Investigations on Magne-Crystallic Action. VI. Further Studies on Paramagnetic Crystals

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INVESTIGATIONS ON MAGNE-CRYSTALLIC ACTION
VI. FURTHER STUDIES ON PARAMAGNETIC CRYSTALS

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CONTENTS

1. Introduction

In some of the earlier papers in this series (Part II, 1933; Part IV, 1936; Part V, 1938) we gave an account of magnetic studies on single crystals of several paramagnetic salts of the rare earth and the iron groups, and a discussion of the results on the basis of the recent theoretical work of Van Vleck (1932 *a*, *b*), and Penney and Schlapp (1932), on the influence of the strong local electric fields acting on the paramagnetic ions in the crystals on their magnetic behaviour. Paramagnetic studies on single crystals are of interest because of the variety of information one can obtain from them under favourable conditions—on such widely different topics as the magnitude and the asymmetry of the electric field acting on the paramagnetic ion in the crystal; the geometry of distribution of the negatively charged atoms immediately surrounding the paramagnetic ion, and

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hence the co-ordination number of the ion; the strength of coupling between the orbital and the spin angular momenta of the electrons in the incomplete shell of the ion; and in those crystals in which the paramagnetic ions are all in the S-state, the magnitude of the Stark separation of the S-levels, which plays an important part in determining the thermal properties of the crystal at very low temperatures ($\doteqdot 0{\cdot}1^\circ$ K); etc. Several examples were given, in the papers referred to, to illustrate these various aspects of the magnetic studies on paramagnetic crystals.

Encouraged by these results we have now made measurements at low temperatures, down to about 90° K, on the anisotropies of some typical salts of the iron and the rare earth groups. The low temperature measurements naturally supply much useful material for an extended application of the theory. We have also made measurements at room temperature on a number of crystals specially selected for their structural or other interest. The present paper gives an account of these magnetic studies.

2. A CRYOSTAT FOR MEASUREMENTS ON THE MAGNETIC ANISOTROPY OF CRYSTALS AT LOW TEMPERATURES

The cryostat. We shall take up first the low temperature measurements. In fig. 1 is given a sketch of the apparatus used, of which the main part is the cryostat for maintaining the temperature of the crystal constant at any desired value. The liquid used as the cryostatic bath is petroleum ether, of boiling-point 30–50° C, which remains sufficiently fluid to about -140° C. It is contained in a long cylindrical silvered Dewar vessel D_1, of about 3 in. external diameter, which is mounted between the large flat pole-pieces PP of the electromagnet, on a wooden block W shaped suitably to receive the bottom of the vessel. The vessel is covered by an ebonite disk E, which is kept in position by a rubber ring R_1. The bath liquid is kept well stirred by a stirrer F driven by a small motor. The shaft of the stirrer is enclosed in a metal sheath passing through E, and is connected to the driving motor by the cross-pinions p_1 and a flexible steel cord C enclosed in a flexible metal sheath s. The stirrer when connected to the motor in this manner runs more smoothly than with the usual pulley and cord connexion.

Temperature control. The control of the temperature of the bath is effected automatically by a constant volume air thermometer. The bulb of the thermometer C_1 is a thin-walled cylinder of copper, which takes up the temperature of the bath with very little time-lag. The bulb has a capacity of 30 c.c., and the volume of dead space of the thermometer is made as small as possible. The bulb is connected to the capillary tube T_1 of pyrex glass through the metal-glass soldered joint J_1, and thence to the pressure rubber tubing t, which is filled with clean mercury. The other mechanical parts in this arm of the apparatus will be clear from the figure, and they serve to adjust the pressure of the air inside the thermometer suitably, and to maintain it constant, and also to adjust the level of the mercury at e_1 at any desired height.

e_1 and e_2 are two tungsten electrodes fused through the glass tube. e_2 is always under the mercury in the tube, while e_1 is just at the mercury level. There are two electric circuits, one or the other of which is closed according as the mercury level is in contact, or loses contact, with e_1.

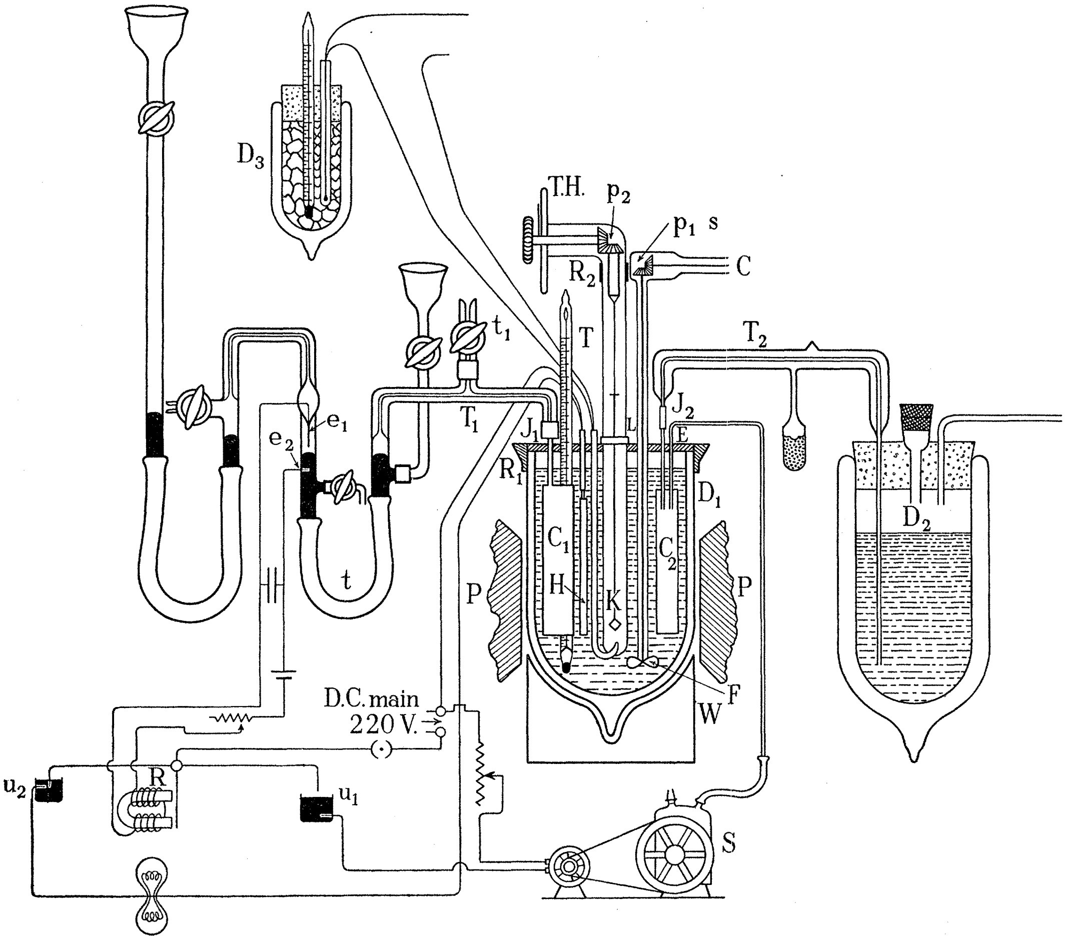

FIG. 1

The first circuit is that through the motor of the air-pump S which slowly sucks liquid air from the Dewar flask D_2 through the thin-walled copper chamber C_2 immersed in the cryostatic bath. The liquid air evaporates in the chamber, and thus cools it and the surrounding bath. The tube T_2 through which the liquid air is delivered to the chamber is double-walled, and the space between the two walls has been well evacuated. It is connected to C_2 through the glass-metal joint J_2.

The second circuit is that through the heating coil H immersed in the bath. The coil is of fine enamelled copper wire wound on a mica sheet, and takes a current of about $\frac{1}{2}$ amp. The leads to the coil have naturally to be well insulated, since any sparking near the bath of petroleum ether is dangerous.

The electrical connexions to the two circuits will be clear from the figure. The current through the relay magnet R is made or broken according as there is contact between e_1 and the mercury or not. The yoke which is connected to the relay arm, and is of the double-contact type, dips accordingly into one or the other of the mercury cups u_1, u_2, and thus closes the first or the second of the two circuits mentioned above.

In order to avoid sparking at the mercury contact at e_1, the mercury surface is covered by a drop of glycerine, and a condenser, of 6 μF capacity, is connected across the terminals e_1 and e_2.

The cryostat in actual working. In order to lower the temperature of the bath, the tap t_1 is opened to the atmosphere, and the mercury level is adjusted so that it just makes contact with e_1. The air pump is now in action, and the bath cools slowly, and the air thermometer takes up the temperature of the bath without appreciable time-lag. Since the air of the thermometer is in communication with the atmosphere, the mercury levels are not altered.

When the bath has cooled down to the required temperature, the tap t_1 is closed. If there is any further cooling, the air in the thermometer will contract, and break the contact at e_1, and close the circuit of the heating coil. The air then expands and pushes the mercury to contact with e_1, thus closing the cooling circuit. In practice the two processes alternate in rapid succession all the time, and the temperature of the bath remains steady to within 0·1° C.

In order to raise the temperature of the bath, t_1 is opened and the mercury level lowered so as to cut off contact with e_1. When the temperature has risen to the desired value, the mercury level is adjusted so as to be just in contact with e_1, and t_1 is closed again.

The thermostat is very economical in its working; about 2 l. of liquid air are sufficient for a complete series of measurements from room temperature to $-140°$ C and back, extending over about 8 hrs.

Measurement of temperature. The temperature measurements in the crystal chamber are made with a copper-constantan thermocouple enclosed in a Pyrex tube, and inserted into the crystal chamber of copper through a suitable airtight copper-glass seal at the bottom of the chamber. The other junction of the thermocouple is kept immersed in a mixture of pure ice and distilled water kept in the Dewar flask D_3. The thermocouple, before insertion in the apparatus, is calibrated at the following temperatures: (1) the temperature of liquid oxygen boiling at atmospheric pressure, namely

$$-183°{\cdot}0\,\mathrm{C}+(p-760)\times 0{\cdot}0126°\,\mathrm{C},$$

where p is the atmospheric pressure in mm. of mercury (the liquid usually contains a little dissolved nitrogen, which slightly lowers the boiling-point; but as the liquid evaporates the nitrogen is progressively removed, and the temperature reaches a steady value, which is the temperature of boiling pure oxygen); (2) the temperature of a mixture of solid carbon dioxide and ethyl ether, namely, $-78°{\cdot}64$ C; (3) the temperature of the room, measured with a calibrated mercury thermometer; and (4) that of steam at about 100° C: the other end of the thermocouple is kept in melting ice all the time. A four-constant formula of the type $E = at+bt^2+ct^3+dt^4$, in which E is the observed potential difference between the two ends of the thermocouple and t is the temperature in ° C of the measuring end, is used for calculating the temperatures.

In the actual experiments a pentane thermometer, previously calibrated with the thermocouple, and immersed deeply in the cryostatic bath, serves to indicate directly the *approximate* temperatures.

Modification of the cryostat for the temperature of boiling oxygen. Below about $-140°$ C the petroleum ether becomes very viscous, and therefore unsuitable for the bath. The only temperature lower than this at which measurements were made was that of oxygen boiling at atmospheric pressure. The cryostatic arrangement for this temperature is naturally simple. The petroleum ether is removed and liquid oxygen in sufficient quantity is directly introduced into the Dewar vessel D_1 and allowed to evaporate at atmospheric pressure. The arrangement for thermostatic control is cut off.

In some of the measurements, we used in the above arrangement, in place of liquid oxygen, a mixture of solid carbon dioxide and ethyl ether, which gives a constant temperature of $-78°\cdot 6$ C.

3. Measurements on magnetic anisotropy

Crystal suspension. The crystal K is suspended in a separate chamber formed by a long thin-walled cylindrical copper tube, of large diameter, closed at the lower end, and immersed in the cryostatic bath as deeply as possible. The copper tube is attached at the upper end to a long glass tube T, which rests on a cup-shaped collar L attached to the copper tube; the junction is sealed airtight with soft wax. The glass tube carries at its upper end a graduated torsion-head, *T.H.*, which is attached to the tube by a piece of large diameter rubber tubing R_2. The axis of the torsion-head is horizontal, and its scale vertical, so that the scale can be read conveniently. The axis of the torsion-head is coupled to the vertical torsion-pin, from which the crystal is suspended, by means of a cross-pinion p_2 having no backlash, so cut that the angle of rotation of the torsion-pin about the vertical axis is accurately the same as that of the pointer on the torsion-head about the horizontal axis.

The crystal is suspended, with any desired direction vertical, from the end of the torsion-pin. The suspension fibre consists of two parts. The upper part is a very thin quartz fibre whose torsional constant has been determined previously. The lower part is a glass fibre which is sufficiently stout, relatively to the quartz fibre, to be regarded as rigid. To the lower end of this glass fibre is attached the crystal, and it lies in the centre of the homogeneous, horizontal magnetic field obtaining between the large flat pole-pieces of the electromagnet. The whole length of the quartz fibre is sufficiently above the cryostat to remain always at room temperature, and its torsional constant thus remains independent of the temperature of the cryostat.* A small horizontal glass fibre, attached centrally to the glass suspension near its upper end, serves as a pointer for observing the rotatory movements of the crystal.

Measurements on magnetic anisotropy. The experimental method adopted by us for measuring the magnetic anisotropy is essentially the same as that used in our previous measurements at room temperature. For any given suspension of the crystal, the anisotropy $\Delta\chi$ in the horizontal plane is determined by finding the critical angle by which the torsion-head has to be rotated from its normal position (corresponding to zero torsion of the fibre when the crystal has taken up its equilibrium orientation in the magnetic field), in order to bring the crystal just to its unstable orientation in the field. For the details of the method the reader may be referred to Part III of this paper, pp. 268–9. In calculating $\Delta\chi$ from the observed critical angle α_c, we used in Part III the simple, but approximate, formula

$$\lambda = \alpha_c - \pi/4, \tag{1}$$

where λ stands for $\Delta\chi m H^2/(2Mc)$. Under the usual conditions of measurement of anisotropy, in which α_c is large, usually several rotations, this formula is a sufficiently good approximation.†

In the present measurements, which concern the variation of $\Delta\chi$ with temperature, $\Delta\chi$ is found to increase in some crystals more than 10 times as we pass from room temperature to that of liquid oxygen; and λ naturally increases in the same ratio. Hence, in order to avoid inconveniently large values of α_c at low temperatures, its value at room temperature has to be kept moderate. In this case the simple relation $\lambda = \alpha_c - \pi/4$ is not sufficiently accurate, and we have to use in its place the more rigorous relation

$$\lambda = (\alpha_c - \pi/4 - \sigma)/\cos 2\sigma, \tag{2}$$

where

$$\sin 2\sigma = 1/(2\lambda) \tag{3}$$

and λ stands for $\Delta\chi m H^2/(2Mc)$, as before.

When the crystal just reaches its unstable orientation in the field, the direction of the largest susceptibility in the horizontal plane will make an angle of $\pi/4+\sigma$ with the direction of the field, and as will be seen from (2) and (3), if α_c is not large, σ may be considerable.

4. THE MAGNETIC ANISOTROPY OF PARAMAGNETIC IONS IN THE S-STATE IN CRYSTALS: INVERSE T^2 LAW

We shall first consider the special class of crystals whose paramagnetic ions are all in the S-state; their magnetic moments are due wholly to the spin moments of their electrons. Since the spin moments are affected little by the crystalline electric fields—

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* Some recent measurements by Mr W. J. John on the torsional constants of quartz fibres at different temperatures show that the temperature coefficient of torsion is very small.

† When $\alpha_c = 2$ rotations $(=4\pi)$ the error involved in using the approximate formula (1) instead of (2) is 0·1 %, and even when α_c is only one rotation, the error is less than $\frac{1}{2}$ %.

in other words since the splitting, in the Stark manner, of the S-levels of the paramagnetic ions under these fields is very narrow—the theory predicts a simple magnetic behaviour for these crystals; particularly when, as in the substances that we are studying, the concentration of the paramagnetic ions is not large. At any given temperature T, the principal susceptibilities of the crystal conform to the simple formulae (Van Vleck and Penney 1934)

$$\chi_i = \frac{C}{T}\left(1+\frac{\Theta_i}{T}\right), \quad i = 1, 2, 3, \tag{4}$$

where the Θ's are small temperatures, of the order of 0·1° K, which are determined by the magnitude and the asymmetry of the crystalline fields acting on the paramagnetic ions, and satisfy the relation

$$\Theta_1+\Theta_2+\Theta_3 = 0. \qquad (5)^*$$

For this class of crystals we should therefore expect the following simple results:

(1) From equations (4) and (5)

$$\chi = (\chi_1+\chi_2+\chi_3)/3 = C/T; \tag{6}$$

i.e. the mean susceptibility of the crystal should conform closely to the Curie law. This result has been verified experimentally by Jackson, de Haas and others, for manganous, ferric and gadolinium salts.

(2) The anisotropy of the crystal is given by

$$\Delta\chi/\chi = \Delta\Theta/T, \tag{7}$$

and should therefore be very feeble. This result also is verified experimentally for both manganous and ferric salts. (Salts of gadolinium will be considered in the next section.) To be more precise, from measurements on the mean susceptibility χ and the anisotropies $\chi_1-\chi_2$ and $\chi_1-\chi_3$ at any one temperature, say at room temperature, we can easily calculate, with the help of relations (4) and (6), the Θ's. For manganous salts, as we showed in Part IV, the Θ's so obtained have nearly the same magnitude as that deduced from the observations of Kürti and Simon on the lowering of the temperature of the crystals when they are demagnetized adiabatically at very low temperatures.

(3) There is another feature of the anisotropy of these salts, which we shall consider here in some detail. It is clear from equation (7) that for given asymmetric fields acting on the paramagnetic ions, the crystal anisotropies $\Delta\chi$ should be proportional to χ/T, i.e. to the inverse square of the temperature. Now the coefficients of thermal expansion of the crystals being small, the distributions of the negatively charged atoms immediately surrounding the paramagnetic ions in the crystals will remain practically unaffected by temperature, and hence also the electric fields acting on the ions. The temperature variation of $\Delta\chi$ for these crystals should therefore conform to the inverse T^2 law.

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* The Θ's being small compared to T at all ordinary temperatures, it is readily seen that equations (4) reduce to the familiar equations $\chi_i = C/(T-\Theta_i)$ of the classical Weiss theory.

With the experimental arrangement described in the previous section we have measured the magnetic anisotropy of the monoclinic crystal $MnSO_4 . (NH_4)_2SO_4 . 6H_2O$ at different temperatures. In our previous measurements on this crystal, which were made at room temperature, we used the crystal in its natural form. The distribution of induced magnetism (of the Poisson type) on the surface of the crystal will be asymmetric, and since the magnetic fields used are not ideally homogeneous, there may be a small disturbing couple tending to rotate the crystal. In order to eliminate it the crystal was kept surrounded by a liquid of the same volume susceptibility as the crystal. Since it is not convenient to use this technique at low temperatures, the crystals are used in the present measurements in the form of cylinders cut with their axes along different known directions in the crystal, and suspended in the horizontal magnetic field with the cylinder axes vertical.

The results of the magnetic measurements on the crystal are given in Table I. The crystal is monoclinic, having the axial elements $a:b:c = 0{\cdot}740:1:0{\cdot}493$; $\beta = 106^\circ\,51'$. χ_1 and χ_2 are the two principal susceptibilities in the (010) plane, and χ_3 is that along the "b" axis. They refer to one gram molecule, and are expressed in the usual unit, 10^{-6} c.g.s. e.m.u. ψ denotes the angle which the χ_1-axis makes with the "c" axis of the crystal, the positive direction of ψ being defined by the condition that the χ_1-axis makes with "a" the angle $\beta-\psi$, where β is the obtuse angle between the "c" and the "a" axes.

TABLE I

Mode of suspension	Orientation in the magnetic field	$\Delta\chi$ 303° K	194°·5 K	90° K
"b" axis vertical	$\psi = -16^\circ$ at all the three temperatures	8·7	21	93
"a" axis vertical	"b" axis normal to the field	3·4	6·7	21

From these data we obtain the following values for the anisotropy.

TABLE II

Temp. ° K	$\chi_1-\chi_2$	$\chi_1-\chi_3$	ψ
303	8·7	6·0	−16°
194·5	21	13	−16°
90	93	49	−16°

That ψ has the same value at all the three temperatures justifies our assumption that the crystal fields remain practically unaffected by changes in temperature.

The values of $\chi_1-\chi_2$ and $\chi_1-\chi_3$ entered in Table II, particularly those at room temperature, require correction for the anisotropy of the diamagnetism of the crystal. To a first approximation the latter anisotropy may be taken to be the same as that of the diamagnetic crystal $MgSO_4 . (NH_4)_2SO_4 . 6H_2O$, or $ZnSO_4 . (NH_4)_2SO_4 . 6H_2O$, which is isomorphous with the manganese salt. The corrections for $\chi_1-\chi_2$ and $\chi_1-\chi_3$ will then be 1·0 and 0·6 respectively (see Part IV), to be subtracted from the values given in Table II.

The corrected values of $\chi_1 - \chi_2$ at the three temperatures bear the ratios

$$7\cdot7 : 20 : 92 = 1 : 2\cdot6 : 11\cdot9,$$

and those of $\chi_1 - \chi_3$ the ratios

$$5\cdot4 : 12\cdot4 : 48\cdot4 = 1 : 2\cdot3 : 9\cdot0.$$

With these may be compared the ratios of the inverse squares of the temperatures,

$$1 : 2\cdot4 : 11\cdot3.$$

In view of the low values of the anisotropies at room temperature and their consequent sensitiveness to the diamagnetic correction, which is not known with certainty, the agreement between the experimental and the inverse T^2 ratios may be regarded as satisfactory.

5. The magnetic anisotropy of $Gd_2(SO_4)_3 . 8H_2O$

The Gd^{+++} ion is in the S-state (^8S) and has a large magnetic moment. Its salts are therefore very suitable for use as working material in demagnetization experiments at very low temperatures, and were used in the classic experiments of Giauque. The magnetic and the thermal properties of these salts have been studied extensively at these temperatures. It would be of interest to study their magnetic anisotropies also, which naturally should be expected to be very feeble.

Through the kindness of Professor Giauque we were able to obtain some good crystals of the octahydrated sulphate, $Gd_2(SO_4)_3 . 8H_2O$. The crystal is monoclinic, having the axial elements $a : b : c = 3\cdot009 : 1 : 2\cdot007$, $\beta = 118^\circ 2'$. The results of our magnetic measurements on the crystals, used in the form of suitably cut cylinders, are given in Tables III and IV; they refer to a gram molecule having the formula $Gd_2(SO_4)_3 . 8H_2O$, i.e. to a mass of the crystal containing two gram ions of Gd^{+++}.

Table III

Mode of suspension	Orientation in the magnetic field	$\Delta\chi$		
		303° K	194°·5 K	90° K
"*b*" axis vertical	$\psi = +15\frac{1}{2}^\circ$ at all the three temperatures	750	1960	8100
(001) plane horizontal	"*b*" axis along the field	710	1640	5840

Table IV

Temp. °K	$\chi_1 - \chi_2$	$\chi_3 - \chi_2$	ψ
303	750	745	$+15\frac{1}{2}^\circ$
194·5	1960	1730	$+15\frac{1}{2}^\circ$
90	8100	6220	$+15\frac{1}{2}^\circ$

Considering first the room temperature values, we find that the crystal, though monoclinic, is nearly uniaxial magnetically, the axis of magnetic symmetry being along the χ_2-axis, i.e. along a direction in the (010) plane which makes with the "*a*" and the "*c*" axes angles of $12\frac{1}{2}°$ and $105\frac{1}{2}°$ respectively.

Measurements on the mean susceptibility of the crystal at room temperature gave

$$\chi = (\chi_1+\chi_2+\chi_3)/3 = 52{,}300 \text{ at } 30^\circ\,\text{C},$$

which corresponds to a magnetic moment of 8·00 Bohr magnetons for the Gd^{+++} ion, as compared with the theoretical value of 7·94 for the ^8S-state. Comparing with this value the data given in Table IV, we find that at room temperature the anisotropy of the crystal, namely $\chi_1-\chi_2$ or $\chi_3-\chi_2$, is only 1·4 % of the mean susceptibility.

According to the data supplied by Professor Giauque the specimen of gadolinium from which the salt was prepared contained as impurity 0·5 % samarium and 1 % terbium. Because of the low susceptibility of the Sm^{+++} ion, its presence will not contribute appreciably to the observed anisotropy. The effect of the terbium impurity cannot be calculated exactly at present, since no measurements have been made on the anisotropy of terbium salts. We can, however, fix an upper limit to its contribution, and conclude that for the octahydrated sulphate of gadolinium at 30° C

$$(\chi_1-\chi_2)/\chi = (\chi_3-\chi_2)/\chi = 0{\cdot}014 \pm 0{\cdot}003.$$

From these values for the anisotropy and the relations (4) and (6), we obtain

$$\Theta_1 = \Theta_3 = -\tfrac{1}{2}\Theta_2 = (1{\cdot}4 \pm 0{\cdot}3)^\circ\,\text{K}.$$

We shall presently show that these values for the Θ's, though small, are yet considerably higher than what we should expect from the known temperature variation of the entropy of the salt at very low temperatures.

Assuming a cubic symmetry for the crystalline fields acting on the Gd^{+++} ions in the crystal and denoting by δ the *over-all* Stark separation of the ^8S-levels of Gd^{+++} under these fields, Hebb and Purcell (1937) find that the value

$$\delta = 0{\cdot}98\,\text{cm.}^{-1} = 1{\cdot}4^\circ\,\text{K}$$

fits well with the experimental entropy-temperature curve over the whole of the available range, namely 0·25° to 1·5° K. But actually, judging from the large observed magnetic anisotropy of the octahydrated sulphates of the other rare earths, which are isomorphous with $Gd_2(SO_4)_3.8H_2O$, the crystalline fields acting on the Gd^{+++} ions should deviate considerably from cubic symmetry. Nevertheless the over-all Stark separation δ, under these asymmetric fields, which would fit the experimental entropy-temperature data, should be of the above order of magnitude.

Now we should expect the Θ's, which define the asymmetry of the crystalline fields, to be considerably smaller than the over-all separation δ. For the following reason the observed Θ's may be still smaller. Since the unit cell of the crystal contains more than one Gd^{+++} ion (probably eight), and since the principal axes of the crystalline fields acting on these different Gd^{+++} ions may not be parallel to one another, the observed anisotropy of the crystal, and hence the Θ's deduced therefrom, may be smaller than would correspond to the actual asymmetry of the fields acting on the Gd^{+++} ions.

But actually the Θ's for the crystal are of nearly the same magnitude as δ, i.e. the Θ's are much larger than we should expect from the thermal properties of the crystal at low temperatures. This result suggests that much of the observed anisotropy of the crystal must arise from causes other than the splitting of the S-levels by the crystalline electric fields. If the Gd^{+++} ions in the crystal are not sufficiently widely separated, and if their arrangement in the crystal lattice does not conform to cubic symmetry, then the crystal may exhibit an anisotropy in the magnetic field; and at the same time, *in the absence of the applied magnetic field*, the internal *magnetic* fields acting on the Gd^{+++} ions due to the neighbouring Gd^{+++} ions, i.e. the local magnetic fields of the Onsager type, may be so small that the resulting separation of the S-levels, and the contribution to the entropy in the absence of the external magnetic field, may be very little.*

At present we have not enough information regarding the positions of the Gd^{+++} ions in the unit cell which would enable us to estimate the anisotropy that may arise in the above manner, i.e. from the mutual interaction of the magnetic moments. If the large observed anisotropy is really due to this cause, we should expect it to diminish rapidly as the crystal is diluted magnetically, in contrast with the behaviour of the manganous salts which we have studied previously (Part IV), in which the effect of magnetic dilution on the anisotropy is not large. We are trying to grow mixed crystals of gadolinium sulphate with yttrium sulphate, which is diamagnetic, in order to verify this result.

Whether the anisotropy is due to the splitting of the S-levels of Gd^{+++} under the asymmetric electric fields of the neighbouring negative charges, or under the asymmetric magnetic fields of the neighbouring Gd^{+++} ions, in either case it should vary approximately as the inverse square of the temperature. This is actually so, as will be seen from the data given in Table IV. The values of $\chi_1-\chi_2$ at the three temperatures bear the ratios $750:1960:8100 = 1:2\cdot6:10\cdot8$, and those of $\chi_3-\chi_2$ the ratios $745:1730:6220 = 1:2\cdot3:8\cdot4$, as compared with the ratios of the inverse squares of the temperatures, $1:2\cdot4:11\cdot3$.

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* Professor Giauque has kindly informed us that demagnetization experiments on gadolinium salts at low temperatures also suggest a large magnetic interaction. The exchange interactions between the spins of the neighbouring Gd^{+++} ions, which fall off exponentially with their separation, in contrast with the magnetic interactions which vary as the inverse cube of the separation, will be small in the hydrated crystals. Even if it is not small, it will not produce an anisotropy.

6. The influence of the orbital angular momenta of paramagnetic ions on their magnetic behaviour in crystals

It is well known that in many of the salts of the iron group the "effective" magnetic moment of the paramagnetic ion conforms closely to the spin-only value. The inference sometimes drawn from this observation that the orbital angular momentum of the paramagnetic ion plays an insignificant part in determining its magnetic behaviour is, however, incorrect. It is true that the orbital angular momentum is more or less completely quenched by the crystalline electric fields, and is not therefore capable of orienting in the applied magnetic field and thus contributing directly to the magnetic moment developed in the crystal; and that practically the whole of this moment is contributed by the spin momentum of the paramagnetic ion. But *indirectly* the frozen orbital momentum, by virtue of its coupling with the spin momentum, can exercise a large orienting couple on the latter, and thus influence the magnetization. The older way of regarding these local orienting couples acting on the spins as arising from certain internal magnetic fields, whose origin was not properly understood, but which were presumed to be of the same nature as the local fields in ferromagnetics, is in a large measure responsible for the insignificant part assigned to the orbital momentum in determining the magnetic behaviour of the crystal. It is now well established that the local couples tending to orient the spin momentum are ultimately due to the internal electric fields in the crystal, which are generally strong and asymmetric. The spin momentum is not directly affected by these fields to any appreciable extent, but indirectly it is, as we mentioned just now, owing to its coupling with the orbital momentum, which is easily affected. The magnetic anisotropy of the crystal, and the deviations from the simple Curie law, of the temperature variation of its principal susceptibilities, are the results of this indirect influence exercised by the asymmetric crystalline fields on the spin momentum through the spin-orbit coupling. Both these effects, viz. the anisotropy and the deviations from the Curie law, should therefore be the greater the stronger the spin-orbit coupling; and conversely, from observations on the principal susceptibilities of the crystal or its anisotropy at different temperatures, it should be possible to calculate the strength of the spin-orbit coupling.

7. The coupling between the orbital and the spin angular momenta in Ni^{++} evaluated from magnetic measurements

The theoretical expressions necessary for such a calculation come out simple for nickel salts, and have been worked out by Schlapp and Penney (1932). For any given plane in the crystal the anisotropy $\varDelta\chi$, i.e. the difference between the maximum and the minimum susceptibilities in the plane, per gram molecule, is given by the relation

$$\varDelta\chi = \frac{8N\beta^2}{3kT}\left(8\lambda - \frac{2\lambda^2}{kT} - 3kT\right)\varDelta\alpha, \tag{8}$$

where λ is the constant of spin-orbit coupling, $\beta = eh/(4\pi mc)$ is the Bohr magneton, N is the Avogadro number, and k is the Boltzmann constant. $\Delta\alpha$ is a constant which depends on the crystalline electric fields acting on the paramagnetic ions in the unit cell of the crystal, and on the inclination of the selected plane to the principal axes of these crystal fields. At present we have not enough knowledge of these fields to be able to calculate $\Delta\alpha$ directly. We may, however, assume as before that these fields, and therefore $\Delta\alpha$ also, will be practically independent of temperature. By comparing the values of $\Delta\chi$ at any two convenient temperatures we can then eliminate $\Delta\alpha$ and calculate the constant of spin-orbit coupling λ.

For this purpose measurements at the temperature of the room and that of liquid oxygen, which are the two extreme temperatures in our experiments, would be very suitable. We have made such measurements with the hexahydrated selenate and sulphate of nickel, $NiSeO_4 . 6H_2O$ and $NiSO_4 . 6H_2O$, which are both tetragonal, and the results are given in Table V. ρ denotes the ratio of the anisotropy at $-183°·0$ C to that at $21°·0$ C.

TABLE V

Crystal	ρ	λ
$NiSeO_4 . 6H_2O$	4·76	-330 cm.$^{-1}$
$NiSO_4 . 6H_2O$	$4·8_1$	-340 cm.$^{-1}$

In obtaining the ratios ρ we made the room temperature measurements both before and after the low temperature measurements. While for the selenate the ratio obtained was independent of the order of the measurement, for the sulphate the value obtained by making the room temperature measurement first, and then the low temperature measurement, was considerably lower than that obtained by making the measurements in the reverse order. This result was found to be due to an appreciable dehydration of the sulphate at the low temperature, and the formation of a thin whitish crust of the dehydrated micro-crystals on the surface. The value $4·8_1$ given above is that obtained by making the low temperature measurement first, since this will approximate more closely to the real value than the one obtained from measurements made in the reverse order.

For this reason the value of λ obtained for the sulphate is not entitled to the same weight as that obtained for the selenate, and we may adopt the latter value, namely

$$\lambda = -330 \text{ cm.}^{-1},$$

as the result of our magnetic measurements.

Spectroscopically, the Ni^{++} ion is in the $^3F_4$ state, and the over-all multiplet width, according to Laporte (1928), is 2347 cm.$^{-1}$. From this we obtain, using the relation $\lambda S(2L+1) = 2347$ cm.$^{-1}$, $\lambda = -335$ cm.$^{-1}$. It is gratifying that the value deduced from the magnetic data agrees well with this value.

8. Temperature variation of the magnetic anisotropy of nickel salts

We have also made measurements of the anisotropy of these two nickel salts at several intermediate temperatures, and the results are given in Tables VI and VII. ρ denotes the ratio of the anisotropy at the given temperature T to that at 21°·0 C. The theoretical values of ρ, calculated from equation (8) using for λ the value -330 cm.$^{-1}$, are also given in the tables for comparison with the experimental values.

The measurements on the sulphate were made with increasing temperatures, beginning at about $-130°$ C, and care was taken not to keep the crystal unduly long at temperatures below $-80°$ C, where dehydration is appreciable. For the selenate it was immaterial whether the measurements were made with increasing or with decreasing temperatures.

Table VI. $NiSeO_4.6H_2O$

Temp. ° K	ρ Obs.	ρ Calc.
294·1	(1·000)	(1·000)
270·9	1·096	1·096
268·4	1·110	1·108
251·2	1·192	1·195
248·6	1·207	1·209
240·0	1·261	1·261
231·0	1·321	1·319
221·6	1·389	1·387
212·0	1·462	1·464
207·8	1·494	1·500
203·4	1·544	1·540
190·3	1·673	1·674
175·3	1·863	1·860
171·0	1·917	1·921
168·5	1·955	1·958
164·0	2·023	2·029
148·8	2·309	2·310
147·2	2·345	2·345
145·0	2·389	2·392

Table VII. $NiSO_4.6H_2O$

Temp. ° K	ρ Obs.	ρ Calc.
294·1	(1·000)	(1·000)
272·7	1·090	1·087
251·9	1·190	1·191
232·7	1·307	1·308
230·5	1·323	1·323
225·5	1·364	1·358
210·2	1·477	1·479
191·0	1·667	1·666
170·8	1·925	1·924
151·0	2·262	2·265
146·7	2·355	2·355

As will be seen from the tables, the agreement between the experimental and the theoretical values of ρ is very satisfactory, and may be taken as a quantitative verification of Schlapp and Penney's theory.

Regarding the absolute values of the anisotropy, we may mention that at 21° C $\chi_{\perp}-\chi_{\parallel}$ is about 92 for the selenate and 112 for the sulphate. These anisotropies should be regarded as very feeble, since they are less than 3 % of the mean susceptibilities of the crystals at this temperature. They give for $\Delta\alpha$ reasonable magnitudes, as we showed in Part V.

We may further mention here that measurements on the temperature variation of the principal susceptibilities can also serve for the verification of the theory. The principal susceptibilities are given by

$$\chi_1 = \frac{8N\beta^2}{3kT}(1+8\lambda\alpha_1+\theta_1/kT)-8N\beta^2\alpha_1, \tag{9}$$

where $$\theta_1 = 2\lambda^2(\alpha_2+\alpha_3-2\alpha_1)/3, \tag{10}$$

and two similar expressions. The α's are determined by the crystalline fields and the inclinations to one another of the field axes associated separately with the different Ni^{++} ions in the unit cell of the crystal. Like $\Delta\alpha$, the α's also will be practically independent of temperature.

Experimentally, however, the temperature variations of the principal susceptibilities are more difficult to measure accurately than the temperature variations of the anisotropies. Moreover, in the expressions for the principal susceptibilities, namely equation (9), the predominant term is independent of λ and α, unlike the predominant term in the expression for $\Delta\chi$.

9. The feeble anisotropy of chromic salts

The chromic salts also lend themselves to a simple discussion on the basis of the theory of Schlapp and Penney. The ground state of the Cr^{+++} ion is an F state, as in Ni^{++}, but with a spin moment of 3/2 instead of the moment 1 in Ni^{++}. The over-all multiplet width of Cr^{+++}, according to Laporte, is 912 cm.$^{-1}$, from which we obtain for the constant of spin-orbit coupling $\lambda = +87$ cm.$^{-1}$. This is numerically only a fourth of the value for Ni^{++}. In the expression for the anisotropy of a chromic salt, analogous to (8) for a nickel salt, the λ^2 term will therefore be negligible; moreover, the other two terms, which will be of comparable magnitudes, will have opposite signs. The anisotropy should therefore be much smaller than that of nickel salts, and when we remember that even for the latter salts it is only 2–3 % of the mean susceptibility, for the chromic salts it should be very small indeed.

We have measured the anisotropy of one such salt, namely ammonium chromium oxalate, $(NH_4)_3Cr(C_2O_4)_3 . 3H_2O$, and the results are given below. The crystal is monoclinic prismatic; $a:b:c = 0{\cdot}983:1:0{\cdot}387$; $\beta = 95° 18'$. At 30° C:

$$\chi_1-\chi_2 = 4{\cdot}3,$$
$$\chi_1-\chi_3 = -10{\cdot}3,$$
$$|\psi| = 29°,$$
$$\chi = (\chi_1+\chi_2+\chi_3)/3 = 5440.$$

The maximum anisotropy, namely $\chi_3-\chi_2 = 14{\cdot}6$, is only $\frac{1}{4}$ % of the mean susceptibility. This is not much higher than the anisotropy which might be expected even from the direct influence of the crystalline fields on the spins, as distinguished from the influence exerted on them indirectly through the spin-orbit coupling, which we have considered here. The low anisotropy predicted by the theory is thus verified.

In fact the observed anisotropy of the crystal is of the same order of magnitude as its diamagnetic anisotropy, as will be clear from the following data for the anisotropy of the diamagnetic crystal $K_3Al(C_2O_4)_3 . 3H_2O$, which is isomorphous with the above chromic salt (see Part IV of this paper, p. 351):

$$\chi_1 - \chi_2 = 6{\cdot}9,$$
$$\chi_1 - \chi_3 = 13{\cdot}1,$$
$$\psi = +19^\circ.$$

The low anisotropy of the salts of trivalent chromium—nearly as low as if the Cr^{+++} ion were in the S-state, instead of in ^4F—is very significant, and explains the suitability of these salts as working material for the production of low temperatures by the Debye-Giauque method.

The close conformity of the mean susceptibility of crystal to the spin-only value is generally taken as a criterion for judging its suitability for this purpose. This is not, however, a reliable test, since it only ensures the efficient quenching of the orbital momenta, and the consequent inability of the latter to contribute directly to the effective magnetic moment of the ion. Indirectly, as we remarked in the previous section, the orbital momenta, by virtue of their coupling with the spins, can appreciably hamper the freedom of rotation of the latter. On the other hand, a very feeble anisotropy for the crystal (except of course when it is due to a cubic or a pseudo-cubic symmetry in the structure of the crystal or in the crystal field) is a more reliable and sensitive test for the freedom of rotation of the spin-moments, and hence of the suitability of the crystal for the production of low temperatures by demagnetization.

Coming back to ammonium chromic oxalate, we have also studied the temperature variation of its anisotropy for two suspensions of the crystal. With the "*b*" axis vertical, we find firstly that the value of ψ changes by about 78° as the temperature is lowered from 30° to -183° C, and the value of $\chi_1 - \chi_2$ increases 1·9 times. The large variation in ψ and the small increase in $\chi_1 - \chi_2$ are both to be expected, since the diamagnetic part of the anisotropy, which is a large part, will be independent of temperature, and the values of ψ will not be the same for the diamagnetic and the paramagnetic parts.

With the "*c*" axis vertical, the anisotropy in the horizontal plane increases about 12 times as we pass from room temperature (30° C) to that of liquid oxygen.

Before closing this section we should mention that the mean susceptibility of 5440 at 30° C observed for the crystal, or 5660 after correcting for its diamagnetism, gives for the magnetic moment of Cr^{+++} 3·72 Bohr magnetons, as compared with the spin-only value of 3·87. Now, theoretically, the effective moment of Cr^{+++} in the crystal should bear to the spin-only moment approximately the ratio $1 - 2\lambda/(5Dq)$, where Dq

is the constant of the cubic part of the crystalline field, which would be the predominant part. The above experimental value for the magnetic moment of Cr^{+++} corresponds to $Dq \doteqdot 900\,\text{cm.}^{-1}$, which is of reasonable magnitude.

10. THE CURIE-WEISS LAW AND THE TEMPERATURE VARIATION OF MAGNETIC ANISOTROPY

As we mentioned in a previous section the crystalline electric fields acting on the paramagnetic ions may be regarded as producing an orienting couple on the magnetic dipoles, and to this extent they will simulate a local magnetic field. But there is this essential difference between the inner magnetic field of the Weiss theory and this field, namely that, in general, the latter field will not be proportional to the intensity of magnetization. The Weiss law of temperature variation, $\chi = C/(T-\Theta)$, has not therefore much significance on the new theory.

Experimentally also, the validity of the Weiss law is very limited. In order to realize this properly one has to remember that the so-called "cryomagnetic anomalies", which occur at low temperatures, are really deviations from the Weiss law, and it is only at low temperatures that the conditions are suitable for a proper test of the law. Even at ordinary temperatures, where the test is not stringent, deviations from the law are not uncommon, and in particular if we follow the temperature variations of the three principal susceptibilities of the crystal separately, instead of the variation of their mean value, the deviations from the Weiss law,

$$\chi_i = C/(T-\Theta_i), \quad i = 1, 2, 3, \tag{11}$$

where the Curie constant C should be the same for all the three principal directions, while the Θ's may be different, become more conspicuous. On the new theory, on the other hand, these deviations are not only to be expected but receive a natural explanation.

But the most striking success of the new theory is in explaining the anisotropy and its variation with temperature. We shall consider here one particular feature of the temperature variation of anisotropy. Whereas according to (11), at all ordinary temperatures, the anisotropy $\Delta\chi$ should increase with fall of temperature, on the new theory the temperature variation of $\Delta\chi$ is not so simple. Since the energy levels of the paramagnetic ions have already separated under the influence of the crystalline fields, and the lower levels may not always correspond to larger magnetic moments, the anisotropy $\Delta\chi$ may, under suitable conditions, even decrease with fall of temperature. If the natural multiplet width of the free ion is not large, then also we may expect similar results.

This is well illustrated by the ethylsulphates of praseodymium and samarium; as the temperature is continually lowered their anisotropies first increase, pass through a maximum and then diminish.

11. Ethylsulphates of praseodymium and samarium

The magnetic anisotropies of some of the rare earth ethylsulphates, having the formula $M_2(C_2H_5SO_4)_6 . 18H_2O$, have been studied by Fereday and Wiersma (1935) over a wide range of temperatures. (The crystals are hexagonal, and we shall denote their susceptibilities along the hexagonal axes, and perpendicular to the hexagonal axes by $\chi_\parallel$ and $\chi_\perp$ respectively, per gram molecule—containing two gram ions of M^{+++}.) Among them, the ethylsulphate of praseodymium is of special interest. At liquid hydrogen temperatures its anisotropy $\chi_\parallel - \chi_\perp$ has a large negative value, about $-36{,}900$ at 14°·44 K, and as the temperature is raised the value increases (algebraically) rapidly, reaching -3610 at 77°·8, -19 at 137°, 370 at 167°·6 and 318 at 290°. The anisotropy, besides changing sign, thus passes through a maximum, in contrast with the behaviour of the other ethylsulphates studied by them, for which $\chi_\parallel - \chi_\perp$ is always positive and decreases continually with increase of temperature.

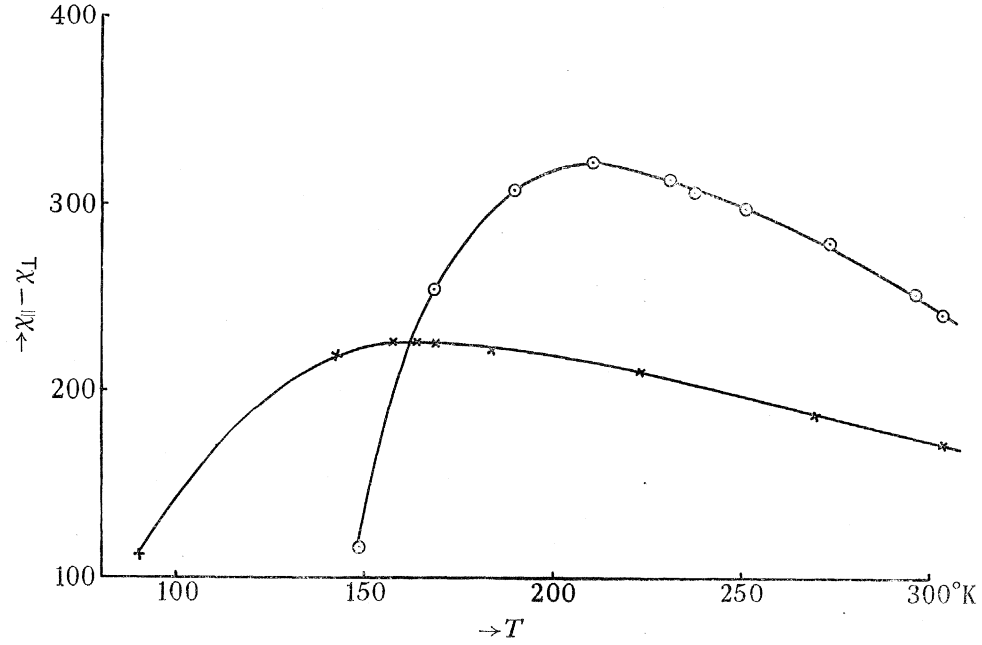

FIG. 2. The circles refer to praseodymium ethylsulphate and the crosses to samarium ethylsulphate.

We had made some low temperature measurements on this crystal. Though our temperature range is much smaller, it includes the region on either side of the maximum of anisotropy, and since only two of the observations of Fereday and Wiersma lie in this region, our detailed measurements in this region may be of some interest. The results are given in Table VIII, and they are plotted in Fig. 2.

Now the normal state of the Pr^{+++} ion is $^3H_4$, and in the Stark pattern produced by the crystalline fields the lowest level is a singlet, which corresponds to a smaller magnetic moment than the higher levels. As the temperature falls, and the population in the ground level increases, the effective magnetic moment of the Pr^{+++} ion naturally diminishes, and the increase in susceptibility is therefore much less than in the inverse proportion to the temperature. Now the diminution in the effective magnetic moment is much greater when the applied magnetic field is along the hexagonal axis than when it is perpendicular to it. In other words $\chi_{\parallel}$, which at room temperature is greater than $\chi_{\perp}$, increases much less slowly than $\chi_{\perp}$, the result being that $\chi_{\parallel}-\chi_{\perp}$ passes through a maximum and then diminishes rapidly, reaching a large negative value, as experimentally observed.

TABLE VIII. $Pr_2(C_2H_5SO_4)_6 . 18H_2O$

Temp. °K	$\chi_{\parallel}-\chi_{\perp}$
303·1	241
296·0	252
273·0	279
250·9	297
237·1	306
230·6	313
210·0	322
189·7	307
168·1	254
148·7	116

TABLE IX. $Sm_2(C_2H_5SO_4)_6 . 18H_2O$

Temp. °K	$\chi_{\parallel}-\chi_{\perp}$
303·1	172
269·4	187
223·0	210
183·3	221
168·4	226
163·4	226
157·2	226
142·2	219
90·1	112

The results for samarium ethylsulphate are given in Table IX. This crystal has not been studied previously. The normal state of the Sm^{+++} ion is $^6H_{5/2}$ and the higher multiplet level with $J = 7/2$ is also occupied to some extent at room temperature; in considering the redistribution of the ions consequent on a change of temperature, we have therefore to take into account not only the Stark levels corresponding to the 5/2 state, but also those of the 7/2 state.

The magnetic behaviour of this crystal is very similar to that of the praseodymium salt, and it is probable that at sufficiently low temperatures $\chi_{\parallel}-\chi_{\perp}$ may become negative for this crystal also.

12. HEXAHYDRATED CHLORIDES OF THE RARE EARTHS

We shall now take up the room temperature measurements, on the anisotropy of some of the chlorides of the rare earth and the iron groups.

The absorption spectra of several rare earth salts of the type $M_2(SO_4)_3 . 8H_2O$ and $MCl_3 . 6H_2O$ have been studied in detail at different temperatures, and from a preliminary analysis of the spectra it has been inferred that the electric fields acting on the rare earth ions in these crystals should be nearly cubic in symmetry. A direct result of such a cubic symmetry is that the crystals should be magnetically isotropic, even when crystallographically they do not belong to the cubic system. In the sulphates, which have been studied magnetically, this result is not verified; they exhibit a marked anisotropy (Part V) showing that, in these salts at any rate, the crystalline fields deviate considerably from cubic symmetry.

Some of the features of the absorption spectra of these crystals also point to this conclusion. If we take the absorption lines which form a close group, many of which are presumably the Stark components originating from the same line of the *free* rare earth ion, the lines are in general strongly polarized, some of them along one, and some along another, of the principal axes of the optical ellipsoid of the crystal (Krishnan and Chakrabarty 1938).

If then in the sulphates, which are octahydrated, the crystalline fields are not cubic in symmetry, there seems to be a general impression that at least in the chlorides, which are hexahydrated, they should be so (Kynch 1937). Since there are just six water molecules associated with each rare earth ion, the octahedron formed by them is presumed to be regular, with the rare earth ion in the centre, and hence the electric field acting on the latter is presumed to be cubic.

In order to test the above surmise we have measured the magnetic anisotropies of some of these chlorides, using the same methods as were adopted by us in our earlier measurements. The results are given in Table X.

TABLE X

Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$\Delta\chi$	Magnetic anisotropy
$NdCl_3 . 6H_2O$	Monoclinic	"*b*" axis vertical	(100) plane at 78°·6 to the field	860	$\chi_1-\chi_2=860$
		"*c*" axis vertical	"*b*" axis normal to field	230	$\chi_1-\chi_3=265$
		(100) plane horizontal	"*c*" axis normal to field	560	$\lvert\psi\rvert=\begin{cases}78°\cdot6 \text{ obs.}\\78°\cdot4 \text{ cal.}\end{cases}$ Temp. = 26° C
$SmCl_3 . 6H_2O$	Monoclinic *a* : *b* : *c* = 1·471 : 1 : 1·218 β = 93° 26′ (Pabst 1931)	"*b*" axis vertical	(100) plane at 59°·1 to the field	340	$\chi_1-\chi_2=340$ $\chi_1-\chi_3=50$
		"*c*" axis vertical	"*b*" axis along field	42	$\lvert\psi\rvert=\begin{cases}59°\cdot1 \text{ obs.}\\58°\cdot9 \text{ cal.}\end{cases}$
		(100) plane horizontal	"*b*" axis along field	200	Temp. = 30° C
$ErCl_3 . 6H_2O$	Monoclinic, with nearly the same axial elements as the samarium salt	"*b*" axis vertical	(100) plane at 64°·1 to the field	8650	$\chi_1-\chi_2=8650$ $\chi_1-\chi_3=7600$
		"*c*" axis vertical	"*b*" axis normal to field	5900	$\lvert\psi\rvert=\begin{cases}64°\cdot1 \text{ obs.}\\63°\cdot8 \text{ cal.}\end{cases}$
		(100) plane horizontal	"*b*" axis normal to field	640	Temp. = 31° C

All the three crystals are monoclinic and isomorphous. In the particular specimens on which our magnetic measurements were made the side faces were not properly developed, and we were not therefore able to fix the sign of the angle ψ, i.e. to decide whether the χ_1-axis lies in the obtuse or the acute angle β between the "*a*" and the "*c*" axes.

With the "*b*" suspension (see Table X) both ψ and $\chi_1-\chi_2$ are determined, and with one other suspension $\chi_1-\chi_3$ also. We made, however, measurements with one more suspension of the crystal, so as to have a check on the results. From the measured anisotropies for the three suspensions the value of ψ is calculated, and compared with its value as measured directly with the "*b*" suspension. The two values agree well, as will be seen from the last column of the table.

In Table XI we give for the hydrated chlorides the values of the maximum anisotropy, i.e. the difference between the maximum and the minimum susceptibilities of the crystal. Similar values for the corresponding hydrated sulphates, taken from Part V, are also given in the table, for comparison with the chloride values.

Table XI. Values of the maximum anisotropy

	$MCl_3.6H_2O$	$\frac{1}{2}\times M_2(SO_4)_3.8H_2O$
M = Nd	860 (26° C)	500 (30° C)
Sm	340 (30° C)	220 (30° C)
Er	8650 (31° C)	4440 (30° C)

As will be seen from the table the chlorides have much larger anisotropies per rare earth ion than the corresponding sulphates. When we remember that even in the sulphates the anisotropies are by no means small, it is easy to realize that in the chlorides also the crystalline electric fields acting on the rare earth ions should be highly asymmetric.

As we mentioned in an earlier part of this paper, the proper measure of the asymmetry of the electric field acting on the rare earth ion is not the anisotropy of the crystal as a whole, but the anisotropy of the ion in its actual surroundings of negatively charged atoms. The latter anisotropy cannot be less than that of the crystal, but may be much greater, since the unit cell of the crystal contains more than one rare earth ion,* and the principal axes of the electric fields acting on the different ions in the cell will not, in general, be parallel to one another. The asymmetry of the electric fields acting on the rare earth ions may therefore be even larger than is suggested by the observed magnetic anisotropy of the crystal.

For the same reason, namely, that the crystal anisotropy gives only a lower limit to the anisotropy of the rare earth ion, and therefore to the asymmetry of the electric field acting on it, the higher crystal anisotropies observed for the chlorides as compared with the sulphates cannot be taken to imply that the electric fields in the chlorides are necessarily more asymmetric than in the sulphates. From the values given in Table XI we can, however, definitely conclude that in both the salts the asymmetry should be large.

13. Dihydrated cupric alkali chlorides

We have also measured at room temperature the anisotropies of some of the double chlorides of copper with the alkali atoms, of the type $R_2CuCl_4.2H_2O$, where $R = NH_4$, K or Rb. The crystals are tetragonal, and their structures have been studied by X-ray methods by Hendricks and Dickinson (1927) and by Chrobak (1929). A detailed discussion of the structures is given in a recent paper by Chrobak (1934). Two alternative structures are proposed, between which it seems to be difficult to decide from the

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* Actually eight in the sulphates (Zachariasen 1935); no data are available for the chlorides.

available X-ray data. According to the first, which is essentially that proposed by Hendricks and Dickinson, each Cu^{++} ion in the crystal is in the centre of an octahedron, formed by two oxygen atoms at the opposite corners and four chlorines, the diagonal joining the two oxygens being along the "*c*" axis. According to the second structure, each Cu^{++} ion in the crystal is in the centre of a cube formed by eight chlorine atoms. (The centres of two opposite faces of the cube are occupied by two oxygens, the line joining them being along the "*c*" axis.) Chrobak finds, after a detailed Fourier analysis, that though in the ammonium salt it is not possible to decide uniquely between the two structures, in the potassium salt the X-ray data favour the first structure.

The magnetic data for these crystals should throw some light on this question. Following Van Vleck, we may represent the potential of the electric field acting on the Cu^{++} ion by the expression

$$\Phi = D(x^4+y^4+z^4)+Ax^2+By^2-(A+B)z^2, \tag{12}$$

where the fourth power terms refer to the cubic part of the field and the quadratic terms to the rhombic part. The first structure, which corresponds to an octahedral distribution of six negative charges around the Cu^{++} ion, will give a positive value for D, the second a negative value (Gorter 1932); and a change in the sign of D will be equivalent to an inversion of the Stark pattern. Van Vleck has shown that for a given field, i.e. for a given sign of D, the Stark pattern for Cu^{++} is inverted with respect to that of Fe^{++}. Hence the pattern for Cu^{++} with negative D will be similar to that of Fe^{++} with positive D. Now since the spin-orbit coupling in Cu^{++} (852 cm.$^{-1}$) is much stronger than in Fe^{++} (100 cm.$^{-1}$), we should expect the anisotropy, $\Delta\chi/\chi$, of Cu^{++} with negative D to be much greater than that of Fe^{++} with positive D; and since experimentally the anisotropies of Cu^{++} and Fe^{++} in hydrated sulphates, selenates, etc., in which D is positive, are of comparable magnitude, we may conclude that the anisotropy of Cu^{++} should be much greater in crystals with negative D than in crystals with positive D; assuming of course, as we might justifiably, that the rhombic parts of the field are of comparable magnitude in the two classes of crystals. Thus an experimental study of the anisotropy of our double chlorides to find whether the anisotropy is of the same order of magnitude as in the hydrated sulphates and selenates, or is much higher, should enable us to decide whether the crystal has the first or the second of the structures proposed.

Feytis has measured the mean susceptibilities of the ammonium and the potassium salts, and finds that for both of them $\chi = 1370$ at 17° C.

TABLE XII. MAGNETIC ANISOTROPY OF $R_2CuCl_4.2H_2O$

Crystal	$\chi_\perp - \chi_\parallel$	Temp. ° C
$R = NH_4$	260	31·0
K	268	31·5
Rb	265	31·5

On comparing these values for the hydrated double chlorides with the corresponding values for the hydrated sulphates and selenates of copper, given in Parts II and V of this paper, we find (1) that their mean susceptibilities are the same as in the latter salts; and (2) that their anisotropies also are of the same order of magnitude as in the latter salts. The magnetic data for our double chlorides are thus decisively in favour of the first structure, namely that of Hendricks and Dickinson, which gives a positive D, as against the second.

The magnetic data further show that the crystals are typical double salts, whose composition can be represented by the formula $2R\text{Cl}.\text{CuCl}_2.2\text{H}_2\text{O}$, rather than a complex salt.

We have much pleasure in expressing our thanks to Professor W. F. Giauque for the gift of gadolinium sulphate, and to Dr S. Banerjee and Mr N. Ganguli for helping us in making some of the low temperature measurements.

14. Summary

The magnetic anisotropies of some typical salts of the rare earth and the iron groups have been measured at low temperatures down to about 90° K. A simple cryostat, with automatic temperature control, suitable for measurements of the magnetic anisotropies of crystals at low temperatures, is described. The results are discussed on the basis of the theory of paramagnetism in crystals developed by Van Vleck, Penney and Schlapp.

1. In those crystals in which the paramagnetic ions are all in the S-state, e.g. $\text{Gd}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$, $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2.6\text{H}_2\text{O}$, the anisotropy $\Delta\chi$ is found to vary inversely as the square of the absolute temperature.

2. In $\text{Gd}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$ the maximum anisotropy, though only 1·4 % of the mean susceptibility at room temperature, is still much larger than should be expected from the Stark separation of the S-levels of Gd^{+++} under the crystalline electric fields. The bulk of the observed anisotropy appears to arise from the magnetic interaction between the neighbouring Gd^{+++} ions.

3. Chromic salts have a very feeble anisotropy, almost as feeble as if the Cr^{+++} ion were in the S-state. The criterion for judging the suitability of a paramagnetic salt as working material in the production of low temperatures by the Debye-Giauque method is discussed.

4. From measurements on the magnetic anisotropy of nickel salts at different temperatures, the strength of the coupling between the orbital and the spin angular momenta of Ni^{++} is calculated, and is found to agree with the spectroscopic value.

5. Praseodymium and samarium ethylsulphates are of special interest. As we go down to low temperatures their anisotropies increase at first, reach a maximum, and then diminish rapidly.

6. The crystal fields in the rare earth chlorides, which are hexahydrated, are as strongly asymmetric as in the sulphates, which are octahydrated.

7. Magnetic measurements on the cupric alkali chlorides enable us to decide between the alternative structures proposed for these crystals from X-ray studies.

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