{++} ions agree better with this rather than the " spin-only " formula (Class IV). The Curie law holds for this class of compounds also.

Class III. Spin and orbital momenta free and $h\nu(J_0 \rightarrow J_1)$ comparable with kT. (Nitric oxide type.) The expression for calculating μ in these circumstances is complicated owing to the necessity for taking into account a Boltzmann distribution between various energy levels.[1] Good illustrations of this class are nitric oxide and the Sm^{+++} and Eu^{+++} ions.[24, 25] Unlike Classes I and II, large departures from Curie's law are observed. With NO, for example, the moment gradually increases, with rising temperature, towards a limiting value, but above 250° the increase with temperature is very small.

Class IV. Spin momenta free but orbital momenta almost entirely quenched. (Iron-group elements.) The formulæ given in I and II reduce to $\sqrt{4S(S+1)}$ when the orbital contribution is neglected entirely. It is characteristic of an atom in an S state, *i.e.*, when $L = 0$; the best examples of this in paramagnetic compounds are obtained when a sub-shell is half filled—containing three p, five d, or seven f electrons. Both Fe^{+++} and Mn^{++} satisfy these conditions (see Table 3). The quenching of the orbital contribution arises from the effect of crystalline fields and is discussed on p. 402. " Quenching of the orbital momenta " means that when an external magnetic field is applied the orbital momenta remain fixed under the influence of the crystalline fields in the lattice or complex ion. This formula is often simply expressed as $\mu = \sqrt{n(n+2)}$, where $n =$ number of unpaired electrons, because $S = n/2$.

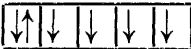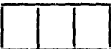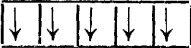*Class* V. Spin coupling owing to strong covalent bond formation.
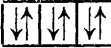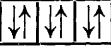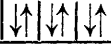
[24] W. Albertson, *Phys. Review*, 1935, **47**, 370.
[25] P. W. Selwood, ref. 4, p. 84.

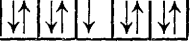(Covalent-bond type.) The metal ions of many of the first transition elements show a large decrease in moment when the ion is co-ordinated with certain ligands ; e.g., the Fe^{+++} ion in hexahydrates contains five unpaired electrons but in the complex cyanide $K_3Fe(CN)_6$ the moment falls to 2·35 B.M., indicating one unpaired electron only. Pauling [26] explains this by the hypothesis that certain groups, notably the cyanide ion, have such a marked capacity for covalent bond formation that unpaired electrons are forced to pair off to provide $3d$ orbitals for bond formation. This is shown in Fig. 1. The implications of this theory are discussed on p. 387, where the alternative Van Vleck explanation is given.

FIG. 1

Electronic configurations and magnetic moments of iron complexes

Ion or compound	Electronic configuration				Unpaired electrons	Magnetic moment* (B.M.)
	$3d$	$4s$	$4p$	$4d$		
Fe^{++} (Free ion)	[↑↓][↓][↓][↓][↓]				4	4·90
Fe^{+++} (Free ion)	[↓][↓][↓][↓][↓]				5	5·92
Fe(II) (Octahedral $4s4p^34d^2$ bonds)	[↑↓][↓][↓][↓][↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓][↑↓]	4	4·90
Fe(II) (Octahedral $3d^24s4p^3$ bonds)	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]		0	Diamag.
Fe(III) (Octahedral $4s4p^34d^2$ bonds)	[↓][↓][↓][↓][↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓][↑↓]	5	5·92
Fe(III) (Octahedral $3d^24s4p^3$ bonds)	[↑↓][↑↓][↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]		1	1·73

* Calculated on the spin-only formula.

Class VI. Hund's rules inapplicable. (Heavy-atom type.) In discussing the metals of the first transition series it is freely assumed that the arrangement of electrons will be in accord with Hund's rules, the first of which requires that in filling up a sub-shell, e.g., the $3d$, the maximum number of orbitals will be singly filled before electron pairing occurs. Thus Fe^{+++} has five unpaired electrons as in Fig. 1. However, we cannot be sure that Hund's rules are necessarily applicable to the metals of the second and third transition series. It has been suggested [27, 28] that even in the simple salts of these metals maximum electron pairing may occur because the lowest energy state is not an S one, i.e., maximum multiplicity is not obeyed. The

[26] L. Pauling, " Nature of the Chemical Bond ", Cornell Univ. Press, New York, 2nd Edn., 1945, p. 112, and refs. therein.

[27] R. B. Janes, *J. Amer. Chem. Soc.*, 1935, **57**, 471.

[28] J. H. Van Vleck, ref. 1, p. 312.

fact that salts of the platinum metals with oxy-anions did not have the high magnetic moments expected for free ions had been regarded as some evidence in support of this view.   As against this, since these metals have a high capacity for covalent bond formation, the explanation could be that covalent bonds are formed.   In solution the platinum metals are hydrated and it is known that even the $[Co(H_2O)_6]^{+++}$ ion is diamagnetic, showing that even Co(III) can form strong covalent bonds with water molecules. With Co(III) one must prepare the complex fluoride K_3CoF_6 in order to observe the maximum multiplicity of four unpaired electrons.[29]   Again, the fact that K_2PtF_6 is diamagnetic [30] might be regarded as evidence that the Pt^{++++} ion disobeys Hund's rules.   Here again the bonds might be regarded as covalent, as in K_2NiF_6 which is also diamagnetic.[31, 32]   However, the small moment of K_2OsCl_6 (1·4 B.M.[33]) suggests that here a break-down of Hund's rules has occurred since the expected μ for octahedral covalent binding is 2·83 B.M. [cf. Fe(IV) in Table 3].   Nevertheless, the evidence for differentiating between Classes V and VI is still meagre.

Class VII.   Small temperature-independent paramagnetism.   (Permanganate type.)   Several compounds, *e.g.*, $KMnO_4$, $K_2Cr_2O_7$, some cuprous salts, and certain cobaltammines have a small magnetic moment (*ca.* 1 B.M.) after allowance has been made for the diamagnetism of the rest of the molecule.   The accepted structures for these molecules involve no unpaired electrons and hence the origin of the small moment is puzzling.   The paramagnetism is temperature independent.   Van Vleck [34] attributes this to an unbalanced orbital contribution which may be regarded as arising from the different rates at which L and S precess about J.   Datar and Datar [35] have questioned this explanation and suggest that spin coupling may be imperfect.   This partial freedom of electron spin is considered to account for the observed paramagnetism of Cr(VI) in chromates.   Against this must be weighed the temperature independence of this paramagnetism. For our purposes it is, however, unimportant because it is of practically no diagnostic value in inorganic chemistry.

(*d*) **Other Kinds of Magnetic Behaviour.**—Ferromagnetism is observed in a lattice of magnetic particles with loose interatomic binding and with parallel spins.   This is characterised by a large value of χ, field strength dependence of χ, and the existence of a Curie temperature.   The last may be regarded as that temperature above which ferromagnetism changes over to paramagnetism.   The term anti-ferromagnetism is used to describe a lattice similar to that of ferromagnetic substances except that the spins are anti-parallel.   Unlike paramagnetic substances, the susceptibility of anti-ferromagnetics decreases as the temperature is lowered.   MnO and

[29] J. T. Grey, *J. Amer. Chem. Soc.*, 1946, **68**, 605.

[30] R. S. Nyholm and A. G. Sharpe, *J.*, 1952, 3579.

[31] W. Klemm, personal communication to Nyholm and Sharpe quoted in ref. 30 ; cf. ref. 66.

[32] R. Hoppe, *Angew. Chem.*, 1950, **62**, 339.

[33] W. P. Groves, Thesis, London, 1941.

[34] *Phys. Review*, 1928, **31**, 587.   Cf. ref. 5, p. 43.

[35] *Nature*, 1946, **158**, 518 ; *Indian J. Phys.*, 1949, **23**, 153.

MnSe are examples of compounds which display anti-ferromagnetism. Klemm [36] has summarised the various important kinds of magnetism with a table of their properties.

Applications of Paramagnetic Susceptibilities

In inorganic chemistry these measurements are useful for three main purposes. Provided that the number of *unpaired electrons* can be deduced from the magnetic moment, it is possible to infer from the former, (i) the *valency*, (ii) the *bond type*, and (iii) the *stereochemistry* of the metal atom. Use can be made of the size of the *orbital contribution to the moment*, in the case of first transition elements, to obtain information concerning the stereochemistry of the metal atom.

(i) **Valency Problems.**—This is the best known application of magnetic susceptibility measurements. Having inferred the number of unpaired electrons, we can then distinguish different possible valency states provided that they contain different numbers of unpaired electrons. The decision is specially easy with first transition elements because Hund's rules are obeyed for the simple ions. Thus Fe^{+++} contains 5 unpaired electrons whilst Fe^{++} has only four (cf. Fig. 1); these correspond to moments of 5·9 and 4·9 B.M. respectively. Similarly Cu(I) and Cu(II) may be distinguished because the former is diamagnetic; it is even possible to estimate the relative amounts of Cu(I) and Cu(II) in a compound if allowance for diamagnetism is made.[37] When electron pairing occurs, valency states may be distinguished if one involves diamagnetism and the other contains one unpaired electron. These conditions obtain for those compounds of the first transition series for which maximum electron pairing occurs, *e.g.*, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, and for practically all of the small number of paramagnetic compounds of the second and third transition series, *e.g.*, Pd(III) in PdF_3 which contains one and not three unpaired electrons; [30] both Pd(II) and Pd(IV) are diamagnetic. A few compounds fall in between these two extremes, *e.g.*, Ru(IV) and certain Cr(II) complexes which contain two unpaired electrons rather than four or nil. The reason for this will be discussed under bond types. The magnetic criterion of valency is so reliable today that unless paramagnetism is observed in a compound for which the valency state should have an odd number of electrons, then the ascribed valency must be regarded with some suspicion. The valency of an element when spin coupling between two like atoms occurs is often debatable, *e.g.*, as in the Hg_2^{++} ion. Instances may be quoted where spin coupling occurs in the solid state to give in effect a higher valency state than in solution or in the gas phase. This will be referred to in discussing the compounds of empirical formulæ $K_2Ni(CN)_3$, $K_3Co(CN)_5$, and ClO_3.

The certainty with which one can decide the number of unpaired electrons in a compound depends upon the class of paramagnetism which it displays. Classes I to IV are usually straightforward, provided that the compound is magnetically dilute. If the distance between two paramagnetic

[36] *Z. Elektrochem.*, 1945, **51**, 14.   [37] R. S. Nyholm, *J.*, 1951, 1767.

atoms is comparable with atomic diameters, partial spin coupling becomes feasible. Cupric acetate monohydrate exhibits this effect, the moment [38] being only 1·45 B.M. at 31° as compared with the usual value for Cu(II) compounds of about 1·9 B.M. Bleaney and Bowers [39] conclude from paramagnetic resonance studies that metal ion–metal ion interaction occurs. Support for this hypothesis has been obtained by Niekerk and Schoening,[40] who have shown by X-rays that the Cu–Cu distance is only 2·64 Å, little larger than the Cu–Cu distance in metallic copper. The two copper atoms are connected by bridging acetate groups.

(ii) **Type of Bond in Metal Complexes.**—Magnetic moments can be used to distinguish between two types of binding in metal complexes, particularly those of the first transition series. This division has long been recognised on chemical grounds alone ; a freely dissociable Co(II) ammine is known as a " normalkomplexe " while the more robust Co(III) ammines, which do not undergo reversible thermal dissociation, are examples of " durchdringungskomplexe" (penetration complexes). In the case of Fe(III) (see Fig. 1), the first class (e.g. ferric trisacetylacetone) have moments of 5·9 B.M., indicating five unpaired $3d$ electrons ; the second class (e.g., potassium ferricyanide) have moments of 2·3—2·4 B.M., a little greater than the spin-only value for one unpaired electron. Two main theories have been advanced to explain this difference in moment. Pauling [26] suggested that the bonds in the first class are essentially electrostatic (" ionic bonds "), whilst in the latter, $3d$ orbitals are involved in the binding ($3d^2 4s 4p^3$ " covalent bonds "). The two $3d$ orbitals required for bond formation are supposed to be made available by electron pairing, leaving only one unpaired $3d$ electron. In the first case the five $3d$ electrons are unaffected by complex formation. Van Vleck [41] showed that strong crystalline forces * could also bring about electron pairing ; in the ferricyanides, for example, strong forces were believed to upset the Russell–Saunders coupling giving the minimum number of unpaired spins. If the attached ligands are not held strongly to the Fe atom, the spin multiplicity is unaffected. Pauling [26] pointed out that on Van Vleck's theory one might expect spin pairing in $K_3 FeF_6$ because strong electrical fields should be present. Van Vleck agreed that in this instance, at least, the Pauling and the molecular-orbital approach are both more satisfactory on empirical grounds. Orgel,[42] after re-examining the relation between the Pauling and the Van Vleck theory, has shown that these are really only two different ways of approaching the problem ; the qualitative similarity is demonstrated, and it is pointed out that both theories should in all cases lead to the same conclusion. In comparing the effect of a CN^- as against a F^- ion, the polarisability of the ion, rather than the intensity of the field at its surface, is of paramount importance in determining the resultant crystalline field. This weakens Pauling's

[38] B. C. Guha, *Nature*, 1945, **155**, 364 ; *Proc. Roy. Soc.*, 1951, A, **206**, 353.
[39] *Ibid.*, 1952, A, **214**, 451.   [40] *Nature*, 1952, **171**, 36.
[41] *J. Chem. Phys.*, 1935, **3**, 807.   [42] *J.*, 1952, 4756.
* Electrical fields which arise from the regular arrangement of charged ligands around the paramagnetic atom.

argument against Van Vleck's picture. It is satisfactory to know that there is really no conflict between these two theories because Pauling's approach is easier for most purposes and has found general acceptance. It will be used widely in the following discussion of stereochemistry. Recent work has done much to remove certain objections (based as much as anything on terminology) to Pauling's original theory. It had been pointed out, *e.g.*, by Sugden,[43] that the physical properties of compounds like ferric trisacetylacetone were incompatible with the view that the bonds were " ionic ". Later, Pauling [44] emphasised that the term ' ionic " was not to be taken too literally, and envisaged a type of covalent binding in the above compound in which four $4s4p^3$ bonds resonated among six positions in an ionic octahedral complex. Because they were considered to be too unstable for bond formation, Pauling [45] rejected Huggins's suggestion [46] that $4d$ orbitals might be used in combinations such as $4s4p^34d^2$ for octahedral binding. Huggins's proposals have been re-examined by several workers. Taube [47] refers to the two types of complex as " inner d orbital type " ($3d^24s4p^3$ bonds) and " outer d orbital type " ($4s4p^34d^2$ bonds). A similar proposal has been put forward by Burstall and Nyholm [48] in discussing the magnetic behaviour of dipyridyl and ditertiary arsine complexes of the transition metals. Overlap calculations provide theoretical support for the view that $4d$ orbitals may be used for σ-bond formation in so-called " ionic " complexes.[49, 50] The fact that $4d$ orbitals are well elongated means that good overlap occurs at relatively greater distances from the metal atom than occurs when $3d$ orbitals are used. Hence the electron cloud of the bonding electron pair lies further over towards the ligand, *i.e.*, the bond is more polar. Thus the difference between the terms " ionic " or " higher level covalent bonds " is not as great as it seems at first sight. However, the possibility of exchange owing to the size of the overlap integral is explicit in the latter but not in the former.

The above ideas enable one to understand why some atoms are more effective than others in causing electron pairing. The more electronegative atoms (F, O) favour " higher level covalent binding " because they tend to concentrate the electron pair closer to the ligand, resulting in the use of $4d$ orbitals. On the other hand, the groups of low electronegativity (*e.g.*, P, As) utilise more readily the $3d$ orbitals and hence give rise to " lower level covalent bonds ". In the binding of groups of low electronegativity such as the CN, NO_2, and AsR_3 ligands, it is probable that double (π) binding makes a significant contribution to the strength of the bond. These π bonds could increase the bond strength for three reasons : they increase the number of bonds between the metal and ligand ; they provide a mechanism whereby the improbably high negative charge on the metal atom may be de-localised ; finally, partly as an outcome of the latter, they

[43] *J.*, 1943, 328.   [44] *J.*, 1948, 1641.   [45] *Op. cit.*, p. 115.
[46] *J. Chem. Phys.*, 1937, **5**, 527.   [47] *Chem. Reviews*, 1952, **50**, 69.
[48] *J.*, 1952, 3570.   [49] L. E. Orgel, quoted by R. Wilkins, *Nature*, 1951, **167**, 434.
[50] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, in the press,

provide a method for strengthening the σ bond. Detailed references to work on this subject are given by Burstall and Nyholm.[48]

When it is not possible to free $3d$ orbitals for bond formation by pairing $3d$ electrons, Pauling [45] suggests that " promotion " of electrons to higher levels *above* the bonding orbitals occurs. Such a promotion is postulated in octahedral covalent Co(II) complexes for which the binding is apparently $3d^24s4p^3$; this is shown in Fig. 2. It can be seen that no such promotion

FIG. 2

Electronic configuration of cobaltous complexes

| Type of compound | Electronic arrangement | | | | Unpaired electrons | Magnetic moment* |
	$3d$	$4s$	$4p$	$5s$		
Co³⁺ (Free ion)	⤊⤊⤊ ↓ ↓	☐	☐ ☐ ☐	☐	3	3·88
Co(II) (Octahedral $3d^24s4p^3$ bonds)	⤊⤊⤊⤊⤊	⤊	⤊⤊⤊	↓	1	1·73
Co(II) (Square $3d4s4p^2$ bonds)	⤊⤊⤊↓↑	⤊	⤊⤊ ☐	☐	1	1·73

* Calculated on the spin-only formula.

is necessary for square complexes. In the octahedral complex the promoted electron is assumed to occupy an exposed $5s$ orbital and hence should be lost easily by oxidation to yield a diamagnetic Co(III) complex. This corollary has proved both a strength and a weakness of the theory. The chemical behaviour of some complexes, *e.g.*, the $[Co(NO_2)_6]^{4-}$ ion, supports the assumption, but in certain other cases where promotion has been assumed the evidence is unconvincing, *e.g.*, Cu(II) (see p. 392).

(iii) **Stereochemistry.**—The stereochemistry of an atom follows logically from a knowledge of the bond type and the co-ordination number. The relationship between stereochemistry and different combinations of atomic orbitals is discussed elsewhere ; [22, 51] Table 2 lists only the common shapes

TABLE 2.   *Some common stereochemical arrangements and orbital combinations*

Co-ordn no	Shape	Bond orbitals	Co-ordn no	Shape	Bond orbitals
2	Linear Angular	sp p^2	4	Square planar Tetrahedral	dsp^2 sp^3, d^3s
3	Triangular plane Pyramidal	sp^2 p^3	5	Bipyramid Square pyramid	$nsnp^3nd$ $(n-1)dnsnp^3$
			6	Octahedral	d^2sp^3

[51] G. E. Kimball, *J. Chem. Phys.*, 1940, **8**, 194.

with which we are concerned in this article. For the effect of lone-pair contributions to stereochemistry, see Lennard-Jones and Pople.[52]

Pauling's theory of the stereochemistry of the first transition series (also applicable, with limitations, to the second and third) may be summarised as follows : (i) If the magnetic moment of a complex is essentially the same as that of the free ion * (*i.e.*, no spin coupling occurs) the bonds do not involve $3d$ orbitals ; however, the moment is not diagnostic of $4s4p^3$ as against $4s4p^24d$ bonds. (ii) Spin coupling with a reduction of either two or four in the number of unpaired electrons is caused by the formation of strong covalent bonds using one or more $3d$ orbitals ; this necessitates the transfer of unpaired electron(s) originally occupying orbitals now used for bond formation : usually these displaced electron(s) pair off with other $3d$ electrons. (iii) If no vacant $3d$ orbital(s) are available to accommodate electron(s) displaced from $3d$ orbitals required for bond formation, these electrons may be promoted to vacant orbitals *above* those used for bond formation ; such promoted electrons will occupy the orbitals of lowest energy. (iv) The stereochemistry of a complex ion is decided by the orbitals used for bond formation.

Table 3 summarises calculated and observed moments for various types of complex of the first transition series. It may also be used to obtain calculated moments for the third and second transition series.

Survey of the Periodic Table

Only the more recent developments in valency and stereochemistry are discussed, the first transition series receiving most attention.

Group I.—*The Alkali Metals.* In their chemical compounds these are invariably univalent and hence diamagnetic ; certain higher oxides, *e.g.*, KO_2, are paramagnetic,[53, 54] but the unpaired electron is on the O_2^- ion.

Copper, Silver, and Gold. Each of these metals has one s electron more than a completed d sub-shell and hence univalent compounds are diamagnetic (see Table 3 and Fig. 3). The univalent compounds are either two- or four-covalent, using linear sp or tetrahedral sp^3 bonds. A gradual change in the preferred co-ordination number from four to two occurs in passing from copper through silver to gold. The bivalent compounds contain an odd number of electrons and hence are paramagnetic. Both Cu(II) and Ag(II) compounds contain one unpaired electron [55, 56] but no Au(II) compounds are known. The apparently bivalent gold complex with the empirical formula $(C_7H_7)_2S,AuBr_2$ (benzyl sulphide—dibromogold) has been

[52] *Proc. Roy. Soc.*, 1951, *A*, **210**, 190.

[53] E. W. Neumann, *J. Chem. Phys.*, 1934, **2**, 31.

[54] W. Klemm and H. Sodomann, *Z. anorg. Chem.*, 1935, **225**, 273.

[55] A. A. Noyes, K. S. Pitzer and C. L. Dunn, *J. Amer. Chem. Soc.*, 1935, **57**, 1229.

[56] S. Sugden, *J.*, 1932, 161.

* Provided that the free ion contains *more* than three $3d$ electrons. This proviso is necessary because magnetic moments do not distinguish between $4s4p^34d^2$ and $3d^24s4p^3$ octahedral binding when only three unpaired electrons are present, *e.g.*, as in Cr(III) complexes.

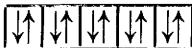TABLE 3   Magnetic properties of first transition series (μ in B M)
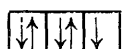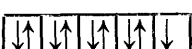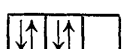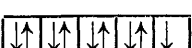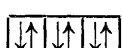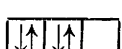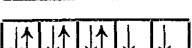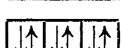
Element and valency	Spectroscopic normal state	No electron pairing Free ion or if using higher bonding orbitals ($4s4p^3$ $4s4p^24d^2$)			Calc from $g\sqrt{J(J+1)}$	Calc from $\sqrt{L(L+1)+4S(S+1)}$	Calc from $\sqrt{4S(S+1)}$	O S	Electron pairing Covalent bond orbitals — Calc from Square $3d^44s4p^2$ $\sqrt{4S(S+1)}$	Octahedral $3d^24s^44p^3$ $\sqrt{4S(S+1)}$	Obs
		L	S	J_0							
K^I, Ca^I, Sc^{III}, Ti^{IV}, V^V, Cr^{VI}, Mn^{VII}	$^1S_0$	0	0	0	0	0	0	Diamag	0	0	Diamag
Ti^{III}, V^{IV}, Cr^V, Mn^{VI}	$^2D_{3/2}$	2	$\tfrac{1}{2}$	3/2	1 55	3 01	1 73	1 7—1 8	1 73	1 73	1 7—1 8
Ti^{II}, V^{III}, Cr^{IV}, Fe^{VI}	$^3F_2$	3	1	2	1 63	4 49	2 83	2 8—3 1	2 83	2 83	2 8—3 1
V^{II}, Cr^{III}, Mn^{IV}	$^4F_{3/2}$	3	3 2	3/2	0 70	5 21	3 87	3 85—3 9	3 87	3 87	3 85—3 9
Cr^{II}, Mn^{III}, Fe^{IV}	$^5D_0$	2	2	0	0 00	5 50	4 90	4 8—4 9	4 90	2 83	2 9—3 1
Cr^I, Mn^{II}, Fe^{III}, (Co^{IV})*	$^6S_{5/2}$	0	5/2	5 2	5 92	5 92	5 92	5 85—5 95	3 87	1 73	2 1—2 4
Mn^I, Fe^{II}, Co^{III}, Ni^{IV}	$^5D_4$	2	2	4	6 71	5 50	4 90	5 0—5 6	2 83	0	Diamag
Co^{II}, Ni^{III}	$^4F_{9/2}$	3	3/2	9/2	6 63	5 21	3 87	4 3—5 3	1 73	1 73	1 9—2 4 B M
Co^I, Ni^{II}, Cu^{III}	$^3F_4$	3	1	4	5 59	4 49	2 83	2 9—3 4	0	0	Diamag
(Ni^I),* Cu^{II}	$^2D_{5/2}$	2	$\tfrac{1}{2}$	5/2	3 55	3 01	1 73	1 9—2 1	1 73	3 87(?)†	1 9—2 4
Cu^I, Zn^{II}	$^1S_0$	0	0	0	0	0	0	Diamag	0	0	Diamag

* Moments corresponding to valency states shown in parentheses have not yet been observed
† If all three promoted electrons are unpaired

391

FIG. 3

Electronic configuration and magnetic moments of copper complexes

Ion or compound	Electronic configuration				Unpaired electrons	Magnetic moment* (B.M.)
	3d	4s	4p	4d		
Cu⁺ (Free ion) .	[↑↓][↑↓][↑↓][↑↓][↑↓]	[ ]	[ ][ ][ ]	[ ]	0	Diamag.
Cu(I) (Linear 4s4p bonds)	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]	[↑↓]		0	Diamag
Cu(I) (Tetrahedral 4s4p³ bonds) . .	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]		0	Diamag.
Cu⁺⁺ (Free ion) .	[↑↓][↑↓][↑↓][↑↓][↑]	[ ]	[ ][ ][ ]	[ ]	1	1·73
Cu(II) (Square 3d4s4p² bonds) .	[↑↓][↑↓][↑↓][↑↓][↑]	[↑↓]	[↑↓][↑↓][↑]		1	1·73
Cu(II) (Square 4s4p²4d bonds) .	[↑↓][↑↓][↑↓][↑↓][↑]	[↑↓]	[↑↓][↑↓]	[↑↓]	1	1·73
Cu(II) (Octahedral 4s4p³4d² bonds) .	[↑↓][↑↓][↑↓][↑↓][↑]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓][↑↓]	1	1·73
Cu(III) (Square 3d4s4p² bonds) .	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓]		0	Diamag.
Cu(III) (Octahedral 4s4p³4d² bonds) .	[↑↓][↑↓][↑↓][↑][↑]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓][↑↓]	2	2·83

* Calculated on the spin-only formula.

shown by Brain, Gibson, Jarvis, Phillips, Powell, and Tyabji [57] to contain equal numbers of Au(I) and Au(III) atoms, hence the observed diamagnetism. The location of the unpaired electron in Cu(II) and Ag(II) compounds has been the subject of much speculation. Since all Cu(II) complexes whose structures have been determined are square planar, Pauling [58] assumed that the bonds are $3d4s4p^2$ (see Fig. 3), one unpaired electron being promoted to a $4p$ orbital, but there are serious objections to this hypothesis. First, promotion of the electron to a $4p$ orbital should result in facile oxidation of square Cu(II) complexes to the tervalent state—which is not observed in practice. Also, theoretical work [49, 50] leads to the conclusion that fairly electronegative groups like H_2O and NH_3 [which do give square Cu(II) complexes] are more likely to use $4d$ than $3d$ bond orbitals. In the case of Ni(II), for example, where the diamagnetism is diagnostic of the square arrangement, groups of low electronegativity are required to form $3d4s4p^2$ square bonds. Huggins's [46] suggestion that the bonding orbitals are $4s4p^24d$ without electron promotion has been re-examined by Ray and

[57] *J.*, 1952, 3686,   [58] L. Pauling, *op. cit.*, p. 121.

Sen,[59] who obtained the susceptibilities of a large number of Cu(II) complexes at various temperatures and calculated μ on the Curie–Weiss law. The moments fell roughly into two classes, some between 1·8 and 1·9 B.M. and others between 1·9 and 2·2 B.M., but the division was by no means sharp. The first group are believed to involve $3d4s4p^2$ bonds with electron promotion, and the second are considered to be either $4s4p^3$ tetrahedral or $4s4p^24d$ square planar. The smaller moment of compounds in the first group is attributed to the greater quenching effect of the crystalline field upon the exposed electron ; however, there is no evidence to support the claim that electron promotion really occurs. Finally, the existence of octahedral Cu(II) complexes, e.g., $[Cu(NH_3)_6]X_2$.[60] is more easily explained by the formation of $4s4p^34d^2$ bonds, without electron promotion, than by the improbable $3d^24s4p^3$ combination requiring the promotion of three electrons. The former combination follows logically from a square $4s4p^24d$ complex by completing the octahedron.

The tervalent state of these elements is of considerable interest. The well-known Au(III) complexes are square planar and the diamagnetism is consistent with the use of $5d6s6p^2$ bonds.[61] Both Cu(III) and Ag(III) are also known. Malatesta [62, cf. 63] has described a Cu(III) periodate of the formula $K_nH_{(7-n)}Cu(IO_6)_2,nH_2O$ which is diamagnetic. Also, Scholder and Voelskow [64] have prepared the compound $Ba(CuO_2)_2,H_2O$; as it is diamagnetic it is concluded that it is probably polymeric, two oxygen atoms forming a bridge between successive square-co-ordinated Cu(III) atoms. The corresponding potassium salt, $KCuO_2$, has been described by Wahl and Klemm ; [65] this also is diamagnetic. In these compounds the electronegativity of the oxygen atoms appears to have been reduced sufficiently by bridge formation to permit the Cu(III) atom to make use of $3d$ orbitals. Quite a different result is obtained when Cu(II) fluoride is oxidised with fluorine. Hoppe [32, cf. 66] has prepared K_3CuF_6 as a green solid but, unlike the oxy-anions above, this substance is paramagnetic with a moment corresponding to two unpaired electrons. This leads to the conclusion that the bonds are octahedral $4s4p^34d^2$, the two unpaired electrons being in the $3d$ shell. Silver also forms compounds of the type $K_nH_{(7-n)}Ag^{III}(IO_6)_2$ which are diamagnetic.[62, 63] Other diamagnetic, and hence presumably square, Ag(III) complexes have been prepared by using organic ligands.[67]

Group II.—*The Alkaline-earth Metals.* These elements are invariably bivalent and hence diamagnetic in their simple salts and complex compounds. The paramagnetism of certain higher oxides arises from the presence of unpaired electrons in the anion. The sub-group elements (Zn, Cd, and Hg) are diamagnetic in the common bivalent state. The apparent univalency

[59] *J. Indian Chem. Soc.*, 1948, **25**, 473.   [60] G. Peyronel, *Gazzetta*, 1941, **71**, 363.

[61] R. S. Nyholm, *Nature*, 1951, **168**, 705.

[62] L. Malatesta, *Gazzetta*, 1941, **71**, 467, 580.

[63] A. Malaprade, *Compt. rend.*, 1940, **210**, 504.

[64] *Z. anorg. Chem.*, 1951, **266**, 256.   [65] *Ibid.*, 1952, **270**, 69.

[66] W. Klemm and E. Huss, *ibid.*, 1949, **258**, 221.

[67] P. Ray and K. Chakravarty, *J. Indian Chem. Soc.*, 1944, **21**, 47 ; 1950, **27**, 619 ; *Nature*, 1943, **151**, 643.

of mercury arises from the presence of the $[-Hg^{II}-Hg^{II}-]^{++}$ cation which is diamagnetic. This kind of metal–metal bond is probably more common than is usually supposed.[68]

Group III.—In the A sub-group (B, Al, Sc, Y, and the lanthanons) tervalency is the rule and in this valency state diamagnetism is observed for all compounds of all elements except the lanthanons. Moments of the latter have been discussed. Claims for univalency, particularly of Al[69, 70, 71] have been advanced but magnetic data are of no value because both uni- and ter-valent aluminium are diamagnetic. In the B sub-group (Ga, In, Tl) uni- and ter-valency are well known and both are diamagnetic. Compounds in which these elements appear to be bivalent, e.g., Tl_3I_4[72] and $TlCl_2$,[73] are diamagnetic and hence contain both uni- and ter-valent thallium.

Group IV.—Compounds of the main group elements (C, Si, Ge, Sn, and Pb) in the bi- and the quadri-valent state are invariably diamagnetic. However, paramagnetism is displayed by free radicals of the type $Ph_3C\cdot$ which contain one unpaired electron.[74] In the sub-group (Ti, Zr, Hf) the really interesting behaviour of the first transition series begins, because titanium is the first transition element to show paramagnetism. In the usual quadrivalent state Ti is diamagnetic but Ti(III) and Ti(II) contain one and two unpaired electrons respectively.[75, 76] This confirms the valency but tells nothing about the stereochemistry owing to the number of vacant $3d$ orbitals. Much less is known of the magnetochemistry of hafnium and zirconium ; it has been pointed out that they fall into the most neglected group in the Periodic Table.[77]

Group V.—The main-group elements (N, P, As, Sb, and Bi) are diamagnetic in the usual ter- and quinque-valent states and few paramagnetic compounds of these elements are known. Nitrogen, however, forms some paramagnetic compounds, notably the oxides NO_2 and NO ; the moment of the latter shows unusual temperature dependence (see Class II). Special interest attaches to the magnetic properties of complexes containing the NO group. When present as the NO^+ cation, as in $[NO]^+[NO_3]^-$, it is diamagnetic. It also behaves as the NO^- group, e.g., in certain Co(III) complexes. Two types of nitrosopentamminocobalt(III) salts are known,[78, 79] a stable red form having the formula $[Co(NH_3)_5NO][NO_3]_2$, which is diamagnetic, and an unstable black form with the formula

[68] L. Pauling, *Chem. Eng. News,* 1947, **25**, 2970.

[69] W. Klemm and E. Voss, *Z. anorg. Chem.,* 1943, **251**, 233.

[70] A. S. Russell, V. E. Martin, and C. N. Cochran, *J. Amer. Chem. Soc.,* 1951, **73**, 1466.

[71] J. P. McGeer, *J. Chem. Educ.,* 1952, **29**, 534.

[72] A. G. Sharpe, *J.,* 1952, 2165.

[73] D. J. Meier and C. S. Garner, *J. Chem. Phys.,* 1950, **18**, 237.

[74] N. V. Sidgwick, " The Chemical Elements and Their Compounds ", Oxford Univ. Press, 1950, London, p. 534.

[75] W. Klemm and L. Grimm, *Z. anorg. Chem.,* 1942, **249**, 198.

[76] C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Review,* 1940, **58**, 977.

[77] P. W. Selwood, ref. 4, p. 103.

[78] S. P. Ghosh and P. Ray, *J. Indian Chem. Soc.,* 1943, **20**, 409.

[79] J. L. Milward, W. Wardlaw, and W. Way. *J.,* 1938, 233.

$[Co(NH_3)_5NO]Cl_2$. The latter is paramagnetic with a moment a little less than that required for one unpaired electron. In the diamagnetic compound the NO^- group apparently uses up one of the valencies of the (tervalent) cobalt. If in the second compound the NO were attached by a co-ordinate link to a Co(II) atom, four unpaired electrons are expected if the bonds to the Co(II) atom are "ionic" or two if they are covalent $3d^24s4p^3$, one electron being on the NO in each case. As pointed out by Mellor and Craig,[80] Co(II) is unlikely to show electron pairing when attached to five NH_3 groups. Ray and Ghosh [78] conclude that the Co atom is tervalent, the compound being a mixture of two forms—one diamagnetic with the NO in a singlet state and the other paramagnetic with the NO in a triplet state (containing two unpaired electrons). The solution to this problem will now most probably be obtained by using spectroscopic infrared techniques. The diamagnetism of Sb in K_2SbCl_6 [81] is also puzzling since Sb(IV) should contain an odd number of electrons. Pauling considers that equal numbers of diamagnetic $[Sb^{III}Cl_6]^{---}$ and $[Sb^VCl_6]^-$ ions are present.[26] The compound is isomorphous with K_2PtCl_6, and Jensen [82] has discussed alternative methods of spin pairing more consistent with this observation.

In the sub-group (V, Nb, and Ta) vanadium has valencies of 2, 3, 4, and 5. Magnetic moments show that in no case does spin pairing occur, the spin-only value being observed except in magnetically concentrated compounds.[30] The moment is very useful here in the assignment of valency. Nb and Ta have received much less attention ; [77] as usual, moments are smaller than for V. Thus the moments of K_3VF_6, VF_3, and TaF_3 are respectively 2·79, 2·55, and 1·4 B.M.[30]

Group VI.—In the main group (O, S, Se, and Te) both O_2 and S_2 are unusual in being paramagnetic.[83] The presence of two unpaired electrons is most easily understood in terms of the molecular orbital theory of valency.[84] In practically all other compounds (e.g., in valency states of 2, 4, and 6) these elements are diamagnetic. The sub-group elements (Cr, Mo, and W) are interesting owing to variable valency and paramagnetism. Diamagnetism is expected for Cr(VI) but weak temperature-independent paramagnetism is observed.[35] Cr(V) occurs in compounds such as $KCrOF_4$, the moment of which indicates one unpaired electron.[30] All Cr(III) compounds contain three unpaired electrons but the moment is not diagnostic of $3d^24s4p^3$ as against $4s4p^34d^2$ octahedral binding. However, the slow rate of exchange of H_2O with the $[Cr(H_2O)_6]^{+++}$ cation suggests that the former is the more common.[85] Cr(II) in simple salts, and in most complex compounds, has a moment close to the spin-only value for four unpaired electrons ; [86] with the —CN group [86] or with dipyridyl,[48]

[80] J. Proc. Roy. Soc., N.S.W., 1944, **78**, 25.
[81] K. A. Jensen, Z. anorg. Chem., 1937, **232**, 193.
[82] Ibid., 1944, **252**, 317.   [83] A. B. Scott, J. Amer. Chem. Soc., 1949, **71**, 3145.
[84] C. A. Coulson, op. cit., p. 100.
[85] R. A. Plane and H. Taube, J. Phys. Chem., 1952, **56**, 33.
[86] D. N. Hume and H. W. Stone, J. Amer. Chem. Soc., 1941, **63**, 1200.

six-covalent complexes are formed containing two unpaired electrons only and in this case the binding is $3d^24s4p^3$. Unlike either of these compounds, chromous acetate has a moment of less than 1 B.M.; [87] even this may arise from impurity. King and Garner [87] suggest that this indicates $3d^34s$ tetrahedral bonds but no X-ray studies in support of this hypothesis are available. The explanation could be the same as for cupric acetate mono-hydrate (see p. 387). An important development is the recent announcement by Hein and Herzog [88] of the isolation of a Cr(I) complex having the formula $[Cr(dipyridyl)_3]ClO_4$, obtained by reduction of the bivalent complex $[Cr(dipyridyl)_3][ClO_4]_2$. The univalency ascribed to the chromium atom is supported by the magnetic moment of 2·1 B.M., indicating only one unpaired electron. The unexpected feature of the compound is the high co-ordination number of six proposed for a univalent metal. The moment indicates covalent $3d^24s4p^3$ bonds; further work on this compound should prove of interest. Mo(III) has the expected three unpaired electrons in its complex compounds, but in other valency states both Mo and W form strong covalent bonds and are generally diamagnetic or contain one un-paired electron according as the valency is even or odd. The data are summarised by Selwood.[89]

Group VII.—The compounds of the halogens are paramagnetic only when the valency is *even* and the compound is monomeric. Chlorine dioxide, ClO_2, for example, is paramagnetic with one unpaired electron. Chlorine trioxide, however, in the liquid state is diamagnetic; this is consistent with the dimeric formula Cl_2O_6 attributed to this compound. This difference in magnetic behaviour of ClO_2 and Cl_2O_6 illustrates how the formation of a dimer can eliminate an unpaired electron. The problem of assigning a formal valency to certain elements is well illustrated by the behaviour of Cl_2O_6. The physical properties of this compound leave no doubt that it should be formulated as $O_3Cl \cdot ClO_3$, the chlorine having a valency of seven; in the gas phase, however, the substance is monomeric and here the valency is six.[90] In the gas phase the compound should be paramagnetic [cf. $K_3Co(CN)_5$ solid and in solution]. The sub-group elements (Mn, Tc, and Re) have valencies from one to seven. No unpaired electrons are expected in Mn(VII), but a small temperature-independent paramagnetism is observed for the same reason as in chromates. Mn(VI) has the expected moment corresponding to one unpaired electron.[91] Mn(IV) occurs in certain complex compounds and, like the iso-electronic Cr(III), contains three unpaired electrons. A good example is K_2MnF_6[29]; Mn(IV) also occurs with three unpaired electrons in complex heteropolymolybdates.[92] Depending upon the attached groups, Mn(III) compounds contain either four or two unpaired electrons; manganese trisacetylacetone illustrates the former, and $K_3Mn(CN)_6$ the latter.[43, 91] Mn(II) shows electron pairing in the complex

[87] W. R. King and C. S. Garner, *J. Chem. Phys.*, 1950, **18,** 689.
[88] *Z. anorg. Chem.*, 1952, **267,** 337.   [89] *Op. cit.*, p. 106.
[90] N. W. Taylor, *J. Amer. Chem. Soc.*, 1926, **48,** 855; P. W. Selwood, *op. cit.*, p. 123.
[91] N. Goldenberg, *Trans. Faraday Soc.*, 1940, **36,** 847.
[92] P. Ray, A. Bhaduri, and B. Sarma, *J. Indian Chem. Soc.*, 1948, **25,** 51.

cyanide but practically all other compounds contain five unpaired electrons. Mn(I) has been reported in the complex cyanide ; [91] the weak paramagnetism of this is probably due to impurity. Treadwell and Raths [92a] have recently prepared pure $K_5Mn(CN)_6$. They find it to be diamagnetic. Little has been published concerning the magnetochemistry of technetium compounds; many of the results available for rhenium are anomalous and require further investigation.[93, 94]

Group VIII.—Recent developments in this group are best surveyed with the magnetochemistry of Fe, Co, and Ni as the background. The behaviour of Fe(II) and Fe(III) has been referred to ; electron pairing occurs readily with the CN group and other groups of low electronegativity.[48] The magnetic properties of the haematin compounds of iron have been reviewed by Hartree.[95] Magnetochemical confirmation of the existence of Fe(VI) in the $[FeO_4]^{--}$ ion has been obtained by H. J. Hrostowski and A. B. Scott,[96] who had the difficult task of disentangling ferro- and para-magnetism in the same specimen because the K_2FeO_4 was only 97% pure. The susceptibility was measured at different field strengths and then extrapolated to zero field strength, thereby eliminating the ferro-magnetic contribution. As expected, the $[FeO_4]^{--}$ ion contains two unpaired electrons. For cobalt, the valency states of 2, 3, and 4 may be confirmed by magnetic measurements. Co(II) forms both tetrahedral ($4s4p^3$) and octahedral ($4s4p^34d^2$) complexes in which no electron pairing occurs and square planar ($3d4s4p^2$) and octahedral ($3d^24s4p^3$) complexes which contain only one unpaired electron ; hence magnetic moments enable one to distinguish readily between square and tetrahedral *four*-covalent complexes.[97, 98, 99] The moment may also be used to decide the type of bond in octahedral complexes. The puzzling problem of the complex cyanide of Co(II) has recently been cleared up. The solid, which is diamagnetic, is not $K_4Co(CN)_6$ but $K_3Co(CN)_5$; apparently spin pairing takes place in the solid state. In aqueous solution, however, the compound is paramagnetic with one unpaired electron.[100, 101] Adamson [100, 101] considers that the ionic species in solution is $[Co(CN)_5]^{3-}$ and not the monoaquopentacyanide. Co(III) is diamagnetic in practically all of its complexes but has the expected number of unpaired electrons for a Co^{+++} ion in K_3CoF_6.[29] The magnetic moment of the Co(IV) complex K_3CoF_7 has not yet been published. Calvin, Bailes, and Wilmarth [102] have studied the magnetic properties of the complexes formed when certain square Co(II) compounds absorb oxygen.

[92a] W. D. Treadwell and W. E. Raths, *Helv. Chim. Acta*, 1952, **35**, 2259.
[93] W. Klemm and H. Schuth, *Z. anorg. Chem.*, 1934, **220**, 193.
[94] W. Klemm and G. Frischmuth, *ibid.*, 1937, **230**, 220.
[95] *Ann. Reports*, 1946, **43**, 287.
[96] *J. Chem. Phys.*, 1950, **18**, 105.
[97] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc., N.S.W.*, 1940, **74**, 495.
[98] L. Pauling, *op. cit.*, pp. 97, 118.
[99] P. Ray and S. P. Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 323.
[100] A. W. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.
[101] A. W. Adamson, J. P. Welker, and M. Volpe, *ibid.*, 1950, **72**, 4030
[102] *Ibid.*, 1946, **68**, 2254.

The square compounds contain one unpaired electron but become diamagnetic on complete oxygenation. If the product contained one molecule of oxygen per Co atom, the product would still be paramagnetic because the total number of electrons would still be odd. The diamagnetism is most easily accounted for by the assumption that an —O—O— bridge between two Co(III) atoms is formed. Paramagnetism [103] corresponding to one unpaired electron is observed in the polynuclear Co complexes of the type $\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\O_2\end{smallmatrix}Co(NH_3)_4\right]X_4$. It has frequently been assumed that the Co atom is quadrivalent but the unpaired electron is probably associated with the oxygen molecule, both cobalt atoms being tervalent.

Fig. 4

Electronic configuration and magnetic moments of nickel complexes

Type of compound	Electronic configuration			Unpaired electrons	Magnetic moment, B.M.*
	3d	4s	4p		
Ni^{++} (Free ion)	↑↓ ↑↓ ↑↓ ↑ ↑	☐	☐ ☐ ☐	2	2·83
Ni(II) (Tetrahedral 4s4p³ bonds)	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	2	2·83
Ni(II) (Octahedral 4s4p³4d² bonds)	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓ 4d: ↑↓ ↑↓	2	2·83
Ni(II) (Square 3d4s4p² bonds)	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓	0	Diamag.
Ni(II) (Octahedral 3d²4s4p³ bonds)	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓ 5s: ↑↓	0	Diamag.
Ni(III) (Octahedral 3d²4s4p³ bonds)	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓ ↓	1	1·73
Ni(IV) (Octahedral 3d²4s4p³ bonds)	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	0	Diamag.
Ni(0) (Tetrahedral 4s4p³ bonds)	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	0	Diamag.

* Calculated on the spin-only formula.

Magnetic measurements have proved of considerable value in confirming the newer valency states of nickel. The relationship between the valency, stereochemistry, and magnetic behaviour of nickel in its complexes has been reviewed elsewhere [104] and need only be summarised here. In short, nickel has well-defined valency states of 0, 2, 3, and 4 and a less certain univalent state. The electronic configurations are given in Fig. 4.

[103] N. V. Sidgwick, *op. cit.*, p. 1421.
[104] R. S. Nyholm, *Chem. Reviews*, 1953, **51,** in the press.

In the bivalent state, the magnetic moment enables one to distinguish between *tetrahedral* * four-covalent complexes and *square* four-covalent complexes, the former being para- and the latter dia-magnetic. Two kinds of octahedral Ni(II) complex are known and the magnetism is here diagnostic of bond type. The usual type, *e.g.*, $[Ni(NH_3)_6]Cl_2$, contains two unpaired $3d$ electrons and involves $4s4p^34d^2$ bonds ; the second type, *e.g.*, $[Ni(diarsine)]_3 [ClO_4]_2$ is diamagnetic, which is interpreted [48] to indicate $3d^24s4p^3$ binding with the promotion of two $3d$ electrons to a $5s$ orbital in which the electrons are paired. Support for this hypothesis is provided by the fact that the complex may be oxidised under suitable conditions—as should follow if promotion does take place. Octahedral and five-covalent Ni(III) complexes have been described, *e.g.*, $[NiCl_2(diarsine)_2]Cl$ [105] and $[NiBr_3, 2(C_2H_5)_3P]^0$.[106] These contain one unpaired electron, rather than the three expected by Hund's rules for a Ni^{+++} ion. The location of this unpaired electron and the bonding orbitals used in the five-covalent tervalent complex have been discussed elsewhere.[104, 106] In the octahedral Ni(III) complexes the unpaired electron appears to be promoted to a $5s$ orbital ; removal of this gives a diamagnetic Ni(IV) complex.[105] Since diamagnetism is also characteristic of the square planar Ni(II) arrangement, from which most Ni(III) and Ni(IV) complexes are prepared, it is often doubtful whether the nickel atom or the ligand has undergone oxidation in some reactions. Ni(I) is believed to exist in the complex cyanide of empirical formula $K_2Ni(CN)^3$. This compound, however, is diamagnetic [107] even in aqueous solution.[108] The diamagnetism is unexpected since Ni(I) should contain one unpaired electron ; Mellor and Craig [108] suggest that a Ni–Ni bond is involved between two Ni(II) atoms, the anion being dimeric, *i.e.*, $K_4[(CN)_3Ni-Ni(CN)_3]$. Until paramagnetism has been observed the univalency must remain doubtful. Recently, Nast and Pfab [108a] have shown that the anion in $K_2Ni(CN)_3$ is dimeric, two square-co-ordinated nickel atoms being bridged by two CN groups. The carbon atoms of these bridging groups are each three-covalent, similar to those in the bridging CO groups in $Fe_2(CO)_9$. Nast and Roos [108b] have shown that $K_2Ni(CN)_3CO$ is also diamagnetic. They conclude that the anion is dimeric and suggest that in both $[Ni_2(CN)_6]^{4-}$ and $[Ni(CN)_3(CO)]_2^{4-}$ the diamagnetism arises from some kind of metal-metal interaction as in the diamagnetic carbonyl $Co_2(CO)_8$.

The remaining elements of Group VIII never contain more than two unpaired electrons in their complex compounds ; [109] as a rule they are diamagnetic if the number of electrons is even and contain one unpaired electron only if the total number of electrons is odd. Compounds of Ru and

[105] R. S. Nyholm, *J.*, 1950, 2061 ; 1951, 2602.

[106] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.

[107] L. Szego and P. Ostinelli, *Gazzetta*, 1930, **60**, 946.

[108] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc.*, *N.S.W.*, 1942, **76**, 281.

[108a] R. Nast and W. Pfab, *Naturwiss.*, 1952, **39**, 300.

[108b] R. Nast and H. Roos, *Z. anorg. Chem.*, 1953, **272**, 242.

[109] D. P. Mellor, *J. Proc. Roy. Soc.*, 1943, **77**, 145.

* Evidence in favour of the tetrahedral rather than a $4s4p^24d$ square arrangement is discussed elsewhere.[104]

Os in valency states 2, 6, and 8 are diamagnetic. Ru(III) has the usual paramagnetism for one unpaired electron, as in covalent $3d^24s4p^3$ Fe(III) complexes. No Ru(III) compound containing five unpaired electrons is known. Quadrivalent Ru and Os have unusual magnetic properties ; Ru(IV) in K_2RuCl_6 [109] has the expected two $4d$ unpaired electrons but the hydroxy-pentachlororuthenate(IV) of empirical formula $K_2[RuCl_5(OH)]$ is diamagnetic.[109] It has been shown by Mathieson, Mellor, and Stephenson [110] that this compound is really the monohydrate of the dimer $[(Cl_5Ru—O—RuCl_5)_2]^{4-}$, some kind of spin coupling taking place. Os(IV) is similar to Ru(IV) except that moments are generally smaller ; thus, K_2OsCl_6 has a moment of 1·4 B.M.[109] as compared with 2·8 B.M. for the Ru compound. A temperature-dependence study of the susceptibility is necessary in the former because the simple Curie law is almost certainly not applicable in this case, the moment having been calculated on the (probably erroneous) assumption that the Curie law holds good. All known Rh(III) and Ir(III) compounds are diamagnetic, but Rh(IV) and Ir(IV) complexes contain the expected unpaired electron.[30, 109] The anomalous diamagnetism [109] of Rh(II) and Ir(II) compounds is being investigated ; [111] it now seems probable that in these compounds Rh(I) and Rh(III) atoms are present in equal numbers. In the usual bi- and quadri-valent states both Pd and Pt are diamagnetic. The tervalent state is less common than is often supposed ; the so-called $PtCl_3$, for example, contains Pt(II) and Pt(IV) atoms in equal numbers.[112] However, Pd(III) does occur in the fluoride PdF_3, as the moment indicates the required unpaired electron.[30]

The Trans-uranic Elements.—Magnetic properties have helped in the assignment of the electronic configurations of these elements. There has been some doubt as to whether the elements following actinium * (atomic number 89 ; $1s^2 \ldots 4f^{14}5s^25p^65d^{10}6s^26p^66d^17s^2$) are built up by adding electrons to a $5f$ shell, as with the rare earths, or to a $6d$ shell, as for the transition elements. Unlike previous applications in which the ground-state configuration is assumed and valency inferred from the moment, here the elements are compared in suitable valency states and the way in which μ varies with atomic number is examined. Howland and Calvin [113] examined the cations of elements 93—95 in aqueous solution in various valency states to obtain ions containing from one to six electrons in excess of the radon (inert gas) core. They found that the susceptibilities changed along the sequence in the same way as do the susceptibilities of the corresponding rare-earth compounds. Using the mean of figures given by Lister,[114] together with Howland and Calvin's figure for Am(III) in aqueous solution, one obtains the relationship shown in Fig. 5. The similarity with the rare earths is striking and must be taken as confirming the conclusion from spectroscopic work that the $5f$ shell is being filled. If these elements

[110] *Acta Cryst.*, 1952, **5**, 185.
[111] B. Figgis and R. S. Nyholm, unpublished experiments.
[112] Y. K. Syrkin and V. I. Belova, *J. phys. Chem.*, *U.S.S.R.*, 1949, **23**, 664.
[113] *J. Chem. Phys.*, 1950, **18**, 239.   [114] *Quart. Reviews*, 1950, **4**, 20.
* Th (90), Pa (91), U (92), Np (93), Pu (94), Am (95), Cm (96), Bk (97), Cf (98).

behaved like those of the first transition series (see Table 3) the moments should rise to a maximum with *five* unpaired electrons and then fall steadily again ; on the other hand, similarity with the other two transition series would most likely lead to moments corresponding to one or nil unpaired electrons according as the number of electrons is odd or even. In all cases the moments are less than the calculated values, with which the rare earths agree closely. This deficiency is attributed by Howland and Calvin to partial quenching of the orbital contribution by the surrounding electrical field, the $5f$ electrons being regarded as less effectively screened than in the rare earths ; alternatively, Russell–Saunders coupling is regarded as not
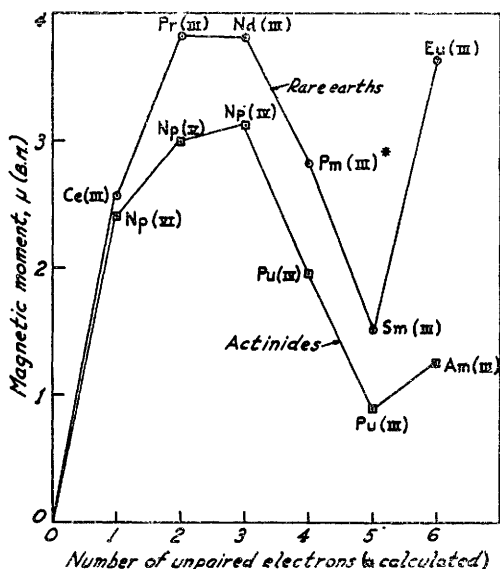

FIG. 5

fully applicable to these elements. For many U(IV) compounds the magnetic moment is sufficiently close to the spin-only value for two unpaired electrons to suggest a $6d^2$ rather than a $5f^2$ arrangement. Lister points out, however, that most of these spin-only values are restricted to magnetically concentrated compounds like UO_2, for the moments of U(IV) sulphate and oxalate agree better with the $5f^2$ arrangement. However, Dawson [115] has measured the moment of UF_4 (in solid solution in ThF_4) and concludes that the U(IV) ion has the $6d^2$ configuration ; magnetic dilution is obtained by using a solid solution. A similar moment for Pu(VI) in sodium plutonyl acetate leads Dawson [115] to suggest that Pu(VI) also has a $6d^2$ configuration. He concludes that for only two unpaired electrons the $6d^2$ arrangement is more stable than the $5f^2$. Nevertheless, the unusual behaviour of Cr(II) and Cu(II) acetates suggests that the latter result should be interpreted with

[115] J. K. Dawson, *J.*, 1952, 1185 ; 1952, 2705.

caution. It is concluded by Lister that, taken as a whole, the magnetic data for the trans-uranic elements undoubtedly support the $5f$ structures. Hutchison and Elliott [116] have reached the same conclusion. Chemical evidence for the elements preceding uranium suggests that thorium is a Group IV, and protoactinium a Group V, element. These deviations from " rare-earth " behaviour can be understood when it is borne in mind that $5f$ electrons are less firmly bound than $4f$ electrons. A serious difference between the rare-earth and the actinide series is observed in comparing Pu(III) with Sm(III) and Am(III) with Eu(III). The smaller moments of the actinide series are attributed by Howland and Calvin to wide multiplet splitting, in which case the calculated Sm(III) and Eu(III) value, based on narrow multiplet separation, is no longer applicable. To sum up, magnetic data support the view that the actinides have electronic configurations similar to those of the rare earths, possibly excepting those with only one or two unpaired electrons ; greater variation owing to magnetic concentration and chemical reactivity, however, is observed.

Orbital Contribution and Stereochemistry

A study of the factors affecting the size of the orbital contribution to the magnetic moment of compounds of the first transition series promises to yield information of diagnostic value for inorganic stereochemistry. As mentioned earlier, the reduction in the magnetic moment of these elements to nearly the spin-only value is attributed to quenching of the orbital contribution by the electric field created by the surrounding atoms. This crystalline field causes a separation of the degenerate energy levels of the D or F states of these ions (but not of an S state since here $L = 0$). Consider as an example the Co^{++} ion, containing three unpaired electrons, ground state term $^4F_{9/2}$. It was shown by Bethe [117] that a cubic field (as occurs when the Co^{++} ion is at the centre of a perfect octahedron of H_2O molecules) splits an F state into three energy levels, the separation between successive levels being about 10^4 cm.$^{-1}$ (see Fig. 6). Usually, small departures from cubic symmetry occur owing to slight distortion of the octahedron of H_2O molecules ; this may be regarded as equivalent to imposing on the cubic field a small component of lower symmetry, e.g., tetragonal or rhombic.* This rhombic component causes a further splitting of two of the three energy levels into triplets, the energy separation between which is of the order of kT (200 cm.$^{-1}$ at room temperature). This gives seven levels in all. In a similar way, a D state is split by a cubic field into two levels with an energy difference of about 10^4 cm.$^{-1}$; these two levels are further split by a rhombic component into a doublet and a triplet respectively. The distribution of the atoms between the possible energy levels depends upon the energy separation between these levels and its value relative to kT at the temperature of investigation. This energy level diagram, known as a
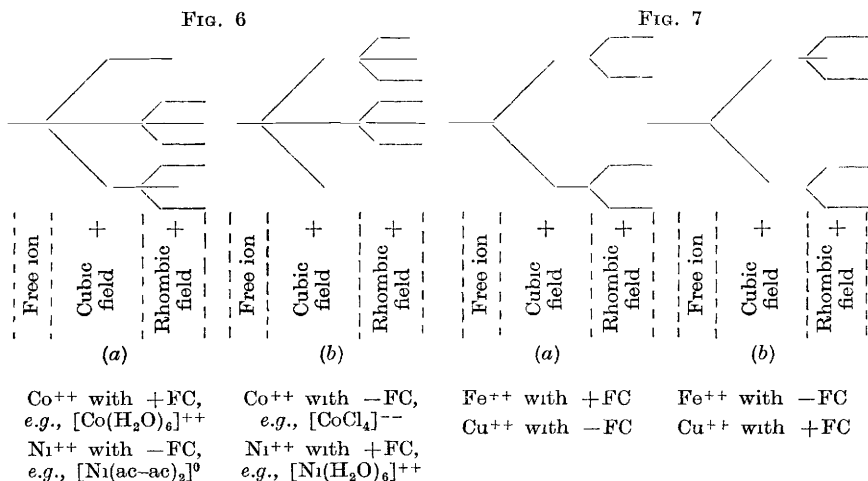
[116] *J. Chem. Phys.*, 1948, **16**, 920.

[117] *Ann. Physik*, 1929, **3**, 133 ; *Z. Physik*, 1930, **60**, 218.

* Cubic field : three axes at right angles, all equal. Tetragonal field : three axes at right angles, two equal. Rhombic field : three axes at right angles, all unequal.

" Stark Pattern ", is given for F and D states under certain conditions in Figs. 6 and 7, respectively. The diagrams are not to scale.

The Stark pattern is inverted when the sign of the field constant (FC) changes from positive to negative. The field constant is the coefficient of the cubic field but will not be discussed further.[1, 117, 118, 119] Gorter [120] has shown that FC is positive when Co^{++} is surrounded by six identical negative

Fig. 6

Fig. 7

| (a) | (b) | (a) | (b) |

Co++ with +FC, e.g., $[Co(H_2O)_6]^{++}$

Co++ with −FC, e.g., $[CoCl_4]^{--}$

Fe++ with +FC
Cu++ with −FC

Fe++ with −FC
Cu++ with +FC

Ni++ with −FC, e.g., $[Ni(ac–ac)_2]^0$

Ni++ with +FC, e.g., $[Ni(H_2O)_6]^{++}$

charges at the corners of an octahedron (e.g., $[Co(H_2O)_6]^{++}$) and is negative when the Co^{++} is at the centre of a tetrahedron of negative charges (e.g., $[CoCl_4]^{--}$). The important difference between 6(a) and 6(b) is that in the latter the singlet level lies lowest and there is a large energy difference between it and the next energy level. Since in 6(a) there is a low-lying triplet with energy separations comparable with kT, all three levels will be occupied and a large orbital contribution can be expected ; for 6(b), however, much closer approximation to the spin-only formula is to be expected. Table 4 gives typical data for octahedral and tetrahedral Co^{++} complexes,

TABLE 4.   *Magnetic moments of " ionic " cobaltous complexes.*[124]

Octahedral complexes		Tetrahedral complexes	
Compound	μ (B M)	Compound	μ (B M)
$[Co(H_2O)_6]Cl_2$	4·94	$(pyH)_2[CoCl_4]$	4·74
$[Co(H_2O)_6][ClO_4]_2,6H_2O$.	4·93	$(pyH)_2[CoBr_4]$	4·67
$[Co(NH_3)_6][ClO_4]_2$ . .	5·04	$Hg[Co(CNS)_4]$	4·33
$[Co(py)_6][ClO_4]_2$ . . .	4·87	$[CoCl_2,2(C_2H_5)_3P]^0$ . . .	4·48
$[Co(dipy)_3][ClO_4]_2$ . . .	4·86		

[118] J. H. Van Vleck, *Phys. Review*, 1932, **41**, 208.
[119] W. G. Penney and R. Schlapp, *ibid.*, p. 194 ; 1932, **42**, 666 ; 1933, **43**, 486.
[120] *Ibid.*, 1932, **42**, 437.

illustrating the effect of the change in stereochemistry.   There is fairly wide variation in both classes but the moments of tetrahedral complexes are certainly lower than in octahedral compounds.   Nevertheless, the theory is obviously over-simplified because the tetrahedral compounds have moments much larger than that expected for the spin-only value of 3·88 B.M.

The magnetic moments of the blue and the violet form of the compound $CoCl_2,2py$ illustrate the effect of stereochemistry on magnetic behaviour.   Barkworth and Sugden [121] have shown that the moments of these are respectively 4·62 and 5·33 B.M.   Formluæ such as $[CoCl_2,2py]^0$, $[Copy_4][CoCl_4]$, and a polymerised structure involving octahedrally co-ordinated Co(II) with chlorine bridges, suggest themselves.   Clearly, an understanding of the way in which asymmetry affects the moment will assist in the solution of this problem.*

It has been shown that Ni(II) should behave in the opposite manner to Co(II), *tetrahedral* Ni(II) complexes having the higher moments.[119, 120]   In general, the moments of tetrahedral Ni(II) complexes are larger than those of octahedral complexes containing six identical ligands, but if the six groups attached to the Ni(II) atom are not identical the moment is often much larger than the spin-only value.   Thus the moments of tetrahedral Ni(II) bisacetylacetone, octahedral hexamminonickel(II) perchlorate and octahedral Ni(II) bisacetylacetone dihydrate are respectively 3·39, 3·15, and 3·42 B.M.[124]   Hence, in distinguishing octahedral Ni(II) from tetrahedral Ni(II) results are less conclusive, probably because the moment is more sensitive to slight departures from cubic symmetry in the crystalline field.[122, 125]

A study of the way in which various factors affect the size of the orbital contribution for bivalent transition elements has been made by Kanekar.[124]   It is found that : (i) changing only the *anion* in complexes of the type $[Co(NH_3)_6]X_2$ or $[Ni(NH_3)_6]X_2$ has practically no effect upon the orbital contribution ; the influence of the anion upon the crystalline field is negligible compared with the octahedron of closer NH_3 molecules ; (ii) changing the *ligand* in octahedral complexes of the above kind, *e.g.*, $NH_3 \rightarrow$ $H_2O \rightarrow$ ethylenediamine, has a small but significant effect ; this seems to be related to the relative electronegativities of the attached groups and hence the field which they create ; (iii) changing the co-ordination number (stereochemistry) has a very marked effect which is in the sense predicted by the crystalline field theory as discussed above ; (iv) changing the halide in complexes of the type $[CoX_4]^{--}$ causes a fall in the moment along the sequence $\mu_{Cl} > \mu_{Br} > \mu_I > \mu_{CNS}$.   As with (ii), this is apparently related to the relative electronegativities.

For ions in D states with the triplet lying lowest (*e.g.*, the $[Fe(H_2O)_6]^{++}$

[121] *Nature*, 1937, **139**, 374.   [122] P. L. Mukherjee, *Z. Krist.*, 1935, **91**, 504.
[123] G. A. Barclay, T. Christie, and R. S. Nyholm, unpublished experiments.
[124] Thesis, London, 1953.   [125] A. Bose, *Indian J. Phys.*, 1948, **22**, 25, 33, 57.
* A recent investigation [123] has shown that the blue form almost certainly has the formula $[CoCl_2,2py]^0$ whilst the violet form is probably a bridged polymer of octahedral bivalent cobalt.

ion) as in 7(b), a considerable orbital contribution is to be expected for the same reason as with 6(a). However, in the case of octahedrally co-ordinated Cu^{++}, a doublet lies lowest, and although one might expect this to give rise to a considerable orbital contribution, yet Bethe [117] has pointed out that such a doublet is essentially " non-magnetic " and should not result in any orbital contribution. In practice it is observed that the magnetic moment in one direction in the $CuSO_4,5H_2O$ crystal is equal to the spin-only value, but a considerable orbital contribution is observed along other axes. This has been explained by a further energy-level splitting owing to the complicated crystalline field operating (see next section).

No reference has been made to the size of the orbital contribution in complexes in which electron pairing occurs. Thus we find that octahedral covalent Co(II) complexes, e.g., $K_2CaCo(NO_2)_6$,[126] have moments of the order of 1·9 B.M., whereas square Co(II) complexes have much larger moments in the range 2·1—2·5 B.M. This is at least consistent with Pauling's theory that the unpaired electron in the first instance is in a 5s orbital where the orbital contribution should be zero. However, considerably more information is necessary before any general statements can be made about covalent compounds. In particular, we need much more data about the separation of energy levels, and knowledge of the way in which the magnetic susceptibility varies with temperature. Finally, the measurement of magnetic anisotropies will be of great value. Valuable data of this kind for salts of Fe, Co, Ni, and Cu have been obtained by Guha.[38]

Paramagnetic Resonance Absorption

This subject has developed rapidly of late owing to improvements in the technique of generating and studying micro-waves. It is now one of the most active fields of research in physics.[127-133] The measurements are of importance for our purposes because of the information obtained about energy levels and magnetic moments. When a paramagnetic salt is placed in a steady magnetic field of the order of a few thousand oersteds, which field may be varied at will, and an oscillating electromagnetic field is applied at right angles to the former, marked absorption of energy by the specimen occurs at certain values of the field strength. The position of these peaks, in terms of the frequency of the oscillating field and of the steady magnetic field, provides information concerning both nuclear and electronic spin of the atom ; we are concerned solely with the latter. An absorption peak is observed whenever the separation of the energy levels of the paramagnetic ion is equal to the quantum of energy $(h\nu)$ corresponding to the radio

[126] P. Ray and H. Sahu, *J. Indian Chem. Soc.*, 1946, **23**, 161.
[127] R. L. Cummerow, D. Halliday, and G. E. Moore, *Phys. Review*, 1947, **72**, 1233.
[128] D. M. S. Bagguley, B. Bleaney, J. H. E. Griffiths, R. P. Penrose, and B. I. Plumpton, *Proc. Phys. Soc.*, 1948, **61**, 542, 551.
[129] Y. Ting and D. Williams, *Phys. Review*, 1951, **82**, 507.
[130] C. J. Gorter, " Paramagnetic Relaxation ", Elsevier, Leiden, 1947.
[131] C. Kikuchi and R. D. Spence, *Amer. J. Physics*, 1950, **18**, 167.
[132] B. Bleaney, *Brit. J. Appl. Phys.*, 1952, **3**, 337.
[133] D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Roy. Soc.*, 1950, *A*, **204**, 188.

frequency. Hence a direct comparison of $h\nu$ and kT is possible. The advantages of this method over others for the study of paramagnetic ions have been summarised by Bleaney and his co-workers [128] as follows : (i) no corrections for diamagnetism or diamagnetic impurities are needed ; (ii) direct measurements of g values are possible (leading to magnetic moments) ; (iii) small splittings of the order of 1 cm.$^{-1}$ can be observed ; (iv) direct observations can be made of the different paramagnetic ions in a unit cell ; (v) very small spin-lattice relaxation times of the order of 10^{-10} sec. may be observed. Needless to say, the main disadvantage is the technical difficulty of working with micro-waves. The technique is fully discussed elsewhere,[127–131] wherein detailed references to other workers are given.

The wave-length of the oscillating field is of the order of 3 cm. and the magnetic field is varied between 0 and 15,000 oersteds. If m is the magnetic quantum number, transitions of considerable intensity can occur between levels provided that the change in m is $\pm$ 1. The relationship between the frequency of the radiation ν, the magnetic field H, and the Landé splitting factor g is given by $h\nu = g\beta H$, where β is the Bohr magneton. Of the large number of compounds so far examined few fail to show the phenomenon of absorption maxima at room temperatures. Failure to do so has been attributed [128] to (a) too large an initial splitting of the orbital levels by the crystalline field, or (b) too broad an absorption line owing to the very short spin relaxation time. The latter difficulty can be overcome by working at low temperatures ; thus Ti(III) salts show no absorption until the temperature is reduced to that of liquid helium. Following a preliminary survey of more than 100 salts of the iron group,[128] more detailed studies have been made of chrome alum,[133] manganese salts,[134] various cobaltous salts,[135, 138] and some bivalent nickel salts.[137] As an illustration A. Abragam and M. H. L. Pryce [136] have studied in detail the paramagnetic resonance spectrum of copper Tutton salts ($CuSO_4,M^I_2SO_4,6H_2O$) and conclude that the data can be interpreted by assuming that a crystalline field of tetragonal symmetry is operating. Pauling's view of the structure (four $3d4s4p^2$ bonds) is considered to be incompatible with their findings. Lack of sufficient crystal-structure determinations to enable theories to be checked is a handicap, but striking advances have been made in the determination of energy levels and the correlation of stereochemistry with magnetic moment.

[134] B. Bleaney and D. J. E. Ingram, *ibid.*, 1951, *A*, **205**, 336.
[135] A. Abragam and M. H. L. Pryce, *ibid.*, 1951, *A*, **206**, 173.
[136] *Idem, ibid.*, p. 164.
[137] J. H. E. Griffiths and J. Owen, *ibid.*, 1952, *A*, **213**, 459.
[138] B. Bleaney and D. J. E. Ingram, *ibid.*, 1951, *A*, **208**, 143.