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The Magnetic Properties of Some Paramagnetic Crystals at Low Temperatures.

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List of Crystals Studied.

$Mn(NH_4)_2(SO_4)_26H_2O$

$K_3Fe(C_2O_4)_33H_2O$

$Fe[(CH_3CO)_2CH]_3$

$(NH_4)_3Cr(C_2O_4)_33H_2O$

$Cr[(CH_3CO)_2CH]_3$

$NiSO_46H_2O$

$NiSeO_46H_2O$

$NiSO_47H_2O$

$NiRb_2(SO_4)_26H_2O$

$NiRb_2(SeO_4)_26H_2O$

$NiCs_2(SO_4)_26H_2O$

$NiTl_2(SO_4)_26H_2O$

$NiTl_2(SeO_4)_26H_2O$

$Ni(NH_4)_2SO_4SeO_46H_2O$

$CoSeO_46H_2O$

$CoSO_47H_2O$

$CoRb_2(SO_4)_26H_2O$

$CoRb_2(SeO_4)_26H_2O$

$CoCs_2(SO_4)_26H_2O$

$CoTl_2(SO_4)_26H_2O$

$FeSO_47H_2O$

$CuRb_2(SO_4)_26H_2O$

$CuTl_2(SO_4)_26H_2O$

$2NH_4ClCuCl_22H_2O$

$Cu(CH_3COO)_2H_2O$

$K_3Fe(CN)_6$

$KMnO_4$

The Magnetic Properties of Some Paramagnetic Crystals at Low Temperatures.

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Introduction.

A new and convenient method for measuring accurately the magnetic anisotropies and principal susceptibilities of single crystals was developed by Professor K. S. Krishnan and the present writer a few years ago. The chief advantage of the method was that the crystals could be used in their natural form without being ground into spheres, or into cylindrical rods or discs as in the earlier magnetic measurements on single crystals. It is only a few crystals that can be obtained in sizes sufficiently large to be ground in this manner, whereas with the present method the crystals weighing even a few milligrams can be studied for their principal susceptibilities. The results of the measurements made by this method on a large number of diamagnetic crystals, both inorganic and organic, and a detailed discussion of the results in relation to their crystal structure, were reported in a paper (1933). It was shown, in particular, that in the organic crystals of the aromatic class (several of which were

studied in this paper), whose molecules are highly anisotropic magnetically, and the magnetic anisotropies of the crystals give valuable information regarding the orientations of the benzene rings in the lattices of these crystals. This experimental method has been used extensively by Krishnan and Banerjee, and by Kathleen Lonsdale for measurements on the organic crystals, -- aromatic, aliphatic, and heterocyclic. More recently several paramagnetic crystals have been studied by Krishnan and his collaborators both at room temperature and at low temperatures.

The importance of studying the principal susceptibilities of paramagnetic single crystals arises from the following circumstance. The large deviations observed in the magnetic behaviour of the paramagnetic ions in these crystals from the theoretical behaviour of an assemblage of free ions, are due to the large electric fields present in the crystals, and the splitting, of the Stark type, of the energy levels of these ions under the influence of these fields. The study of the principal susceptibilities of these crystals at different temperatures gives us therefore a powerful insight into the magnitudes and the asymmetries of these electric fields and the nature of the splitting of the energy levels in these fields.

In most of the common paramagnetic crystals, as for example in the salts of the rare-earth and the iron groups of elements, the coupling between the spin and orbital moments of the electrons in the incoplete shells of the paramagnetic ions is of the Russell-Saunders

Russell- Saunders type. From the point of view of the Stark splitting of the energy levels of the paramagnetic ions under the crystalline electric fields, these crystals fall naturally, as Van Vleck (1935) has pointed out, into the following three classes: (1) those in which the fields are too feeble to break the coupling between the spin moment of the ion and its orbital moment. The rare earth salts belong to this group. The reason is that the paramagnetism of the rare earth ions arises from the spin and orbital moments of the electrons in the 4f shell, which remains incomplete, whereas some of the outer shells like 5s and 5p are filled up. These latter completed shells will therefore effectively shield the electrons in the former, which account for the observed paramagnetism of the ion, from the electric fields due to the neighbouring charged atoms. (2) To the second class belong crystals in which the internal electric fields are strong enough to break the coupling between the spin moment of the paramagnetic ion and its orbital moment but not strong enough to break the coupling among themselves of the spin moments of the different electrons in the incomplete shell of the ion that gives the resultant spin moment of the ion. This condition is fulfilled in the ordinary ionic salts of the iron group of elements. (3) The third class consists of crystals in which the crystalline electric fields are so large that the Russell-Saunders coupling is broken, and the spin moments of the different electrons in the incomplete shells orient in the applied magnetic field independently of one another, though they will exert strong influence on one another through the remnants of that coupling. Such strong fields would obtain for example in the complex salts in which the binding of the paramagnetic atom to its neighbours is of the covalent type. The interatomic

interatomic distances corresponding to covalent binding, as is well known, are much smaller than the corresponding distances in ionic binding, and hence the electric field in the neighbourhood of the paramagnetic atoms in these crystals will be much stronger than in the corresponding ionic salts. The Stark patterns in these three types of crystalline fields will naturally be widely different, and hence also their effects on the magnetic properties of the paramagnetic ions.

From the point of view of the effects on the magnetic properties, the asymmetries of the crystalline electric fields will be nearly as important as the magnitudes of the fields. For example, a field of rhombic symmetry may produce under favourable conditions, more striking changes in the magnetic behaviour than a cubic field of the same magnitude. In order to eliminate the possible effects of exchange interactions between the spin moments, which will be complicated and difficult to allow for, it is desirable to select magnetically dilute crystals for study. In some of the crystals like the Tutton salts or the highly hydrated sulphates and selenates, usually selected for such studies, there may be as many as twenty or more diamagnetic atoms for each paramagnetic atom present. Many of these crystals have a large water of crystallization, and in such crystals the paramagnetic ion is generally surrounded by six water molecules which occupy the corners of an octahedron and which present their negatively charged oxygen ends towards the central ion. Under these conditions the electric field in the neighbourhood of the central ion will be that due to an octahedral distribution of six equal negative charges at the corners of a nearly regular octahedron. The field will therefore be predominantly cubic in symmetry with a feeble rhombic component super-

superposed on it. All the anisotropic effects observed in these salts will be just those produced by these feeble components. On the other hand, if the negatively charged atoms immediately surrounding the paramagnetic ion are not of the same kind, then their distances from the paramagnetic ion will be different for different atoms, and the field will then show much larger deviations from cubic symmetry than would occur when the surrounding atoms are all of the same kind.

Thus the magnetic properties of the paramagnetic ions in these crystals will be sensitive both to the magnitudes of the crystalline fields, which will be determined by the closeness of approach of the neighbouring charged atoms, and hence ultimately by the nature of the chemical binding between the paramagnetic ion and its neighbours, and to the asymmetry of the fields, which will be determined by the geometry of disposition of these charged atoms.

The present work concerns itself with the study of the principal magnetic susceptibilities of single crystals of a number of salts belonging to the iron group of elements, from room temperature down to about 80°K. In some of these crystals, like potassium ferricyanide and potassium permanganate the bindings of the paramagnetic ion to its neighbours are covalent and the electric fields therefore conform to type (3). The majority of the crystal studied, however, are ionic and the fields in them conform to type (2). In many of them like the Tutton salts and the sulphates and selenates, the field is predominently cubic in symmetry with a small rhombic component, and in others like copper ammonium chloride and cupric acetate the fields deviate much from cubic symmetry. In the acetate and in the other organic salts studied, namely the oxalates and the

acetyl-acetonates of the

the acetyl-acetonates of trivalent chromium and iron, the chemical bonds apparently deviate slightly from the ionic type and the crystalline fields will therefore be intermediate between types (2) and (3) discussed above. Among the crystals studied are thus represented crystalline fields ranging from large to small magnitudes and from nearly cubic to strongly asymmetric ones. The magnetic data obtained are discussed on the basis of the Stark splitting of the energy levels of the ions produced by these fields.

The Influence of Crystalline Electric Fields on the Magnetic Properties of Paramagnetic Ions in Crystals.

That many solid substances are paramagnetic shows that even in the solid state the elementary magnetic moments which are responsible for the paramagnetism of the substance, are capable of rotating and taking up preferred orientations in the magnetic field. Such orientation can not be quite free, but will be restricted. The main effect of any restriction to the free rotation of elementary magnetic moments would be to make the temperature variation of the susceptibility of the substance deviate from the Curie law, namely $\chi = \frac{N\mu^2}{3kT} = C/T$, where χ is the susceptibility per gram molecule or ion and N is the Avagadro number. When the deviations from the law are small, the susceptibility can be expressed as a Taylor Series in powers of 1/T, and if we neglect all the terms of the higher powers than $1/T^2$, the expression for the susceptibility will reduce to the form $\chi = C/(T - \theta)$. Many of the paramagnetic substances that have been studied for the temperature variation of their susceptibilities have been studied at room temperature and higher temperatures which are easily

easily accessible in the laboratory, i.e., for $T \gtrsim 300^{\circ}K$ and therefore fairly large; hence it is not surprising that many of them do confirm roughly a law of the above type. This experimental finding, together with some theoretical predictions made by Weiss regarding the paramagnetism of ferromagnetic substances at temperatures higher than the Curie temperature, namely that this paramagnetism too conforms to the formula $\chi = C/(T - \theta)$, where θ is the Curie temperature of the substance, has led to a greater physical significance being attached to this law, as representing the temperature variation of susceptibility of all paramagnetic substances, than is justified by the experimental finding. Indeed from this circumstance it has been presumed that the deviation from the Curie law in all paramagnetic substances and not merely in ferromagnetic substances above their Curie temperatures was due ~~to~~ essentially to the same mechanism, namely to the presence of "inner magnetic fields" in these substances. This assumption, however, is not justified. First, it is found experimentally that θ occuring in the above expression assumes <u>negative</u> values nearly as frequently as positive values; secondly, it is found that even in substances for which θ is positive, the substances never become ferromagnetic however low the temperature may be lowered below θ ; thirdly, these peculiar conditions that account for the ferromagnetism of substances like iron, cobalt, nickel and some of the alloys, are not present in the ordinary paramagnetic substances; none of these substances is metallic in character and the θ values persist unimpaired even under conditions of high magnetic dilution in which the distances between the paramagnetic atoms are increased enormously and indeed they persist even in the liquid state and in state of solution in suitable solvents. Thus the deviations from the Curie

Curie Law can not be attributed to the presence of inner magnetic fields of the Weiss type as in ferromagnetic bodies.

There are also other features of paramagnetic behaviour which do not receive an explanation on this basis. For example, the postulate of an inner magnetic field will not explain why in the rare earth salts the magnetic moment of the rare earth ion calculated from the observed values of C in the above formula roughly conforms to the moment to be expected for the free ion from its known spectroscopic state, whereas in the salts of the iron group of elements the contribution to the magnetic moment appears to come almost exclusively from the spin moment of the electrons in the paramagnetic ion; nor does it explain why in some of the complex salts the magnetic moment may be very much lower than is to be expected from even the spin moments, and in some of them like the six coordinated cobalt salts, or plane four coordinated nickel salts the moment becomes nothing, thus rendering the salts diamagnetic. Again the postulate of such an inner magnetic field can not explain even in a general way the large magnetic anisotropies exhibited by many of these salts. When we remember that even if all the above features of the paramagnetic behaviour were explained satisfactorily on the postulate of an inner magnetic field, the postulate would not be acceptable because of the difficulty of finding a suitable mechanism that can produce such internal fields; it will be clear that we have to look elsewhere for an explanation of these paramagnetic features.

Such an explanation is indeed forthcoming, as has been shown by Kramers(1930), Bethe (1929,30), Van Vleck (1932), and others, when we regard the disturbing influences inside the crystals as being

being the large electric fields that would be present in the neighbourhood of the paramagnetic ions in these crystals, instead of the magnetic fields contemplated in Weiss's theory. That large electric fields should exist in the neighbourhood of the paramagnetic ion would be clear when we remember that the paramagnetic ion in the crystal would be surrounded by negatively charged atoms, whose charges will be of the order of the electronic charge and whose distances from the paramagnetic ion will be of the order of a few Angstrom units. Though at first sight the influence of these electric fields on the magnetic properties of the ion may not be obvious, a little calculation shows that the electric fields involved must be much larger than are used, for example, in the study of the Stark effects of atoms in the laboratory, and the Stark separation produced by these internal electric fields in crystals should therefore be enormously greater than the separations observed with the electric fields used in the laboratory. Indeed the internal electric fields in many of these crystals are so strong that the over-all separations of the energy levels produced by them are of the order of $10^4 cm^{-1}$. The energies involved thus become comparable with the energies of chemical binding between atoms, and one can understand the profound influence which such fields can have on the magnetic and other properties of these ions.

An extreme case may be taken to illustrate the influence of these electric fields, namely when they are strong enough to break the Russell-Saunders coupling in the ion. As is well known the ferrous ion contains 6 electrons in the 3d shell; the spectroscopic ground state of the ion is $^5D_4$, with its spin and orbital moments corresponding to the quantum numbers S = 2

and L = 2 respectively. The effective magnetic moment of the ion, as defined in the usual manner, will be equal to $g\sqrt{J(J+1)}$ Bohr magnetons, where g is the Landé splitting factor and has the value 1.5, while the quantum number J has the value 4. Hence the effective magnetic moment of free Fe^{++} ion should be equal to $\sqrt{45}$ Bohr magnetons. Now in the presence of a large electric field — sufficiently large to produce the analogue of the Paschen-Back effect with magnetic fields — not only the coupling between the S and L moments, but also the coupling of the spin moments of the six electrons in the 3d shell will be broken. The Stark pattern obtained with such a high field will thus be the pattern characteristic of a single d electron. Such high fields will occur, for example, in the neighbourhood of the Fe^{++} ion in the crystal of potassium ferrocyanide in which the ion will be surrounded by six negatively charged cyanogen groups at the corners of an octahedron.

Representing, as usual, the potential of an electron at any point x y z in the neighbourhood of the paramagnetic ion by the expression $V = D(x^4 + y^4 + z^4) + Ax^2 + By^2 - (A+B)z^2$ the fourth-power terms, representing the cubic part of the field, will be the predominent terms for the above field. The Stark pattern of a 'd' electron in this field will consist of a triplet and a doublet, the separation between them being of the order of $10^4 cm^{-1}$. Further it can be shown that for the type of field contemplated above, the cubic field constant D occuring in the above expression for the potential will be positive, in which case the triplet will be the lower. Now each of the five levels can accommodate 2 electrons, according to Pauli's Exclusion Principle. Since we have 6 electrons to be accommodated in these five levels, only the lower three, forming the triplet , will

will be occupied, each of these levels by a pair of electrons with opposing spin moments, while the upper two levels forming the doublet, whose separation from the lower level is very much greater than kT at even the highest temperatures accessible for experimenting, will not be occupied at all. Hence the Fe^{++} ion under these conditions will have no spin moment at all, and the crystal will therefore be diamagnetic, which is indeed the case; though as we have seen , in the ionic salts of Fe^{++} the effective magnetic moment of Fe^{++} ion is large,.

Similarly in potassium ferricyanide the disposition of the CN groups around the ferric ion will be the same as in ferrocyanide hence the electric field in its neighbourhood and the Stark pattern produced by the field. But the number of electrons in the 3d shell of Fe^{+++} is however 5, instead of 6 in Fe^{++} and these 5 electrons will occupy the three lower levels constituting the triplet, four of them occupying two of the three levels in pairs, and the fifth electron occupying the third level singly. The upper two levels forming the doublet will be left unoccupied as before, and the magnetic moment of the ion will thus correspond to the spin moment of only one of the five electrons in the 3d shell, i.e., to $S = 1/2$, whereas for the free ferric ion the moment would correspond to $S = 5/2$. These predictions from the crystal field theory agree with observation.

The fields considered in the above two crystals, which are strong enough to break the Russell-Saunders coupling, are not typical, and as mentioned previously occur only under the exceptional circumstances that prevail in the complex salts. They serve, however, to illustrate how striking may be the effects even of <u>electric</u> fields, when they are sufficiently strong, on

on the magnetic behaviours of the paramagnetic ions. In the ordinary ionic salts, however, the fields are not so strong, though they may still be sufficient to break the coupling between the L and S moments of the ion. Under such fields, the Stark pattern of the energy levels of the ion will consist of $(2L+1)$ levels, whose over-all separation will be of the order of $10^4 cm^{-1}$; each of the levels will retain a $(2S+1)$-fold degeneracy due to the spin moment of the ion, which will be removed only on the application of the magnetic field. In other words, the orbital part of the degeneracy of the ion would have been removed, either partially or wholly, by the crystalline field, even before the incidence of the magnetic field. The contribution from the orbital moment of the ion to the susceptibility will be frozen , either partially ~~or~~ or wholly, and the extent to which it is frozen will depend on the nature of the distribution of the $(2L+1)$ levels in the Stark pattern, particularly of its low lying levels, i.e., those levels whose energy separations from the ground level are not large compared with kT, since only they will be occupied. When, for example, the lowermost of the $(2L+1)$ levels is so far removed from the upper levels that it will be the only occupied level, then evidently the contribution from the orbital moments to the observed susceptibility will be quite negligible, and the spin moment alone will contribute to it. This explains in a general way the empirical finding by Sommerfeld in the salts of the iron group of elements : the paramagnetic ions behave magnetically as though they were in the S-state, and the more extensive observations to the same effect made by D.M.Bose, namely that their magnetic moments conform roughly to the spin- only value.

On the other hand in the salts of the rare earths, the influence of the crystalline electric fields will not be so striking as in the salts of the iron group, owing to the shielding of the paramagnetic electrons by the electrons in the 5s and other outer shells. Because of this shielding, the crystalline electric fields in these salts are not sufficient to break even the L-S coupling. The result is that the $(2J+1)$ levels of the ion, which in the absence of the crystalline field will all have the same energy, will be separated by the crystalline field. All the $(2J+1)$-fold degeneracy will not be removed, however, by the crystalline field, since the energy levels corresponding to the same values of the magnetic moment, but in the positive directions, will have the same energy. That is why the separation of the energy levels by crystalline field does not produce any magnetization. If now the magnetic field is put on, these degeneracies left over by the electric field will be removed, and in general all the energy levels will be altered, and hence also the relative populations of the ions in these levels; thus accounting for the observed paramagnetism. But it is obvious that the paramagnetism produced under these conditions will be widely different from that to be expected for the free ions, in which case all the $(2J+1)$-fold degeneracy would have been left over to be removed by the magnetic field alone. Thus in the rare earth salts also, though the effects of the crystalline fields may not be as drastic as in the complex salts, or even as marked as in the salts of the iron group, they will be considerable.

Some Striking Applications of the Crystalline Field Theory.

Having shown that the effect of a strong electric field on the magnetic behaviour of paramagnetic ions may be as pronounced as that of strong magnetic fields, and further that in actual crystals such large electric fields can exist, we shall now proceed to show that the internal electric fields in these crystals are sufficient to explain satisfactorily all the observed deviations from the behaviour to be expected for the free ions. In the first place it will be clear from what has been said in the previous section that the orbital angular momenta of the ions play a large part in determining the nature of the Stark pattern, and therefore in determining the deviations from the free ion behaviour. Indeed where there are no orbital angular momenta to be quenched by the crystalline electric fields, as in the case with the S-state ions, the splitting of the energy levels will be extremely narrow, and hence the influence of the crystalline electric fields will be quite negligible except at the lowest temperatures, of the order of $\Delta\nu/k$, where $\Delta\nu$ is the over-all Stark separation of the S-levels. That is why the magnetic behaviours of the S-state ions, e.g. Mn^{++} Fe^{+++}, Gd^{+++} are particularly simple. Single crystals of salts containing these ions have been studied extensively for their magnetic anisotropies and absolute susceptibilities by Krishnan and Banerjee (1936). The susceptibilities of these salts conform almost exactly to the spin-only value, and their temperature variations to the Curie law. Their anisotropies are extremely feeble, the difference between the two extreme susceptibilities in the manganous salts for example, at room temperature, being only

only 1/3000 of the absolute susceptibility. This feeble anisotropy would correspond to an over-all splitting of the order of $0.1cm^{-1}$, in satisfactory agreement not only with the narrow Stark separation to be expected theoretically, but also with the observed specific heats of these salts at temperatures in the neighbourhood of the absolute zero, and the lowering of temperature produced by the adiabatic demagnetization of these salts at these low temperatures.

There is another special case, already referred to, in which though the orbital angular momentum of the paramagnetic ion is considerable, the ion may still behave as though it were zero, i.e. as though the ion were in the S-state. This will be the case under the following special conditions. Let us assume that the crystalline electric field is of the second type referred to in the Introduction, namely one too feeble to break the Russell-Saunders coupling but at the same time is strong enough to break the L-S coupling in the ion. If in the Stark pattern, the lowest level is a singlet and it is sufficiently removed from the other levels to be exclusively occupied by the ions, then it is the $(2S+1)$-fold spin degeneracy of this lowest level that will determine the magnetic properties of the ion at all ordinary temperatures, the contributions from the higher levels being negligible. The ion will thus behave as though it were in the S-state with a spin moment corresponding to S. This is the case for example, with the chromic salts, and to a less close approximation with the nickel salts.

On the other hand, when the orbital angular momentum of the ion is not completely quenched, as in the case considered just now, but

but is quenched partially, that is when the separation of the upper levels from the lowest level is not large in comparison with kT, then the remnants of the orbital angular momentum will play an important part in determining the magnetic properties of the ion. It will be not so much through their direct contribution to the susceptibility, as indirectly by the strong orientative influences which they exert on the spin moments through the spin-orbit coupling. This large influence of the orbital moment, may at first sight appear inconsistent with the statements usually made that in the salts of the iron group, the susceptibility corresponds to the spin-only value. This inconsistency is only apparent, because in the earlier theories, the susceptibility was fitted with a formula of the type $\chi = C/(T - \theta)$, which as we have pointed out, can always be done if the deviation from the Curie law is small, i.e., if $\theta \ll T$; in this expression the value of the constant C will correspond to the spin-only value. The influence of the orbital moment will be confined to determining the value of θ ; since θ was attributed, in the older theories, to some inner magnetic field of unknown origin, the effect of the orbital momentum was naturally overlooked.

But actually the influence of the orbital angular momentum of the ion on the susceptibility is all-important, since ultimately all the influence of the crystalline field — this influence as we have seen may be quite large — is exercised through it. It is through the orientative influences of the orbital moments on the spin moments, and to some extent also on account of the directional asymmetry of its direct contribution to the susceptibility of the crystal, that the crystal exhibits at all a magnetic anisotropy.

We shall now mention some of the striking aspects of the application of the crystal field theory, and illustrate each of these aspects by a typical example. We shall refer first to the interesting prediction made purely on the basis of the crystalline field theory by Krishnan and Mookherji (1936,37,38), regarding the directions of the principal magnetic axes of the crystal of copper sulphate pentahydrate, and the relative magnitudes of the susceptibilities along them. The crystal is triclinic, and its unit cell contains 2 molecules of $CuSO_4 5H_2O$. Each Cu^{++} ion in the crystal is found to be located at the centre of an octahedron of negatively charged oxygen atoms. The octahedron is not a regular one, but is that obtained by elongating symmetrically one of the diagonals of a regular octahedron. The electric field produced in the neighbourhood of the Cu^{++} ion in the centre by this distribution of negative charges will obviously have an axis of tetragonal symmetry. The effect of such a field will be to make the magnetic susceptibility of the ion along the tetragonal axis, say $K_{\parallel}$ per gram ion, differ considerably from the susceptibility along perpendicular directions, say $K_{\perp}$ per gram ion. From the fact that the tetragonal axis of the field is the long diagonal of the tetrahedron; one can further show that $K_{\parallel}$ should be greater than $K_{\perp}$. Since there are two such Cu^{++} ions in the unit cell, the directions of the three principal magnetic axes of the crystal can be immediately predicted: two of them should be the interior, and the exterior bisectors of the angle between the two tetragonal axes, and the third axis will naturally be perpendicular to these two. Denoting the acute angle between the two tetragonal axes by 2θ, the gram ionic susceptibilities of the crystal along the three magnetic axes as determined above will

will evidently be equal to $K_{\parallel} \cos^2\theta + K_{\perp} \sin^2\theta$, $K_{\parallel} \sin^2\theta + K_{\perp} \cos^2\theta$, and $K_{\perp}$ respectively. Actually in the crystal of $CuSO_4 5H_2O$, 2θ is found to be nearly a right angle. Hence besides predicting the directions of the three principal axes, one can further predict that the susceptibilities along the first two axes should be nearly equal, and less than along the third direction. All these predictions have been verified experimentally. The directions of the three axes as determined experimentally, and as calculated from the known distribution of the negative charges round the Cu^{++} ions, are given in the following Table, taken from the paper of Krishnan and Mookherji (1938). The angles given in the Table are the angles which the principal magnetic axes make with the a, b, c, axes of the crystal.

Table

Principal Magnetic Axes of $CuSO_4 5H_2O$.

a = 6.12 Å	$\alpha = 82^\circ 16'$
b = 10.7 "	$\beta = 107^\circ 26'$
c = 5.97 "	$\gamma = 102^\circ 40'$

Magnetic Axis (x<y<z)	Angles which the magnetic axes make with the crystallographic axes					
	a		b		c	
	Calculated	observed	calculated	observed	calculated	observed
x	154	155	64	68	51	50
y	66	66	85	86	42	42
z	80	85	27	22	103	100

The agreement is remarkable particularly since the crystal is triclinic and the magnetic axes are not thus directly related to

to the crystallographic axes. The susceptibilities along these directions have been found by Krishnan and Mookherji to conform nearly to $\chi_{\parallel} = 0.399/(T-2.0)$ and $\chi_{\perp} = 0.486/(T+1.8)$, thus verifying the approximate uniaxial magnetic symmetry also predicted from the structure of the crystal.

As a second example, we shall take the striking contrast observed by Krishnan and Mookherji (1937,38), between the magnetic properties of isomorphous salts of cobalt and nickel, and again between the properties of ordinary flesh coloured cobalt salts in which the Co^{++} is six-coordinated, and the blue coloured cobalt salts in which the ion is four-coordinated. Both the Co^{++} and Ni^{++} ions are in the F-state, the former with 7 electrons in the 3d shell and the latter with 8 electrons in it. For both the ions the Stark pattern will be the same, and in a cubic field will consist of 2 triplets and a singlet. The singlet level will be one of the extreme levels in the pattern and the other extreme level will of course be one of the triplets. For a given cubic field though the Stark patterns for Co^{++} and Ni^{++} are thus very similar, only there is this essential difference between them that out of the 7 and 8 electrons respectively in the 3d shells of these ions, five form a sub-group for which the resultant orbital moment is zero. This can be seen from the fact that Mn^{++} and Fe^{+++} ions, both of which contain five electrons each in the 3d shell, are in the S-state. Thus the observed orbital angular momenta of L = 2 for Co^{++} and Ni^{++} arise in one case from the two electrons and in the other from the three electrons that are present in the 3d shell in excess of the five that form an orbitally closed sub-group. That the orbital angular momentum is the same for both the ions arises from the circumstance that the number of these extra electrons in Co^{++} and Ni^{++},

and Ni^{++}, namely two and three are complementary, since five electrons will form again a sub-group with zero orbital angular momentum. In view of this complementary nature of the number of electrons in Co^{++} and Ni^{++}, the Stark patterns of the ions in a given cubic field though similar, will be inverted one with respect to the other. In other words, whereas the lowermost level in one of them will be the singlet, in the other it will be a triplet. This will naturally make an enormous difference in the magnetic properties. A singlet ground level separated widely from the upper levels, i.e., by energy intervals much greater than kT, will eliminate most of the effects of the orbital moments and the ion will thus behave as though it were in the S-state, with a moment corresponding to spin-only value; it should have very little magnetic anisotropy. On the other hand, with the triplet level as the ground state, the orbital contribution and the anisotropy of the crystal will be pronounced. Though a priori in a given field, such as exists for example, in the Tutton salts, in which the paramagnetic ion is surrounded by an octahedron of $6H_2O$ molecules, it does not seem possible to predict whether the singlet level should be lowermost in the Stark pattern of Co^{++} or in that of Ni^{++}, yet the observed contrast in the magnetic behaviours of the two salts should evidently be attributed to this inversion, and there is little doubt that it is in Ni^{++} the singlet level is lowermost, since it has a low anisotropy and its principal susceptibilities accord with the Curie law, as contrasted with the large anisotropies, large deviations from the Curie law, and large contributions from the orbital moment to the susceptibilities, observed in cobalt salts of the type considered.

We should refer here to another interesting result namely that

that the erectness or the inversion of the Stark pattern will be determined by the sign of D in the expression for the potential of an electron in the given cubic field. It is only when D is positive that the singlet level is lowermost in the pattern for Ni^{++}, and this is indeed the case, as we have mentioned earlier, when the field is due to an octahedral distribution of six equal negative charges, as in the Tutton salts, and in the ordinary hydrated sulphates, selenates etc. On the other hand, as has been shown by Gorter (1932), if the cubic field is due to a tetrahedral distribution of four equal negative charges, or a cubic distribution of eight, the sign of D becomes negative. Since the effect of a change in the sign of D is equivalent to an inversion of the Stark pattern, it follows that in a cubic field of positive D, i.e., in the six-coordinated salts, the singlet level will be lowermost in Ni^{++} and uppermost in Co^{++}, whereas in a field of negative D, i.e., in tetrahedrally four-coordinated or cubically eight-coordinated salts, the singlet pattern will be lowermost in Co^{++} and uppermost in Ni^{++}. Such a 4-coordination for example, is found in the blue double chlorides Cs_2CoCl_4 and Cs_3CoCl_5, in which, according to the X-ray analysis of their structures by Powell and Wells (1935), the Co^{++} ions are surrounded by 4 negatively charged chlorine atoms which occupy the corners of a tetrahedron. These crystals have been studied for their magnetic properties by Krishnan and his collaborators both at room and low temperatures and they find that these crystals have a low anisotropy, and their susceptibilities deviate much less from the spin-only value and from the Curie Law, than the 6-coordinated salts of cobalt.

This striking contrast in magnetic properties between the salts of cobalt and nickel in a given crystalline field, and the contrast

contrast between the the 6-coordinated and the 4-coordinated salts of cobalt, are difficult to explain on any other basis, and one of the striking achievements to the credit of the crystalline field theory.

Among the more recondite applications of the crystalline field theory may be mentioned the quantitative explanation of the temperature variations of the principal susceptibilities of praseodymium and neodymium sulphates among the rare earth salts, and of nickel and cobalt salts by Schlapp and Penney (1932). Postulating a crystalline field suitably large and asymmetric, and using the known values of the spin-orbit coupling in these ions deduced from the spectroscopic data, they have succeeded in explaining quantitatively the general features of the temperature variation.

Magnetic Measurements at Low Temperatures:

The main part of the apparatus is the cryostat, described by Krishnan, Mookherji and Bose (1939), for maintaining the temperature of the crystal constant at any desired value. It is a cylindrical double-walled round bottomed vessel, closed at both ends, and made of thin sheet of copper. The cryostatic chamber contains a large number of thin copper discs with their planes at right angles to the axis of the cylinder. The discs are perforated by small holes and they are so arranged that the holes in the consecutive discs are not in a line so that when the cold air from the refrigeration chamber is passed through the cryostat, there is uniformity of temperature. The cryostat is kept covered by felt, and is housed inside a long cylindrical Dewar vessel, which is kept in between the large flat pole-pieces of the electromagnet.

The temperature control of the cryostat is made automatically. Three holes are bored in the lid of the cryostatic chamber. One of them serves as the neck of the constant volume air thermometer, a pentane thermometer is inserted in the second hole and through the third cold air from the liquid air chamber is delivered to the cryostat by a double-walled tube, the space between the two walls having been evacuated. The constant volume air thermometer is connected to U tube containing mercury. Two electrodes of tungsten are fused through the glass tube of one of the limbs of the tube, so that one electrode is always under mercury and the other is just at the mercury level. The two electrodes are connected with a sensitive relay that controls an air-pump. The current operating the relay is made or broken according as there is contact between the upper electrode and mercury or not. A glass tap is provided between the

the manometer and the air thermometer, and is used to adjust pressure inside and thence the level of mercury in the manometer. When the temperature is to be lowered, the tap is opened to the atmosphere so that there is contact between the upper electrode and the mercury level. The relay circuit is now completed and the pump is in action, cold air from the liquid air chamber is sucked inside the cryostat. The tap is closed when the cryostat has cooled down to the desired temperature. If there is any further cooling, the air in the thermometer will contract and the circuit will be broken. On the other hand any rise of temperature inside the cryostat will make the air in the constant volume thermometer expand and push up the mercury level, thus making again the electrical circuit working the suction pump. This make and break of the circuit go on alternately in rapid succession and the temperature of the cryostat remains steady to within $0.1^{\circ}C$. The range through which the cryostat can be used is from room temperature to about $80^{\circ}K$.

Measurement of Temperature

A copper-constantan thermocouple is used for the measurement of the temperature of the cryostat. One end of the thermocouple is put inside a Pyrex glass tube upto the bottom of the crystal chamber, the other end being kept in broken ice contained in a thermo-flask. The thermocouple was calibrated with reference to a number of fixed points and a table is made for ready reference. The potential difference is measured by means of a Leeds Northrup standard potentiometer and the corresponding

corresponding temperature is found out from the table.

The approximate temperature inside the cryostatic chamber is read on a pentane thermometer inserted in the chamber.

Measurement of Anisotropy.

A thin-walled cylindrical copper tube, with its lower end closed, is placed vertically and centrally inside the cryostatic chamber, and as deeply inside it as possible. Through the open end of this copper tube is fitted a long glass tube, the junction being made air-tight by means of soft wax. A graduated torsion head is placed ~~is placed~~ at the upper end of the glass tube and a collar of rubber tubing of large diameter is fitted at the joint. The torsion head is of a special type. The plane of the graduated disc of the torsion head is vertical, so that the scale can be read easily, and the torsion is converted with the help of suitable tooth-wheels into a rotation of the vertical pin of the suspension system, over exactly tha same angle as the rotation of the graduated disc.

The suspending system is made of two parts; the upper part, attached to the torsion pin, being a thin fibre of quartz, and the lower being of stout glass carrying at its lower end the crystal and thus forming with it a rigid system. The purpose of making the suspension in two parts as described above is to keep the entire length of the quartz fibre outside the cryostatic chamber and thus keep the torsional constant of the suspended system independent of the temperature of the system. The crystal is suspended with any desired direction vertical, in the centre of a homogeneous, horizontal magnetic field. A small glass pointer attached horizontally to the upper end of the glass fibre serves

serves for observing the rotatary movements of the crystal, since the crystal itself is not directly observable.

Measurements on the anisotropy were made from room temperature down to the lowest temperature obtainable with liquid air, namely 80°K, at intervals of about 15 to 20 degrees. The general principle of the method adopted in these measurements was to compare the magnitude of the maximum couple acting on the crystal, at the temperature of measurement with the magnitude of the couple at room temperature. Since the field is uniform, and the intensity of the field and the torsional constant of the suspension system are both independent of the temperature of measurement, the couples observed at different temperatures are directly proportional to the anisotropies at these temperatures, i.e. proportional to the values of $\chi_I - \chi_{II}$ at these temperatures and since the value of $\chi_I - \chi_{II}$ at room temperature is already known, the values at the lower temperatures also become known. In practice the values obtained at different temperatures were plotted against temperature and the value of $\chi_I - \chi_{II}$ at any desired temperature can be directly read from the graph.

Measurement of Principal Susceptibilities

For the measurement of the principal susceptibilities, it would be sufficient, since we know already the anisotropies at different temperatures, to measure the absolute value of the susceptibility along any one direction in the crystal. The direction selected for this measurement was the direction that set itself along the magnetic field when the crystal was suspended, from one arm of a delicate quartz torsion balance, by a thin quartz fibre. Knowing the direction of suspension of the crystal the direction that

direction that would set itself along the field is known from the previous knowledge of the anisotropy of the crystal. The crystal is suspended at such a height that it will lie in a region of magnetic field where the field is strong and horizontal and its gradient is vertical. Since the thermal coefficient of the crystal is small, it will occupy at all temperatures practically the same region of the magnetic field and hence the value of $H\frac{\partial H}{\partial y}$, (where y is the vertical direction) on which the pull on the crystal depends, may be taken to be independent of temperature. The pull at the temperature of measurement is compared with the pull at room temperature (for which the absolute susceptibility of the crystal along the direction concerned is already known). Thus the value of the absolute susceptibility along this direction at different temperatures is obtained.

In calculating the susceptibilities at different temperatures for a given suspension from the observed pulls at these temperatures, the following corrections have to be applied.

If

F_t is the force at any temperature t^o ,

F_θ is the force at some standard temperature (room temp.) θ ,

χ_t is the susceptibility at t^o ,

χ_θ is the susceptibility at θ ,

$k_{a\theta}$ is the volume susceptibility of air at θ ,

k_θ is the volume susceptibility of the crystal at θ ,

γ is the temperature coefficient of air at t^o,

then the ratio F_t/F_θ can be put in the following elegant form,

$$\frac{F_t}{F_\theta} = \frac{\chi_t}{\chi_\theta}\left\{1 + \frac{k_{a\theta}}{k_\theta}\left(1-\gamma\theta\right)\left(1-\frac{\theta}{t}\right)\right\}.$$

The absolute susceptibilities have all been corrected for

for the diamagnetism of the crystal.

The effective Bohr magneton numbers p_1, p_2 and p_3 along the three principal axes of the crystal, are calculated from the relations

$$\chi_i = \frac{Np_i^2 \beta^2}{3kT}, \qquad i = 1, 2, 3.$$

where β is the Bohr magneton and is equal to $eh/4\pi mc$.

If the susceptibility concerned obeys the Curie law, then the corresponding effective magneton number will be independent of temperature. Hence any deviations of the values of p_1, p_2 and p_3 for the three principal axes of the crystal give a measure of the deviations of the corresponding susceptibilities from Curie law.

Notation Adopted

In the crystals that have an axis of summetry, viz., tetragonal, trigonal and hexagonal crystals, the gram molecular susceptibilities along and perpendicular to the symmetry axis are denoted by $\chi_{\parallel}$ and $\chi_{\perp}$ respectively. In crystals belonging to the orthorhombic class the principal magnetic axes are the crystallographic axes themselves and the gram molecular susceptibilities along these axes are denoted by χ_a, χ_b and χ_c respectively. In the monoclinic system of crystals two of the principal magnetic axes are in the (010)-plane and the susceptibilities along them are denoted by χ_1 and χ_2, the former being the greater of the two. The third susceptibility is along the b-axis and is denoted by χ_3. The χ_1-axis is inclined at an angle ψ to the c-axis and at $(\beta - \psi)$ to the a-axis, β being the obtuse angle between a and c. The (001)-faces of most of the crystals are well-developed, xxxxxxxxx, and hence the inclination θ of the χ_2-axis to this face can in most cases be directly measured. The positive direc-

direction of θ is given by the relation $\beta = \psi + \theta + \pi/2$. When the crystal is suspended in a uniform magnetic fided with b-axis vertical, the inclination of (001)-face to the normal to the field gives θ.

The values of the susceptibilities and anisotropies are to be multiplied by 10^{-6} and expressed in the c.g.s.e.m.u.

The room temperature data for the principal susceptibilities of the crystals, on which the determinations at low temperatures have been based, have in general been taken from the Philosophical Transactions of the Royal Society, 232 (1933), 235 (1936), 237 (1938) and 238 (1939). The room temperature data for $Cu(CH_3COO)_2H_2O$ have been supplied by Mr A. Mookherji.

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Values of Anisotropies at Different Temperatures — Table I

$NiSO_4 7H_2O$

λ is the constant of the spin-orbit coupling.

Temp. °K	$\chi_a - \chi_b$	observed λ	calculated $\lambda = -360 cm^{-1}$	$\chi_a - \chi_c$	observed λ	calculated $\lambda = -370 cm^{-1}$
303	169	1.000	1.000	49	1.000	1.000
280	185	1.095	1.094	53.6	1.094	1.096
260	201	1.190	1.193	58.5	1.194	1.195
240	221	1.308	1.313	64.5	1.316	1.316
220	246	1.456	1.462	71.6	1.461	1.468
200	278	1.645	1.648	81.3	1.659	1.654
180	319	1.888	1.889	93.4	1.905	1.900
160	375	2.219	2.213	110	2.245	2.229
140	451	2.669	2.661	132	2.695	2.685
120	560	3.313	3.316	165	3.367	3.346
100	740	4.379	4.349	216	4.409	4.398
90	864	5.112	5.111	254	5.183	5.171
80	1015	6.006	6.114	303	6.183	6.223

$NiRb_2(SO_4)_2 6H_2O$

Temp. °K	$\chi_1 - \chi_2$	observed λ	calculated $\lambda = -370 cm^{-1}$	$\chi_1 - \chi_3$	observed λ	calculated $\lambda = -350 cm^{-1}$
303	142	1.000	1.000	134	1.000	1.000
280	156	1.096	1.096	146	1.090	1.092
260	170	1.197	1.195	159	1.187	1.191
240	188	1.324	1.316	175	1.306	1.310
220	208	1.465	1.468	195	1.455	1.456
200	236	1.662	1.654	221	1.649	1.638
180	270	1.901	1.900	251	1.874	1.878
160	318	2.240	2.229	293	2.187	2.197
140	383	2.698	2.685	353	2.634	2.638
120	475	3.345	3.346	440	3.284	3.285
100	624	4.394	4.398	577	4.306	4.300
90	735	5.176	5.171	676	5.044	5.051
80	882	6.212	6.223	798	5.955	6.066

Table I

$NiRb_2(SeO_4)_2.6H_2O$

Temp.°K	$\chi_1 - \chi_2$	observed λ	calculated $\lambda = -370\ cm^{-1}$	$\chi_1 - \chi_3$	observed λ	calculated $\lambda = -350\ cm^{-1}$
303	156	1.000	1.000	143	1.000	1.000
280	171	1.096	1.096	156	1.091	1.092
260	187	1.199	1.195	171	1.196	1.191
240	206	1.320	1.316	188	1.315	1.310
220	229	1.468	1.468	209	1.462	1.456
200	259	1.662	1.654	237	1.658	1.638
180	298	1.910	1.900	270	1.888	1.878
160	349	2.238	2.229	315	2.203	2.197
140	421	2.699	2.685	379	2.651	2.638
120	521	3.339	3.346	472	3.301	3.285
100	688	4.411	4.398	619	4.329	4.300
90	803	5.147	5.171	723	5.056	5.051
80	961	6.160	6.223	860	6.014	6.066

$NiCs_2(SO_4)_2.6H_2O$

Temp.°K	$\chi_1 - \chi_2$	observed λ	calculated $\lambda = -340\ cm^{-1}$	$\chi_1 - \chi_3$	observed λ	calculated $\lambda = -330 cm^{-1}$
303	132	1.000	1.000	124	1.000	1.000
280	144	1.091	1.091	135	1.088	1.091
260	156	1.187	1.189	147	1.185	1.187
240	172	1.303	1.305	162	1.306	1.303
220	190	1.440	1.448	179	1.444	1.445
200	215	1.629	1.629	202	1.629	1.625
180	245	1.857	1.863	230	1.855	1.857
160	287	2.174	2.174	268	2.161	2.166
140	344	2.606	2.605	322	2.597	2.594
120	428	3.242	3.237	401	3.233	3.220
100	560	4.242	4.227	522	4.210	4.199
90	656	4.969	4.956	612	4.937	4.922
80	784	5.939	5.944	734	5.920	5.900

$NiTl_2(SO_4)_2.6H_2O$

Temp.°K	θ	$\chi_1 - \chi_2$	observed λ	calculated $\lambda = -335 cm^{-1}$	$\chi_1 - \chi_3$	observed λ	calculated $\lambda = -340 cm^{-1}$
303	27°.0	111.5	1.000	1.000	106	1.000	1.000
280	26°.9	122	1.094	1.091	116	1.094	1.091
260	26°.6	132	1.184	1.188	125	1.180	1.189
240	26°.3	145	1.301	1.305	138	1.302	1.306
220	26°.0	161	1.444	1.448	153	1.443	1.452
200	25°.7	181	1.624	1.629	173	1.632	1.634
180	25°.6	207	1.857	1.863	198	1.868	1.868
160	25°.5	242	2.171	2.174	231	2.179	2.182
140	25°.3	290	2.601	2.605	277	2.613	2.617
120	"	362	3.247	3.237	347	3.273	3.253
100	"	473	4.243	4.227	451	4.255	4.252
90	"	553	4.961	4.956	529	4.991	4.987
80	"	662	5.939	5.944	633	5.971	5.985

Table I

$NiTl_2(SeO_4)_2.6H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	observed λ	calculated λ = -360cm^{-1}	$\chi_1-\chi_3$	observed λ	calculated λ = -350cm^{-1}
303	32.7	121	1.000	1.000	114.5	1.000	1.000
280	"	132	1.091	1.094	125	1.091	1.092
260	"	144	1.199	1.193	136	1.188	1.191
240	"	159	1.314	1.313	150	1.310	1.310
220	"	177	1.463	1.462	167	1.458	1.456
200	"	201	1.662	1.648	188	1.643	1.642
180	"	230	1.905	1.889	215	1,878	1.878
160	33.3	267	2.207	2.213	251	2.193	2.197
140	34.0	324	2.677	2.661	302	2.637	2.638
120	34.7	401 (404)	3.313	3.316	376	3.284	3.285
100	35.4	526	4.349	4.349	491	4.288	4.300
90	35.7	620	5.124	5.111	576	5.030	5.051
80	"	746	6.164	6.144	690	6.026	6.066

$Ni(NH_4)_2.SO_4SeO_46H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	observed λ	calculated λ = -360 cm^{-1}	$\chi_1-\chi_3$	observed λ	calculated λ = -315 cm^{-1}
303	39.2	129	1.000	1.000	114	1.000	1.000
280	40.3	141	1.093	1.094	124	1.087	1.090
260	41.2	154	1.194	1.193	134	1.176	1.184
240	42.1	169	1.310	1.313	147	1.289	1.298
220	43.0	189	1.465	1.462	163	1.430	1.438
200	43.7	214	1.659	1.648	185	1.623	1.614
180	44.4	244	1.891	1.889	210	1.844	1.842
160	45.2	285	2.209	2.213	245	2.149	2.144
140	45.8	344	2.666	2.661	293	2.570	2.563
120	46.4	428	3.318	3.316	363	3.183	3.172
100	"	563	4.364	4.349	473	4.150	4.127
90	"	654	5.069	5.111	550	4.825	4.828
80	"	790	6.124	6.144	660	5.789	5.776

$CoSO_4.7H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	$\chi_1-\chi_3$	
303	69.1	1928	1100	
280	"	2296	1261	
260	"	2716	1485	
240	"	3252	1775	
220	"	3925	2137	
200	"	4733	2590	
180	"	5784	3195	
160	"	7145	4005	
140	"	9026	5136	
120	"	12000	6901	
100	"	16740	9977	
90	"	19510	11714	
80	"	21960	13384	

Table I

$CoSeO_4.6H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	$\chi_1-\chi_3$
299	-52.3	4030	2415
280	"	4407	2638
260	"	4916	2909
240	"	5580	3327
220	"	6431	3827
200	"	7494	4446
180	"	8857	5239
160	"	10670	6289
140	"	13170	7757
120	"	16880	9880
100	"	22370	13077
90	"	25570	14950
80	"	29450	17210

$CoRb_2(SO_4)_2.6H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	$\chi_1-\chi_3$
299	40.5	2400	1246
280	"	2751	1404
260	"	3159	1610
240	"	3667	1867
220	"	4302	2189
200	"	5121	2603
180	"	6165	3138
160	"	7447	3787
140	"	9126	4631
120	"	11210	5670
100	"	14150	7154
90	"	16130	8172
80	"	18760	9550

$CoRb_2(SeO_4)_2.6H_2O$

Temp.°K	θ	$\chi_1-\chi_2$	$\chi_1-\chi_3$
299	35.2	2900	2238
280	35.0	3296	2573
260	34.7	3776	2982
240	34.5	4393	3486
220	34.4	5126	4121
200	34.2	6063	4906
180	34.0	7213	5860
160	33.7	8750	7115
140	33.3	10760	8719
120	33.2	13510	10850
100	33.2	17170	13630
90	"	19400	15270
80	"	21930	16990

Table II

$CoCs_2(SO_4)_2.6H_2O$

Temp.°K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
299	62°	2600	512
280		2952	581
260	no change	3393	666
240		3931	764
220		4593	881
200		5428	1021
180		6449	1200
160		7752	1408
140		9497	1706
120		11900	2242
100		15060	3018
90		16900	3420
80		18970	3950

$CoTl_2(SO_4)_2.6H_2O.$

Temp.°K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
299	54.2	2010	931
280	54.0	2299	1069
260	53.7	2643	1243
240	53.5	3083	1460
220	53.2	3607	1725
200	52.7	4268	2085
180	52.2	5065	2526
160	51.7	6112	3080
140	51.2	7571	3901
120	50.9	9526	4920
100	50.5	12030	6247
90	50.3	13600	7078
80	50.2	15470	8030

Table I

$FeSO_4.7H_2O$

Temp.°K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
303	-7.5	1289	1276
280		1409	1394
260		1552	1538
240	no	1740	1732
220	change	1970	1978
200		2268	2289
180		2638	2679
160		3130	3180
140		3806	3850
120		4805	4837
100		6372	6460
90		7432	7702
80		8670	9498

$CuSO_4.Rb_2SO_4 6H_2O$

Temp.°K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
299	86°	350	100
280	"	372	106
260	"	399	114
240	"	432	127
220	"	470	139
200	"	514	154
180	"	565	170
160	"	629	190
140	87°	713	214
120	"	822	248
100	"	975	288
90	"	1065	308
80	"	1163	330

$CuSO_4.Tl_2SO_4.6H_2O$

Temp.°K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
299	88.2	283	71
280		296	74
260		316	79
240		342	87
220		372	97
200	no	411	111
180	change	456	127
160		515	147
140		584	167
120		673	193
100		796	227
90		872	246
80		961	269

Table I

$2NH_4ClCuCl_2 2H_2O$

Temp. °K	$\chi_{\perp} - \chi_{\parallel}$	Temp. °K	$\chi_{\perp} - \chi_{\parallel}$
304.1	260	160	470
280	283	140	537
260	301	120	627
240	324	100	747
220	351	90	823
180 (200)	421 (330)	80	904

$Cu(CH_3COO)_2 . H_2O$

Temp. °K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
305.1	3.3°	198	133
280		201	135
260	"	201	136
240		200.5	135
220	"	197	133
200		192	130
180	"	183	123
160		170	114
140	"	150	100
120		124	82
100	"	97	65
80		75	45

$K_3Fe(CN)_6$

Temp. °K	θ	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$
303.1	89°	451	123
290		492	139
280		527	153
270		565	169
260		604	183
250	"	653	199
240		704	219
230		765	243
220		828	263
210	"	900	287
200		979	310
190		1070	338
180		1167	369
170	"	1281	398
160		1413	434
150		1564	467
140		1737	500
130	"	1965	539
120		2242	564
110		2558	550
100		2914	504
90		3309	420
80		3739	357

The Ratios of Anisotropies at Different Temperatures - Table II

$KMnO_4$

The anisotropies at room and other temperatures are denoted by $\Delta\chi$ and $\Delta\chi'$.

Temp.°K	Along $\chi_a - \chi_b$	Along $\chi_a - \chi_c$
	$\Delta\chi'/\Delta\chi$	$\Delta\chi'/\Delta\chi$
303	1.00	1.00
280	1.16	1.04
260	1.29	1.08
240	1.43	1.11
220	1.56	1.15
200	1.69	1.19
180	1.81	1.23
160	1.94	1.28
140	2.06	1.34
120	2.18	1.40
100	2.29	1.49
80	2.40	1.63

Susceptibilities and Magnetic Moments at Different Temperatures - Table III.

$Mn(NH_4)_2(SO_4)_2 6H_2O$

Diamagnetic correction - 203

Temp.°K	χ_1	p_1^2
303.9	14000	34.30
242.8	17680	34.61
204.7	20800	34.33
79.7	53340	34.28

$K_3Fe(C_2O_4)_3 3H_2O$

Diamagnetic correction - 192

Temp.°K	χ_1	p_1^2
296.9	14520	34.75
248.9	17350	34.83
198.9	21640	34.69
146.8	29240	34.60
108.2	39790	34.70
96.9	44380	34.66
81.1	53040	34.67

Table III

$Fe[(CH_3CO)_2.CH]_3$

Diamagnetic correction – 164.

Temp. °K	χ_a	p_a^2
302.4	14440	35.21
219.8	19890	35.24
152.8	28730	35.37
83.2	52400	35.14

$(NH_4)_3Cr(C_2O_4)_3.3H_2O$

Diamagnetic correction – 203

Temp. °K	χ_3	p_3^2
303.1	5652	13.81
237.6	7113	13.62
176.8	9371	13.36
140.1	11930	13.16
104.5	15450	13.01
82.9	19180	12.81

$Cr[(CH_3CO)_2CH]_3$

Diamagnetic correction – 164.

Temp. °K	χ_1	p_1^2
302.4	5070	12.37
208.8	7195	12.12
146.4	9916	11.70
88.6	15590	11.14

$NiSO_4.6H_2O$

Diamagnetic correction – 124.

Temp. K	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$	$p_\perp^2$	$p_\parallel^2$	$\bar{p}^2$
303.1	4195	4086	4159	10.24	9.98	10.15
199.4	6337	6157	6277	10.19	9.90	10.09
143.6	8689	8414	8597	10.06	9.74	9.95
111.3	11090	10710	10970	9.95	9.61	9.84
80.6	15290	14660	15080	9.94	9.52	9.80

Table III

$NiSeO_4.6H_2O$

Diamagnetic correction – 132.

Temp.°K	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$	$p_\perp^2$	$p_\parallel^2$	$\bar{p}^2$
298.6	4422	4332	4392	10.67	10.45	10.60
211.8	6216	6082	6171	10.61	10.39	10.54
168.4	7793	7613	7733	10.58	10.34	10.50
110.7	11660	11350	11560	10.40	10.13	10.31
82.1	15580	15030	15400	10.30	9.95	10.18

$NiSO_4.7H_2O$

Diamagnetic correction – 136.

Temp.°K	χ_a	χ_b	χ_c	$\bar{\chi}$	p_a^2	p_b^2	p_c^2	$\bar{p}^2$
304.4	4235	4067	4186	4163	10.40	9.98	10.28	10.22
261.9	4901	4701	4843	4815	10.35	9.93	10.22	10.17
234.4	5468	5242	5402	5371	10.33	9.90	10.21	10.15
189.0	6736	6435	6648	6606	10.27	9.80	10.13	10.07
137.3	9169	8707	9030	8969	10.15	9.64	10.00	9.93
102.3	12190	11480	11970	11800	10.05	9.47	9.88	9.80
78.1	15840	14790	15510	15380	9.97	9.31	9.77	9.68

$NiRb_2(SO_4)_2.6H_2O$

Diamagnetic correction - 213.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
299.9	3473	4229	4237	4280	10.57	10.22	10.24	10.34
229.2	5692	5493	5508	5564	10.52	10.15	10.17	10.28
148.7	8683	8324	8353	8453	10.41	9.98	10.01	10.13
87.1	14470	13700	13770	13980	10.16	9.62	9.67	9.82

$NiRb_2(SeO_4)_2.6H_2O$

Diamagnetic correction – 229.

Temp.°K	χ_1	χ_2	χ_2	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
295.1	4539	4379	4392	4437	10.80	10.42	10.45	10.56
191.1	6986	6710	6734	6810	10.76	10.34	10.38	10.49
136.0	9728	9294	9330	9451	10.67	10.19	10.23	10.36
90.9	14260	13470	13550	13760	10.45	9.87	9.93	10.08

9'87

Table III

$NiCs_2(SO_4)_2.6H_2O$

Diamagnetic correction – 241.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
295.1	4461	4325	4332	4373	10.61	10.29	10.30	10.40
243.4	5405	5237	5247	5296	10.60	10.28	10.29	10.39
159.2	8144	7853	7868	7955	10.45	10.08	10.09	10.21
113.0	11380	10914	10944	11080	10.37	9.94	9.97	10.09
83.6	15280	14540	14590	14800	10.30	9.80	9.83	9.98

$NiTl_2(SO_4)_2.6H_2O$

Diamagnetic correction – 251.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
298.8	4381	4267	4273	4307	10.55	10.28	10.29	10.37
213.4	6103	5935	5944	5994	10.50	10.21	10.23	10.31
152.6	8492	8230	8242	8322	10.45	10.13	10.14	10.24
79.9	15980	15340	15360	15560	10.29	9.88	9.90	10.03

$NiTl_2(SeO_4)_26H_2O$ Diam. Correction – 267.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
297.3	4467	4343	4350	4387	10.70	10.41	10.42	10.51
214.1	6193	6010	6019	6074	10.69	10.38	10.39	10.49
145.5	9001	8694	8712	8802	10.55	10.20	10.22	10.32
83.4	15390	14690	14750	14940	10.35	9.88	9.92	10.05

$Ni(NH_4)_2SO_4SeO_4.6H_2O$

Diamagnetic correction – 210.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
305.1	4390	4262	4275	4309	10.80	10.48	10.52	10.60
225.7	5904	5722	5747	5791	10.74	10.41	10.46	10.54
138.6	9429	9077	9131	9212	10.54	10.14	10.21	10.30
85.3	14980	14290	14390	14550	10.30	9.83	9.90	10.01

Table III

$CoSO_4.7H_2O$

Diamagnetic correction – 136.

Temp. °K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
303.7	10300	8376	9196	9290	25.23	20.52	22.53	22.76
247.5	12560	9556	10970	11030	25.06	19.06	21.89	22.00
188.3	16120	10820	13190	13380	24.46	16.43	20.02	20.30
135.1	22470	12770	16850	17360	24.42	13.91	18.35	18.93
101.3	30260	14060	20660	21990	24.71	11.48	16.88	17.69
78.7	38810	16510	25210	26840	24.62	10.47	16.00	17.03

$CoSeO_4.6H_2O$

Diamagnetic correction – 132.

Temp. °K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
298.6	11440	7360	8990	9263	27.54	17.71	21.64	22.30
255.0	13310	8260	10290	10620	27.36	16.98	21.15	21.83
157.1	21290	10210	14760	15420	26.97	12.93	18.69	19.53
121.0	27480	10880	17700	18680	26.81	10.61	17.27	18.23
100.1	32280	10200	19320	20600	26.06	8.23	15.60	16.63
79.8	39020	9520	21630	23390	25.11	6.12	13.92	15.05

$CoRb_2(SO_4)_2.6H_2O$

Diamagnetic correction – 213.

Temp. °K	χ_1	χ_2	χ_3	$\bar{\chi}$.	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
297.7	11250	8790	10000	10010	27.01	21.11	24.00	24.04
198.4	16500	11290	13850	13880	26.38	18.05	22.15	22.19
146.3	22120	13720	17810	17880	26.10	16.19	21.01	21.10
84.5	36330	19100	27500	27840	24.75	13.01	18.74	18.83

Table III

$CoRb_2(SeO_4)_2.6H_2O$

Diamagnetic correction – 229.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
295.6	12000	9050	9630	10300	28.61	21.57	22.94	24.37
181.3	19220	12120	13420	14920	28.09	17.72	19.62	21.81
133.7	25780	14280	16410	18820	27.80	15.39	17.69	20.29
88.1	38060	18310	22560	26310	27.04	13.01	16.03	18.69

$CoCs_2(SO_4)_2.6H_2O$

Diamagnetic correction – 241.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
294.8	11420	8740	10900	10350	27.14	20.77	25.99	24.60
236.4	14150	10150	13370	12560	26.96	19.34	25.48	23.93
193.7	17180	11430	16080	14900	26.83	17.85	25.12	23.27
147.4	22170	13270	20550	18660	26.35	15.77	24.42	22.18
103.0	30640	16140	27820	24870	25.45	13.41	23.10	20.65
80.8	38230	19430	34310	30660	24.90	12.66	22.35	19.97

$CoTl_2(SO_4)_2.6H_2O$

Diamagnetic correction – 251.

Temp. K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
298.8	10770	8740	9830	9780	25.94	21.06	23.68	23.56
239.7	13200	10130	11720	11680	25.52	19.58	22.65	22.58
185.7	16840	11960	14400	14400	25.22	17.91	21.56	21.56
148.7	20890	13970	17330	17400	25.11	16.75	20.78	20.87
122.8	25020	15920	20330	20420	24.77	15.76	20.12	20.22
101.2	29410	17680	23310	23470	23.99	14.43	19.02	19.15
79.9	36610	20910	28520	28680	23.58	13.47	18.37	18.47

Table III

$FeSO_4.7H_2O$

Diamagnetic correction - 136.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
303.1	11810	10520	10540	10960	28.85	25.69	25.74	26.76
241.9	14690	12980	12990	13550	28.63	25.31	25.32	26.42
186.3	18610	16100	16060	16920	27.95	24.17	24.12	25.41
139.6	24430	20580	20520	21840	27.49	23.16	23.09	24.58
107.4	31070	25400	25320	27270	26.90	21.99	21.92	23.60
82.0	40380	32030	31330	34580	26.69	21.17	20.84	22.90

$CuRb_2(SO_4)_2.6H_2O$

Diamagnetic correction - 213.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
298.9	1663	1313	1563	1513	4.006	3.163	3.765	3.645
257.7	1943	1539	1826	1769	4.036	3.190	3.793	3.673
146.3	3292	2606	3086	2995	3.884	3.075	3.641	3.533
87.4	5556	4468	5242	5089	3.915	3.148	3.693	3.583
84.4	5725	4607	5404	5245	3.895	3.134	3.676	3.568

$CuTl_2(SO_4)_2.6H_2O$

Diamagnetic correction - 251

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
302.1	1691	1411	1621	1574	4.119	3.436	3.949	3.835
207.2	2415	2021	2310	2249	4.034	3.376	3.859	3.756
97.6	5027	4209	4797	4678	3.956	3.311	3.756	3.676
85.3	5793	4877	5541	5404	3.983	3.353	3.811	3.716

Table III

$2NH_4Cl, CuCl_2, 2H_2O$

Diamagnetic correction: – 163.

Temp.°K	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$	$p^2_\perp$	$p^2_\parallel$	$\bar{p}^2$
290.1	1624	1352	1533	3.796	3.162	3.585
227.0	2049	1711	1936	3.748	3.129	3.542
164.0	2726	2265	2572	3.604	2.995	3.401
114.9	3771	3102	3552	3.493	2.887	3.291
85.2	4882	4002	4589	3.353	2.748	3.151

$Cu(CH_3COO)_2 \cdot H_2O$

When a-axis is made vertical, b-axis sets perpendicular to the field.

Volume susceptibility = 7.355, measured along the b-axis, at 32.5°C

χ_1 = 881, χ_2 = 683 and χ_3 = 749 at 32°C.

Diamagnetic correction: – 87.

Temp.°K	χ_1	χ_2	χ_3	$\bar{\chi}$	p^2_1	p^2_2	p^2_3	$\bar{p}^2$
304.4	968	770	835	858	2.385	1.898	2.058	2.114
252.3	996	795	860	884	2.026	1.617	1.749	1.797
219.9	963	766	830	853	1.707	1.326	1.472	1.502
190.7	914	726	787	809	1.406	1.116	1.210	1.244
144.3	772	617	669	686	0.898	0.718	0.778	0.798
108.1	585	477	512	525	0.521	0.416	0.446	0.461
82.8	420	342	372	378	0.280	0.228	0.248	0.252

$K_3Fe(CN)_6$

Diamagnetic correction = -132

Temp. °K	χ_1	χ_2	χ_3	$\bar{\chi}$	p_1^2	p_2^2	p_3^2	$\bar{p}^2$
304.9	2252	1812	2132	2065	5.537	4.454	5.241	5.077
254.9	2646	2011	2454	2370	5.438	4.132	5.042	4.871
193.9	3359	2334	3031	2908	5.250	3.648	4.736	4.546
156.9	3973	2498	3531	3334	5.023	3.159	4.465	4.216
123.6	4890	2710	4332	3977	4.871	2.701	4.315	3.962
81.1	6891	3221	6528	5547	4.512	2.109	4.272	3.631

$K_3Fe(CN)_6$

p^2 values calculated from L. C. Jackson's experimental data.

Temp. °K	p_1^2	p_2^2	Temp. °K	p_3^2
290	5.998	5.067	290.6	5.662
273	5.946	5.282	197.4	5.488
200	5.733	4.543	90.3	4.640
170	5.608	4.165	84.9	4.580
150	5.495	3.894	80.6	4.558
90	4.898	2.786	75.7	4.533
82	4.785	2.613		
75	4.690	2.452		

Discussion of the Results.

There are several interesting points that strike one on a critical examination of the experimental results tabulated in the foregoing pages. Before considering these points, we shall refer to some important results that are already well-known and are amply verified by the extensive data obtained in the present work. The following are some of them.

First, in the case of a paramagnetic ion whose ground state is an S-state, and has no orbital moment to be quenched by the crystalline electric fields, the splitting of the Stark-pattern will be extremely narrow, and hence paramagnetic crystals whose paramagnetism arises from such ions will have very little anisotropy, and secondly their susceptibilities will follow almost exactly the Curie law, and thirdly the effective magnetic moments of the ions in these crystals will be almost exactly $2\sqrt{s(s+1)}$ where s is the spin quantum number. Among the crystals studied here there are three belonging to this class, one a manganous salt and the other two organic salts of iron*; the manganous and ferric ions are both in the state $^6S_{5/2}$. It will be seen from the Tables that in all the three salts, the effective magneton number p is practically independent of temperature and agrees well with the theoretical value of $2\sqrt{5/2.7/2} = \sqrt{35}$. The anisotropies of all the three salts were found to be too feeble to be measurable with our arrangement, as was to be expected.

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* Ordinary ferric salts are not easy to obtain as good crystals, and hene the choice of two organic salts; they grow more easily as large crystals and are more stable.

Considering next the chromic salts, though the Cr^{+++} ion is in the F-state, namely $^4F_{3/2}$, it still behaves to a first approximation as though it were in the S-state, owing to the fact that the lowest level in the Stark-splitting is very far removed from the higher levels, and the lowest level has only the $(2s+1)$-fold degeneracy due to the spin moment, ~~—~~ s being 3/2. As will be seen, the p^2 values for the chromic salts differ only little from the spin-only value of 15, and its variation with temperature, is also small.

The magnetic properties of the nickel salts have been discussed theoretically by Schlapp and Penney (1932), on the basis of the crystal field theory. Denoting the potential due to the crystalline electric field in the neighbourhood of the paramagnetic ion, as usual, by $V = D(x^4+y^4+z^4) + Ax^2 + By^2 - (A+B)z^2$, they find first that in all the ordinary hydrated nickel salts for which the magnetic data are available, the observed magnetic susceptibilities can be explained satisfactorily on the assumption that the crystalline electric field is predominently cubic in its symmetry, with a small rhombic component superposed on it. In other words, the fourth power terms in the expression for the potential V decide the main features of the paramagnetism, and that the influence of the square terms is relatively less important. Secondly, the sign of the constant D defining the potential due to the cubic part of the field has to be assigned a positive sign. This will be the case if the distribution of the negatively charged atoms immediately surrounding the positively charged paramagnetic ion is such that there are six of them occupying the corners of an octahedron. If these six negative charges are all equal, and the octahedron a regular one, the field at the centre will be strictly cubic in symmetry, and will have no rhombic components. Any small deviation from such an ideal distri-

distribution will produce a small rhombic component, as required by observation. Now in all the paramagnetic nickel salts studied, and whose structures are known, the Ni^{++} ion is found to be surrounded by such an octahedron of negatively charged atoms, so that the crystalline fields in all such salts do satisfy the requirements of the theory, namely that the cubic field should predominate, that D should be positive, and that there should also be a small rhombic ~~rhombic~~ component.

Under the influence of such a field, the seven-fold orbital degeneracy corresponding to the $^3F_4$-state of Ni^{++} is found to split up under the cubic part of the field into a singlet, which will be the lowest, and two triplets, the separation of the latter two from the singlet being large, of the order of $10^4 cm^{-1}$. Under the rhombic field, the components of the two triplets will separate out, these latter separations being of the order of $10^2 cm^{-1}$, and thus smaller than the separations produced by the cubic parts. Each of the seven levels will retain all the $(2s+1)$-fold degeneracy, due to their spin moment s (s being equal to 1, since the ground state of Ni^{++} is a ^3F-state). With such a Stark pattern , i.e. with the lowermost level having a three-fold spin degeneracy, and the other levels being sufficiently removed from this level, the nickel ion will naturally behave to a first approximation as though it were in the S-state, like the Cr^{+++} ion.

But actually, owing to the spin orbit coupling in Ni^{++} being large, about 335 cm^{-1} as compared with 87 cm^{-1} for Cr^{+++}, the behaviour will not be so simple as in the latter ion; the orbital moment will exercise an appreciable influence on the magnetic susceptibilities, through its coupling with the spin. Thus though

though the deviation from the Curie Law may still be small, the deviation of the effective magneton number from the spin-only value of $\sqrt{8}$ will become considerable.

The principal magnetic susceptibilities of several Ni^{++} salts measured at room temperature have been utilized by Krishnan and Mookherji (1938) to calculate the crystalline fields in them. They find that not only the cubic part of the field, which is the predominent part, but also the rhombic part, is of nearly the same magnitude in all the nickel salts. This shows that the dispositions of the water molecules, which are the immediate neighbours of the Ni^{++} ion in all these salts, are nearly the same in all these salts.

More recently Krishnan, Mookherji and Bose (1939) have utilized the deviation from the spin-only value, and its variation with temperature which arises from the large value of the spin-orbit coupling λ, to calculate the spin-orbit coupling itself; i.e. to calculate the spectroscopic constant λ purely from the magnetic measurements. In this calculation it is assumed that the crystalline field remains practically independent of temperature, which is a reasonable assumption to make, in view of the low coefficient of thermal expansion in the solid state. The value of the spin-orbit coupling obtained in this manner agrees well with the spectroscopic value.

The extensive data obtained for a large number of nickel salts fully support these conclusions. Using these data and assuming the spectroscopic value of $\lambda = 335\ cm^{-1}$, we have calculated the crystal field constants α_1, α_2 and α_3 for the three principal axes of the crystalline field in the neighbourhood of the Ni^{++} ion,

ion, these axes being assumed to be the same as the principal magnetic axes of the crystal. The α's are related to the constants D, A and B of the crystalline field, and ultimately to the three principal susceptibilities by the relations

$$\alpha_1 + \alpha_2 + \alpha_3 = \frac{3(p^2-8)}{8(8\lambda-3kT)} \quad , \qquad \text{and}$$

$$\frac{\alpha_1 - \alpha_2}{\chi_1 - \chi_2} = \frac{\alpha_1 - \alpha_3}{\chi_1 - \chi_3} = \frac{3kT}{8N\beta^2(8\lambda - \frac{2\lambda^2}{kT} - 3kT)}$$

The values of $\alpha_1 - \alpha_2$, $\alpha_1 - \alpha_3$ and $\alpha_1 + \alpha_2 + \alpha_3$ thus calculated are entered in the following Tables.

Table IV

$NiSO_4.6H_2O$

Temp.°K	$(\alpha_{\parallel} - \alpha_{\perp})10^6$	$-(2\alpha_{\perp} + \alpha_{\parallel})10^6$
300	7.6	243
220	7.6	252
140	7.6	247
80	7.6	234

$NiSeO_4.6H_2O$

Temp.°K	$(\alpha_{\parallel} - \alpha_{\perp})10^6$	$-(2\alpha_{\perp} + \alpha_{\parallel})10^6$
300	6.2	295
220	6.2	305
140	6.2	303
80	6.2	287

$NiSO_4.7H_2O$

Temp.°K	$(\alpha_b - \alpha_a)10^6$	$(\alpha_c - \alpha_a)10^6$	$=(\alpha_a + \alpha_b + \alpha_c)10^6$
300	11.9	3.5	251
220	11.8	3.5	253
140	12.1	3.5	245
80	11.9	3.6	224

Table IV

$NiRb_2(SO_4)_2.6H_2O$

Temp. °K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	9.9	9.4	265
220	10.0	9.4	272
140	10.2	9.4	264
80	10.4	9.4	234

$NiRb_2(SeO_4)_2.6H_2O$

Temp. °K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	10.8	10.0	290
220	11.0	10.1	301
140	11.2	10.1	298
80	11.3	10.1	265

$NiCs_2(SO_4)_2.6H_2O$

Temp. °K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	9.2	8.7	272
220	9.2	8.6	279
140	9.2	8.6	273
80	9.2	8.6	261

$NiTl_2(SO_4)_2.6H_2O$

Temp. °K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	7.8	7.4	270
220	7.8	7.4	277
140	7.8	7.4	278
80	7.8	7.4	266

$NiTl_2(SeO_4)_2.6H_2O$

Temp. °K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	8.5	8.0	286
220	8.5	8.0	299
140	8.7	8.1	291
80	8.8	8.1	269

$Ni(NH_4)_2SO_4SeO_46H_2O$

Temp.°K	$(\alpha_2-\alpha_1)10^6$	$(\alpha_3-\alpha_1)10^6$	$-(\alpha_1+\alpha_2+\alpha_3)10^6$
300	9.0	7.9	295
220	9.1	7.9	301
140	9.2	7.9	290
80	9.2	7.9	261

It will be seen from the Tables that in all the crystals the α's are practically independent of temperature. Further, they are nearly of the same magnitude for not only Tutton salts, but for the other salts also.

Cobalt Salts.

We shall now proceed to consider the new results to which we referred at the beginning of this section.

The cobalt ion is also in the F-state, namely $^4F_{9/2}$, and since its orbital moment is the same as in Ni^{++}, one should expect the Stark patterns of the two ions to be similar as regards the removal of the orbital degeneracy by the crystalline field. This is so, but with this essential difference, namely that for a given field, the Stark pattern for Co^{++} is inverted with reference to the pattern for Ni^{++}. This arises from the circumstance that in Co^{++} the orbital moment L=3, is the resultant contribution from <u>two</u> of the electrons in the 3d shell, whereas in Ni^{++}it is the contribution from

three. That the orbital contributions in the two cases are the same is due to the fact that the resultant orbital moment due to five electrons in the second half of the 3d group is zero. Thus Co^{++} and Ni^{++} are in a sense complementary to one another. Owing to this circumstance the Stark pattern of Co^{++} will be inverted with respect to the pattern for Ni^{++}. As a result of this inversion, the lowest level of the Stark pattern, which in Ni^{++} is a singlet in the kind of cubic field considered, will now be a triplet. This makes the magnetic behaviour of Co^{++} much more complicated than that of Ni^{++}. In particular the contribution from the orbital moment L will be large, and hence the principal susceptibilities will be much more sensitive to the rhombic part of the field than in Ni^{++}. The theoretical calculations of the principal susceptibilities from the known field constants will be complicated, and will involve much labour, but the general trend of the results to be expected can be deduced on the basis of certain simplifying assumptions, for example that one of the rhombic field constants, say B, is zero, so that A becomes equal to $-C$, and the square terms in the expression for the potential V become simply $A(x^2 - z^2)$. Making such an assumption, Schlapp and Penney have made detailed calculations assuming the cubic field to be of the same intensity as in nickel salts, and also taking some typical values for the rhombic field, corresponding to A = 0, 40, 200 and lastly a very high value. We shall state here only their main conclusions. With a purely cubic field, the effective moments along the three principal axes are naturally identical, and they fall with the fall of temperature, slowly at first and rapidly at lower temperatures. Even with the smallest rhombic field considered by

by Schlapp and Penney, namely the one corresponding to say A = 40, the effective moments along the three principal directions become naturally different. It is found that all the three effective moments fall with fall of temperature, two of them in more or less the same way as with a purely cubic field, while the third, corresponding to the largest value of p, say p_1, decreases less slowly. With a further increase of the rhombic field from A = 40 to A = 200, the three principal moments are separated further, i.e., the anisotropy of the crystal is further enhanced. The temperature variations of the effective moments become now very small down to about 200°K; in other words the temperature variation of the principal susceptibilities obeys practically the Curie law down to about 200°K, with different Curie constants for the three directions. Below this temperature, the temperature variations of the effective moments become large. The maximum moment p_1 now <u>increases</u> with fall of temperature while the other two fall in the same manner as for the lower rhombic fields. For a given cubic field, and at all temperatures, the mean value of p^2 is the smaller the larger the magnitude of the rhombic field.

In the calculations of Schlapp and Penney the cubic field is assumed to be the same as in the nickel salts and its magnitude is easy to calculate in these latter salts from the magnetic data. This assumption of the same field as in nickel salts is justified, since practically in all the ionic compounds, in which the six negatively charged atoms surrounding the paramagnetic ion are the same — this is the case with the salts studied here, the surrounding atoms being oxygens of water molecules — the cubic part of the

the field will be nearly the same.

The proper choice of the rhombic part of the field that will fit with the observational data presents some difficulty. There are two striking effects of the rhombic field in cobalt salts which one can use as rough criterion for choosing the magnitude of this field. First the larger the rhombic part of the field, the lower will be the effective magnetic moment corresponding to the mean of the three principal susceptibilities. Secondly with the larger rhombic fields all the three susceptibilities vary slowly with temperature, and at low temperatures p_1^2 may actually rise with fall of temperature.

The second criterion, however, is not always available. The theoretical calculations of Schlapp and Penney refer to the simple case where the principal axes of the electric fields in the neighbourhood of the paramagnetic ions, coincide with the principal magnetic axes of the crystal; in other words to the case when the principal axes of the fields associated separately with the different paramagnetic ions in the crystal are respectively parallel to one another. This will in general be the case only when the unit cell of the crystal contains one cobalt ion, whereas actually the number in the unit cell is rarely one. It is two, for example in the Tutton salts, and four or sixteen in some of the hydrated sulphates and selenates considered here. Hence in general the field axes associated with these diff different ions in the unit cell of the crystal will be inclined to one another, and the three principal susceptibilities of the crystal per gram ion of cobalt will not be the same

same as the principal susceptibilities of the separate cobalt ions per gram ion. The observed value for the crystal will thus be the average of the values for the separate ions. If the principal moments of the cobalt ion determined by the field in its neighbourhood are P_1, P_2, P_3, $P_1 > P_2 > P_3$ and p_1, p_2, p_3 those characteristic of the crystal, then p_1 will in general be smaller than P_1, and p_3 greater than P_3 — in other words the three susceptibilities will tend to approach each other in the crystal, as compared with the three susceptibilities for the ion, to which Schlapp and Penney's calculations refer; $P_1^2 + P_2^2 + P_3^2$ will of course have the same value as $p_1^2 + p_2^2 + p_3^2$. Hence even when the rhombic field is so large that the value of P_1^2 for the ion tends at low temperatures to increase with fall of temperatures, p_1^2 may not show such an increase, since both P_2^2 and P_3^2 fall rapidly with fall of temperature and they also contribute to the value of p_1^2. If inspite of this p_1^2 for the crystal does show an increase at low temperatures it can certainly be regarded as indicating a large rhombic field. The converse, however, is not true, since even when p_1^2 does not show such an increase P_1^2 might, and the rhombic field may therefore be large. Thus the sign of the temperature coefficient of p_1^2 at low temperatures is not a suitable criterion for estimating the magnitude of the rhombic field, except when the coefficient is negative. On the other hand, the low value of $(p_1^2 + p_2^2 + p_3^2)/3$ on which the mean of the susceptibilities of the crystal depends is a more dependable criterion.

An examination of the p_1^2, p_2^2, p_3^2 <u>versus</u> temperature curves shows that in all the cobalt Tutton salts, the mean square of the effective moment falls down from about 23 at room temperature to

to about 19 at 80°K. These values, and also the general trends of the temperature variations of the principal moments show that the rhombic fields in all these salts should be of nearly the same magnitude, the fields in all of them being appreciably greater than would correspond to A = 40, considered by Schlapp and Penney.

In the two simple hydrated salts of cobalt namely $CoSO_4 7H_2O$ and $CoSeO_4 6H_2O$, the rhombic fields are definitely much greater than in the Tutton salts. The mean susceptibilities of these two crystals, particularly of $CoSeO_4 6H_2O$ are much smaller than in the Tutton salts, and further the p_1^2 values in these crystals have much smaller temperature coefficients than in the Tutton salts.

In the hexahydrated cobalt selenate the p^2 value corresponding to the lowest of the three principal susceptibilities falls down so rapidly with decrease of temperature that this susceptibility actually shows a maximum at about 130°K, below which temperature the susceptibility decreases with the lowering of temperature. The condition for the occurrence of such a maximum can be easily investigated. By definition the square of the effective moment is given by $p^2 = \frac{3k}{N} \chi T$, where χ is the corresponding gram molecular susceptibility. Now $d(p^2)/dT = \frac{3k}{N} (\chi + T.d\chi/dT)$. At the temperature corresponding to the maximum of the susceptibility $d\chi/dT$ should be equal to zero. Thus when slope of the p^2 versus T curve exceeds the value p^2/T, the thermal coefficient of susceptibility namely $d\chi/dT$ should become positive, whereas ordinarily it is negative. This criterion can be expressed geometrically in the following manner. Consider any point Q on the p^2 versus T curve. Then the temperature variation

variation of susceptibility at Q will be positive if the slope of the p^2 versus T curve exceeds the slope of the line joining Q and the origin ($T = 0$, $p^2 = 0$). This condition is satisfied at low temperature for lowest of the three principal moments.

There is one other salt among the crystals studied by us that shows a similar maximum in the susceptibility curve, namely copper acetate monohydrate, in which all the three principal susceptibilities show this phenomenon; owing to the effective moments for all the three directions coming down rapidly with fall of temperature. The p^2 vs T curves for all the three principal directions in this crystal have slopes higher than that given by the equation given in the foregoing paragraph.

As against the occurrence of a maximum of susceptibility in the susceptibility versus temperature curve observed above , the curve can exhibit a minimum too under suitable conditions. Such a minimum has been observed for example in samarium salts, at about 400°K. The multiplet intervals for samarium are not large, so that it is not only the levels for which $J = 5/2$ (the lowest possible value of J) but also the immediately higher level of which $J = 7/2$ that will be occupied. Now the higher level corresponds to a considerably larger magnetic moment than the lower level . Starting from low temperatures, as the temperature is raised continually there will come a stsge when the population in the upper level will increase rapidly . The average moment per ion will thus increase sufficiently rapidly with rise of temperature to overbalance direct influence of temperature. If p_1^2 is the value characteristic of the lower level

level and p_2^2 of the higher level, then the value of p^2 will rise from p_1^2 to $\frac{1}{2}(p_1^2 + p_2^2)$ as the temperature is raised. Suppose that at the point Q of inflection the slope of the curve is greater than the critical value deduced above. Then evidently there will be two points A and B, where the slope will have the critical value. If T_A and T_B be the corresponding temperatures, then the $d\chi/dT$ will be normal, i.e., negative for temperature $T < T_A$ or $> T_B$, whereas for temperatures in the interval $T_A < T < T_B$ $d\chi/dT$ will be positive. The temperature T_A and T_B will thus be the positions of minima and maxima of the curve. If $p_1^2 = 0$, i.e. if the lower level is non-magnetic, the susceptibility will fall continually as we lower the temperature from T_A, without exhibiting any minimum.

Fig. 49.

Fig. 50.

Coming back to the crystal of $CoSeO_4 6H_2O$, here too the Co^{++} ion is surrounded by an octahedron of six water molecules, just as in the Tutton salts. That the rhombic field in this crystal should be greater than in the Tutton salts shows that in all of them the octahedron may be more or less regular and account for the cubic part of the field, whereas the rhombic part, which as we have seen is much feebler, may form the next near neighbours. These will naturally be different in the Tutton salts and in the sulphate.

Before we conclude this section on cobalt salts, we should

should draw attention to the abnormal rise in the anisotropy of $CoSO_4 7H_2O$ with decrease of temperature, as compared with the corresponding rise for all the other cobalt salts studied here. The values of $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$ increase seven to eight times as we pass from the room temperature to about 80^oK for all the other salts, whereas for $CoSO_4 7H_2O$ this increase is nearly eleven times for $\chi_1 - \chi_2$ and twelve times for $\chi_1 - \chi_3$. This abnormal rise of anisotropy is evidently connected with the large field present in the crystal

Ferrous Sulphate Heptahydrate.

The ground state of the Fe^{++} ion is $^5D_4$, and in a cubic field of the type considered above, i.e. with a positive coefficient D in the expression for the potential, it splits up into a triplet and a doublet, the triplet being lowermost. Each of the five levels will have a five-fold spin degeneracy. Owing to the lowermost level being a triplet, as in Co^{++}, and for other reasons, the magnetic properties of Fe^{++} ion should be very similar to those of Co^{++}. Measurements have been made on one ferrous salt, namely the monoclinic $FeSO_4 7H_2O$. The squares of the three principal magnetic moments and their variations with temperature show a striking resemblance to those of cobalt salts. Firstly the anisotropies are of nearly the same magnitude and the temperature variation also nearly the same as in cobalt salts. As we pass from room temperature down to 80^oK, the anisotropies $\chi_1 - \chi_2$ and $\chi_1 - \chi_3$ increase nearly seven times, which is roughly the ratio of increase in practically all the cobalt salts. Secondly all the p^2 curves fall down with fall of temperature, p_1^2 more slowly than the

the other two. Lastly the mean p^2 value is lower than the theoretical value for the free ion, by nearly the same amount as in cobalt salts, and it decreases with fall of temperature in nearly the same manner.

There is one other result in connection with $FeSO_4 7H_2O$ to which we might draw attention here. Though the crystal is monoclinic, and there is no tendency in the crystal to exhibit pseudo-symmetry of a higher type, two of the principal susceptibilities of the crystal, namely the two lower ones are nearly equal. In $CoSO_4 7H_2O$, which is isomorphous with $FeSO_4 7H_2O$, there is no such uniaxial magnetic symmetry observed This shows that the crystal itself has no such pseudo-symmetry. The symmetry observed in the ferrous salt and not in the cobalt salt should therefore be attributed to the differences in their Stark patterns. Though in both Fe^{++} and Co^{++} ions the ground level is a triplet, the next higher level, transitions to which determine the orbital contributions to the effective magnetic moments and hence to the anisotropies of the crystals, are not similar in the two cases. In the Stark pattern for Co^{++} this level too is a triplet, whereas in the pattern for Fe^{++} it is a doublet, and this should be responsible for two of its principal susceptibilities being equal.

Incidentally even this difference between the Fe^{++} and Co^{++} salts tends to emphasise the essential similarity between the two in other respects, to which attention has been drawn earlier.

Similarly in all the Ni^{++} salts two of the principal susceptibilities are nearly equal, which are the two lower,

lower, as in $FeSO_4 7H_2O$, in all the Tutton salts of nickel, and the two higher in $NiSO_4 6H_2O$ and $NiSeO_4 6H_2O$.

Copper Salts.

The copper salts studied by us fall into three distinct groups as judged by their magnetic properties. To the first belong the Tutton salts in which though the three principal moments are very different, corresponding to a large anisotropy for the crystal, they are practically independent of temperature. In other words, the temperature variations of all the three principal susceptibilities follow the Curie law $\chi = C_i/T$, the Curie constant C_i being different for the three directions. In this respect they resemble $CuSO_4 5H_2O$, whose anisotropy has been studied at low temperatures by Krishnan and Mookherji (1938) and the principal susceptibilities by A. Bose; in which the p^2 values are different for different directions, but are practically independent of temperature.

The square of the effective moment corresponding to the direction of smallest susceptibility is only slightly higher than the spin-only value of 3, again as in $CuSO_4 5H_2O$; whereas in the other directions the value is considerably higher, pointing in the first place to a large contribution from the orbital moment of the Cu^{++} ion — its ground state is ^2D — and secondly to this orbital contributions being confined to presumably some specific direction with reference to the Cu^{++} ion. It suggests that the non-cubic part of the crystalline field in the neighbourhood

neighbourhood of thr Cu^{++} ion has an axis of symmetry; in which case the orbital moment of the Cu^{++} ion will be conserved along this axis only, and will be practically frozen out along parpendicular directions.

To the second class belongs the double chloride - $2NH_4ClCuCl_2 2H_2O$. Here the three p^2 values at room temperature are roughly of the magnitude as in the Tutton salts. But as the temperature is lowered their values come down , slowly at first, and rapidly at lower temperatures, reminding one of the temperature variation curves for the cobalt and ferrous salts. Indeed at low temperatures, namely 80°K, the smallest of the p^2 values is definitely lower than the spin-only value, showing that for this direction and at these low temperatures the contribution from the orbital moment is opposed to the spin contribution.

To the third class belongs copper acetate monohydrate, in which all the three p^2 values are very small. At room temperature the highest of them is only 2.585, and therefore considerably below the spin-only value of 3, and all of them fall off very rapidly with the lowering of temperature. At the lowest temperature of our experiment, namely 82.8°K, the values of p_1^2, p_2^2 and p_3^2 are 0.280. 0.228 and 0.248 respectively, corresponding to a mean value of $\bar{p}^2 = 0.252$, which is extremely low. Indeed the trend of the curves suggests that a further lowering of temperature by 20° or 30° all the p^2 values might almost vanish.

The striking contrast observed above in the magnetic properties of the three classes of copper salts must evidently

be attributed to the large differences in the crystalline fields in these salts. In the first class, to which the Tutton salts belong, the crystalline field will be predominently cubic in character, with a small non-cubic part (presumably with an axis of symmetry and hence either trigonal or tetragonal) superposed on it. This is due to the field being determined almost wholly by the octahedron of the water molecules immediately surrounding the Cu^{++} ion in these crystals. On the other hand in the double chloride, which is typical of the second class, the distribution of the neighbours is very different. The Cu^{++} ion in this salt, as shown by the X-ray studies of Chrobak (1929, 34), on its structure, is plane 4-coordinated. The four neighbours are two chlorine atoms and two oxygen atoms of water molecules, and they occupy the corners of a rhombus, the opposite corners being occupied by similar atoms. Under these conditions the rhombic part of the field with its principal axes along the two diagonals of the rhombus will be very much stronger than in the Tutton salts. The rapid drop of the principal magnetic moments at low temperatures is evidently due to this circumstance.

In copper acetate monohydrate, which represents the third class, the non-cubic part of the field should have less symmetry than in class II, and its magnitude probably even greater, so as to make the spin and orbital moments oppose each other and practically neutralize each other's effects. This will naturally be particularly marked at low temperatures, whereas at higher temperatures, owing to thermal agitation, this neutralization will not be so effective. We do not know enough of the structure of the acetate to verify the existence of such a strong asymmetric field, but from the composition of the molecule, one can see that there are not enough atoms of the same kind to build

build up a symmetric surrounding for the Cu^{++} ion. If the field has a large rhombic part, the A and B constants defining the rhombic part of the field should be widely different.

Potassium Ferricyanide and Potassium Permanganate.

These two crystals are essentially different from the remaining ones in that the paramagnetic ions in them, Fe^{3+} and Mn^{7+} respectively, are covalently coordinated with their neighbours. Such a covalent binding, as we remarked earlier, will conduce to a much closer approach between the central ion and the surrounding atoms, and hence to a much larger crystalline electric field in the centre than will be the case in the ionic salts. The effect of such a strong electric field will be to break up the Russell-Saunders coupling between the spin and the orbital moments of the individual electrons present in the 3d shell and responsible for the paramagnetic moment of the ion. These electrons will therefore orient themselves in the applied magnetic field independently of one another, and we have therefore to regard the medium as consisting of n separate d electrons per atom, n being equal to 5 in Fe^{+++} for example. It is not the energy levels of the Fe^{+++} ion as a whole that we have to consider now and their splitting in the field, and the relative populations of the available Fe^{+++} ions in these levels; but it is the energy levels of the 3d electrons, their splitting in the field, and the distribution of all the available 3d electrons in these levels.

This makes a great difference to the magnetic properties. The 3d level will correspond to an orbital moment L = 2, and will therefore split up into five levels in the crystalline field, just as the D level of the Fe^{++} ion, but with this difference, namely that in the Stark pattern for the d electron the doublet level will be lowermost, whereas in the pattern for the D-state ion it is the triplet level that will be lowermost. Confining attention now to the former pattern, the upper triplet will be widely separated from the lower doublet. We are to accommodate in these levels 5 electrons per atom of iron. Naturally four of them will occupy the lower doublet level, one pair of electrons occupying each level of the doublet, and thus these four electrons will form a magnetically neutral group. The fifth electron can occupy any of the three upper levels, and it is this odd electron that will be responsible for the observed paramagnetism of the crystal of potassium ferricyanide, and indeed in all covalently six coordinated ferric salts. Since the three components of the upper triplet will be slightly separated from one another due to the asymmetry of the field, the probability of the odd electron occupying these levels will not be the same for the three levels, except at high temperatures. It is the relative probabilities of occupation of three levels by the odd electron that will determine the observed anisotropy and its temperature variation.

A detailed calculation of the principal magnetic moments in this salt has been made by Howard (1935), who finds that the orbital contributions are quite large, and strongly asymmetric, and vary with temperature. These results would also be clear from a priori considerations of the relative probabilities of occupation of the triplet levels.

The principal susceptibilities of the crystal have been

been measured previously by Jackson (1933), from room temperature to 75°K. He cuts discs of suitable size out of the crystal, with the axis of the disc along some selected direction in the crystal, and finds the force acting on them in an inhomogenous field, and thence determine the three principal susceptibilities. Our values of the susceptibilities and the direction of the principal axes, determined in a different manner roughly confirm Jackson's values.

There is one important result, which is not brought out in Jackson's measurements, but is conspicuous in ours owing to the anisotropies being measured here directly. The $\chi_1 - \chi_3$ value rises very sharply, reaches a maximum at about 120°K, and falls equally rapidly on a further lowering of temperature.

Though, as mentioned, there is a general agreement between Jackson's values and ours, this does not extend to the details. For example, the numerical values of p_1^2, p_2^2 and p_3^2 obtained by us are consistently lower than Jackson's. Again our p_3^2 values are practically independent of temperature in the region between 120° and 80°K, whereas Jackson's values fall rapidly with temperature even in this range.

We should also mention here that both Jackson's values and ours fit well with the theoretical calculations of Howard, based on some reasonable assumptions for the field, over the whole range of our measurements.

Regarding $KMnO_4$, since manganese atom contains 7 electrons in the 3d shell, Mn^{7+} should have the argon configuration, and should be diamagnetic. If in potassium permanganate the manganese atom may be regarded as having lost all its 7 electrons, and in Mn^{7+} ion, we should expect the crystal to be diamagnetic.

The paramagnetic susceptibility of the crystal being extremely small, corresponding to $p^2 = 0.25$, as obtained by Mookherji (1943), conforms to this prediction. That there is left over a feeble paramagnetism need not occasion surprise, since the assumption of the presence of the Mn^{7+} ion is only an approximation.

The absolute value of the susceptibility being so small, it was not possible with our arrangement, which was designed for the measurement of ordinary paramagnetic crystals, to measure the temperature variation of the principal susceptibilities; and we could measure only the anisotropies. The temperature variations of the anisotropies $\chi_a - \chi_b$ and $\chi_a - \chi_c$ are interesting. The anisotropies plotted against temperature give almost straight lines which are bent towards each other, $\chi_a - \chi_c$ having much smaller slope than $\chi_a - \chi_b$. The ratios of anisotropies at room and other temperatures are given in Table II#. It will be seen that the values of $\chi_a - \chi_b$ and $\chi_a - \chi_c$ increase 2.4 and 1.6 times respectively as we pass from 300°K to 80°K. It is difficult to estimate how much of the observed feeble anisotropy of the crystal is due to its diamagnetism.

Summary

In the paper is given an account of measurements on the principal magnetic susceptibilities of single crystals of a large number of paramagnetic salts of the iron group, from room temperature down to about 80°K. A discussion of the results is given on the basis of the crystalline field theory. Thefollowing are some of the main results obtained.

In manganous and ferric salts in which the paramagnetic ion is in the S-state, the anisotropies are negligibly small, and the temperature variation of the susceptibility almost exactly follow the Curie law.

In chromic salts also this is so, even though the Cr^{+++} ion is not in the S-state. This is due to the lowest level in the Stark pattern of Cr^{+++}being a singlet, and its being widely separated from the upper levels; the singlet level, however, having a (2s+ 1)-fold spin-degeneracy.

The nickel salts are very similar to the chromic salts in their magnetic behaviour except that the spin-orbit coupling in Ni^{++} is much greater than in Cr^{+++}, which conduces to a much larger deviation from the S-state behaviour than in Cr^{+++}; in other words it leads to an appreciable magnetic anisotropy and deviation from the Curie law. These deviations are utilized to calculate the crystal field constants, and it is found that not only the cubic part of the field which is predominant, but even the rhombic part, which is small, is nearly the. the same in most of the nickel salts, and they are practically independent of temperature.

In both Co^{++} and Fe^{++} salts, owing to the ground level being a triplet, the magnetic properties are more sensitive to the rhombic

rhombic part of the field than in the nickel salts. An estimate is given of the rhombic part of the field.

The copper salts, as judged by their magnetic properties fall into three distinct classes. In the first class all the principal susceptibilities follow the Curie law, but with different Curie constants, i.e., the effective moments are different for different directions, but all of them are practically independent of temperature. To this class belong the Tutton salts. In the second class the principal moments are nearly the same as before, but they all decrease with lowering of temperature, slowly at first and rapidly at later stages. The double chloride of copper and ammonium is a typical example of this class. To the third class belongs cupric acetate monohydrate in which the principal moments are all very low even at room temperature and decrease rapidly as the temperature is lowered. The three classes correspond to the non-cubic part of the crystalline field being very different, lowest in the first class and highest in the third.

Attention is drawn to the occurrence of an axis of magnetic symmetry, in nickel and ferrous salts, even though the crystal structure does not lead to it.

The influence of covalent binding on the strength of the electric field, and ultimately on the breaking of the Russell-Saunders coupling not only between the spin and orbital moments, but also between the spins of the different electrons of the ion, and its effect on the magnetic properties of the ion, is discussed.