Investigations on Magne-Crystallic Action. IV. Magnetic Behaviour of Paramagnetic Ions in the S-State in Crystals

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X—Investigations on Magne-Crystallic Action

IV—Magnetic Behaviour of Paramagnetic Ions in the S-State in Crystals

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Contents

I—Introduction

In Part II* of this paper we gave an account of measurements on the principal susceptibilities of some paramagnetic sulphates and double-sulphates of the iron group of metals. In view of the interest which the subject of crystal magnetism has acquired by the recent theoretical publications of Bethe, Kramers, Van Vleck,

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* 'Phil. Trans.,' A, vol. 232, p. 99 (1933). We wish to correct here some errors that appear in in the earlier Parts. In Part I the principal susceptibilities of naphthalene and anthracene should be as follows:

	$-\chi_1$	$-\chi_2$	$-\chi_3$	ψ
Naphthalene	56·0	146·4	76·6	12°·0
Anthracene	75·5	211·8	102·9	8°·0

In Part III, Table I, the value of θ for phenanthrene should read $-11°\cdot4$ instead of $+11°\cdot4$, and ψ should be equal to $+19°\cdot7$.

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Penney, and others, further extensive studies on paramagnetic crystals were undertaken. The present part of the paper deals with crystals in which the paramagnetic ions are all in the S-state, which are of special interest. Magnetic studies on the other crystals will be described in a later paper.

II—Van Vleck's Theory

Bethe and Kramers have discussed theoretically the problem of the Stark splitting of the energy-levels of an atom or ion under the influence of crystalline fields. On the basis of their results, Van Vleck, Penney, and Schlapp* have developed a general theory of the magnetic properties of paramagnetic crystals, which explains satisfactorily (1) the relative contributions of the orbital and spin moments to the susceptibility, (2) the magnetic anisotropy of the crystals, and (3) the temperature variation of their principal susceptibilities.

The theory is somewhat as follows. Consider an assemblage of *free* paramagnetic ions having an angular momentum J. In zero magnetic field, the $(2J + 1)$ *m*-states of the ion will naturally all have the same energy. On the application of a magnetic field the degeneracy will be completely removed, *i.e.*, the different *m*-states will split up, the distribution of the ions among these states will become unequal, and the ions will, in consequence, have a resultant magnetic moment along the field. This accounts for their paramagnetism. If, however, the ions had not been free, but had been under the influence of strong asymmetric crystalline electric fields, the degeneracy in respect of the *orbital* moments of the ions would already have been removed by these fields. If, further, the corresponding energy separations of the levels were large compared with kT, the distribution of the ions among these levels will remain practically unaffected by the application of the magnetic field, and there will thus be no contribution from the orbital moments to the effective magnetic moments of the ions.

The *spin* moments, on the other hand, are not affected directly by the crystalline fields, though indirectly they would be, through their coupling with the orbital moments. The latter having been frozen, the coupling of the spins with them would be equivalent to subjecting the spins to local fields, which, because of the asymmetry of the crystalline fields responsible for the freezing of the orbital moments, would also be asymmetric. The result would be : (1) the crystal would exhibit a magnetic anisotropy, (2) the temperature variation of its principal susceptibilities would deviate from the Curie law.

III—Theory Applied to Ions in the S-State

If thus the anisotropy of the crystal and the deviations from the Curie law arise from the coupling of the spins with orbital moments which have been frozen by asymmetric crystalline fields, then both these effects should disappear when the orbital

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* *See* Van Vleck, " Theory of Electric and Magnetic Susceptibilities " (Oxford, 1932), chap. xi.

moments are zero, *i.e.*, when the paramagnetic ions are in the S-state. That is, (1) crystals whose paramagnetic ions are in the S-state should be more or less isotropic magnetically, even when the crystals do not belong to the cubic system. This result has been verified by RABI* and by JACKSON† with single crystals of manganous and ferric salts (the ground state for both Mn^{++} and Fe^{+++} ions is $^6S_{5/2}$), for which they find that the three principal susceptibilities do not differ from one another by more than one per cent. (2) The susceptibility should follow the simple Curie law. This result also has been verified for manganous and ferric ions, in the crystal state by JACKSON (*loc. cit.*), and in state of solution by A. BOSE.‡

IV—MAGNETIC ANISOTROPY OF S-STATE IONS

More accurate measurements, however, show that manganous salts do have a definite, though very small, magnetic anisotropy,§ and its explanation offers many points of interest. As we shall show in this paper, a small part of the anisotropy is that of the diamagnetism of the salt, and another part, which should be even smaller, may arise from the mutual influence of the magnetic moments of the Mn^{++} ions. The rest of the anisotropy should be attributed to the following cause: though, as we mentioned in the previous section, the S-levels, to a first approximation, are not affected by the crystalline electric fields, KRAMERS has shown that when higher order approximations are considered, even the S-levels have a feebly separated Stark multiplet structure; this will naturally lead to an anisotropy, as in other paramagnetic crystals, but of course very much feebler.

If then from the observed anisotropy we can separate the small contributions from the first two causes, and obtain that due to the Stark splitting alone, we can use it to calculate the magnitude of the splitting. This will be of great interest in view of the important part played by this splitting at temperatures close to absolute zero, especially since we do not, at present, possess enough knowledge of either the magnitude or the asymmetry of crystalline fields to be able to calculate the Stark splitting directly.

The present paper concerns itself with a detailed study of the magnetic anisotropy of single crystals of manganous and ferric salts. The different causes which contribute to the anisotropy are discussed, and methods are devised for separating their effects. The anisotropy due to crystalline Stark splitting alone is thus obtained, and the magnitude of the splitting is calculated therefrom. The result is discussed in relation to the entropy and the specific heat of the salt at very low temperatures, and in relation to other physical phenomena that are influenced by the splitting.

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* 'Phys. Rev.,' vol. 29, p. 174 (1927).

† 'Proc. Roy. Soc.,' A, vol. 140, p. 695 (1933).

‡ 'Nature,' vol. 133, p. 213 (1934); 'Proc. Ind. Acad. Sci.,' A, vol. 1, pp. 605, 753 (1935).

§ *See* Part II of this paper, 'Phil. Trans.,' A, vol. 232, pp. 105–109 (1933). The values for the magnetic anisotropy of manganous ammonium sulphate crystal given in Part II are too high. *See* Table I of the present paper.

V—MEASUREMENTS ON MANGANOUS AND FERRIC SALTS

We shall first explain the notation adopted in this paper. All the crystals studied were monoclinic. The two principal gram molecular susceptibilities of the crystal in the (010) plane are denoted by χ_1 and χ_2 respectively, χ_1 being greater than χ_2. The third susceptibility, viz., that along the " *b* " axis, 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 " *c* " and " *a* ". Since the (001) faces of the crystals were well-developed, the inclination θ of the χ_2- axis to this face was sometimes directly measured, the positive direction of θ being defined by the relation $\pi/2 + \theta + \psi = \beta$ (obtuse).

The experimental method adopted in the following measurements is the same as that described in Part II of this paper for manganous ammonium sulphate. The measurements consist of two parts.

(1) *The Measurement of the Absolute Susceptibility Along any Convenient Direction in the Crystal*—The crystal is suspended, with its " *b* " axis vertical, at the end of a long, thin quartz fibre, so as to lie between the conical pole-pieces of a magnet, at the same height as the central axis of the magnet, but slightly to one side. The crystal is kept surrounded by a saturated aqueous solution of the substance, which holds in solution suitable amounts of manganous chloride as well. When the field is put on, the crystal turns round so as to bring its χ_1-axis along the field, and further moves laterally along the direction of the field-gradient, either towards the centre of the field or away from it depending on whether the *volume* susceptibility of the crystal along the χ_1-axis is greater or less than that of the liquid bath. Firstly, the torsion-head from which the crystal is suspended is suitably rotated so as to make the torsion on the fibre zero when the χ_1-axis is along the field. Secondly, the concentration of $MnCl_2$ in the bath is adjusted until there is no lateral motion of the crystal. Under these conditions the volume susceptibility of the crystal along the χ_1-axis is the same as that of the solution. The latter is measured by the well-known Gouy method by comparing the weight of the solution in a magnetic field, with that of a standard solution of $NiCl_2$ of known susceptibility in the same field.

(2) *Measurement of Anisotropy*—The conical pole-pieces are now replaced by the usual flat ones in order to obtain a large *uniform* field. The crystal is suspended as before with the " *b* " axis vertical, from the end of the fibre—which has now been calibrated—in the centre of the field; further, it is kept surrounded by the liquid bath described in the previous paragraph, having the same volume susceptibility as the crystal. Before the field is put on, the torsion-head is suitably rotated in order that the (001) plane of the crystal (which is usually well developed*) may be exactly normal to the direction of the field. The field is now put on, and the direction in

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* When any other vertical face (*h*0*l*) was better developed than (001), it was, of course, chosen as the reference plane in preference to (001).

which the crystal tends to rotate is noted—whether the "c" axis, which was originally at an angle of $\beta - \pi/2$ to the field, tends to move towards the field direction or away from it. The torsion-head is rotated in the opposite direction, through an angle α_1, say, so as to bring the (001) plane back to normality with the field. If the rotation of the torsion-head is continued in the same direction, there will come a stage when the χ_1 and χ_2 axes just make 45° with the field, and the couple due to the field is a maximum. With the smallest further rotation of the torsion-head, the crystal suddenly turns round. Let α_2 be the angle of rotation of the torsion-head from its initial position, necessary to bring it to the above critical position. Then from the relations

$$\sin 2\theta = \frac{\alpha_1}{\alpha_2 - \pi/4 + \theta}, \quad \ldots\ldots\ldots\ldots \quad (1)$$

and

$$\chi_1 - \chi_2 = \frac{2Mc}{mH^2}(\alpha_2 - \pi/4 + \theta), \quad \ldots\ldots\ldots \quad (2)$$

where c is the torsional constant of the fibre, H is the field, m is the mass of the crystal, and M is its gram molecular weight, both θ and $\chi_1 - \chi_2$ are known.

Measurement of $\Delta\chi$ for one other direction of suspension of the crystal enables us now to determine $\chi_1 - \chi_3$. Usually measurements were made for a third suspension also, so as to have a check on the values obtained.

VI—Results

The results of the measurements on anisotropy are given in Table I. In addition to the paramagnetic crystals, the isomorphous diamagnetic crystals obtained by replacing the Mn in them by Mg or Zn, and the Fe by Al, were also studied by us for their anisotropy. The magnetic data for the latter crystals also are included in Table I, and they are needed for correcting for the anisotropy of the diamagnetic part of the susceptibility of the former. Measurements on some mixed crystals are reported in Tables V and VI. All the measurements were made at room temperature, but, for the sake of uniformity, the results have all been reduced to 30° C. The susceptibilities are expressed in the usual unit, 10^{-6} c.g.s. e.m.u.

The measurements on the absolute susceptibilities of the paramagnetic crystals are given in Table II. In the last column of the table is given the magnetic moment of the Mn^{++} or Fe^{+++} ion in the crystal; the mean susceptibility of the crystal, given in the penultimate column, was corrected for its diamagnetism, and from the corrected value the moment of the paramagnetic ion was calculated on the assumption that its susceptibility obeys the Curie law, which, as we have seen, is justified since both Mn^{++} and Fe^{+++} ions are in the S-state, viz., ${}^6S_{5/2}$. The theoretical value of the moment is 29·4 Weiss magnetons. Though the experimental values agree closely with this value, the small deviations that occur are consistently on one side, the experimental values being slightly lower. It is difficult to decide whether this

TABLE I

Serial number 1	Crystal 2	Crystallographic data 3	Mode of suspension 4	Orientation in the field 5	$\|\Delta\chi\|$ 6	Magnetic anisotropy 7
1	$Mn(NH_4)_2\ (SO_4)_2 . 6H_2O$	Mcnoclinic prism $a : b : c$ = 0·740 : 1 : 0·493	" b " axis vertical (001) plane horizontal	$\theta = +33°$ " a " axis normal to field	8·7 0·1	$\chi_1 - \chi_2 =$ 8·7 $\chi_1 - \chi_3 =$ 6·0 $\psi = -16°$
		$\beta = 106° 51'$	" a " axis vertical	" b " ,, ,,	3·5	Cal. $\Delta\chi =$ 3·4
2	$MnRb_2\ (SO_4)_2 . 6H_2O$	Monoclinic prism $a : b : c$ = 0·738 : 1 : 0·495	" b " axis vertical (001) plane horizontal	$\theta = +28°$ " a " axis normal to field	8·9 0·7	$\chi_1 - \chi_2 =$ 8·9 $\chi_1 - \chi_3 =$ 6·2 $\psi = -12°$
		$\beta = 105° 57'$	" a " axis vertical	" b " ,, ,,	4·3	Cal. $\Delta\chi =$ 4·2
3	$MnCs_2\ (SO_4)_2 . 6H_2O$	Monoclinic prism $a : b : c$ = 0·727 : 1 : 0·491	" b " axis vertical (001) plane horizontal	$\psi = -12\frac{1}{2}°$ " a " axis normal to field	7·0 0·3	$\chi_1 - \chi_2 =$ 7·0 $\chi_1 - \chi_3 =$ 5·0 $\psi = -12\frac{1}{2}°$
		$\beta = 107° 7'$	" a " axis vertical	" b " ,, ,,	3·1	Cal. $\Delta\chi =$ 3·3
4	$MnTl_2\ (SO_4)_2 . 6H_2O$	Monoclinic prism $a : b : c$ = 0·745 : 1 : 0·496	" b " axis vertical (001) plane horizontal	$\theta = +33°$ " b " axis normal to field	8·9 0·9	$\chi_1 - \chi_2 =$ 8·9 $\chi_1 - \chi_3 =$ 7·2 $\psi = -16\frac{1}{2}°$
		$\beta = 106° 22'$	" a " axis vertical	" b " ,, ,,	4·7	Cal. $\Delta\chi =$ 4·6
5	$MnK_2\ (SO_4)_2 . 4H_2O$	Monoclinic prism $a : b : c$ = 1·032 : 1 : 1·249	" b " axis vertical (001) plane horizontal	$\theta = +66°$ " a " axis along field	4·3 0·8	$\chi_1 - \chi_2 =$ 4·3 $\chi_1 - \chi_3 =$ 1·5 $\psi = -61°$
		$\beta = 95° 0'$ (does not belong to the Tutton series)	" a " axis vertical	" b " ,, ,,	2·0	Cal. $\Delta\chi =$ 2·1
6	$Mn(NH_4)_2\ (SeO_4)_2 . 6H_2O$	Moniclinic prism $a : b : c$ = 0·743 : 1 : 0·499	" b " axis vertical " a " ,,	$\psi = -20°$ " b " axis normal to field	8·9 3·2	$\chi_1 - \chi_2 =$ 8·9 $\chi_1 - \chi_3 =$ 6·3 $\psi = -20°$
		$\beta = 106° 16'$	(001) plane horizontal	" b " ,, ,,	0·6	Cal. $\Delta\chi =$ 0·5

TABLE I—(continued)

Serial number 1	Crystal 2	Crystallographic data 3	Mode of suspension 4	Orientation in the field 5	$\lvert\Delta\chi\rvert$ 6	Magnetic anisotropy 7
7	$MnRb_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +29°$	9·0	$\chi_1 - \chi_2 =$ 9·0
		a : *b* : *c*	(001) plane horizontal	" *b* " axis normal to field	0·4	$\chi_1 - \chi_3 =$ 7·3
		= 0·742 : 1 : 0·501				$\psi = -$ 14°
		β = 105° 9′	" *a* " axis vertical	" *b* " ,, ,,	5·2	Cal. $\Delta\chi$ = 5·2
8	$MnTl_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +29\frac{1}{2}°$	10·2	$\chi_1 - \chi_2 =$ 10·2
		a : *b* : *c*	" *a* " ,,	" *b* " axis normal to field	6·0	$\chi_1 - \chi_3 =$ 8·5
		= 0·746 : 1 : 0·499				$\psi = -$ 14°
		β = 105° 29′	(001) plane horizontal	" *b* " ,, ,,	0·8	Cal. $\Delta\chi$ = 0·8
9	$K_3Fe(C_2O_4)_3 . 3H_2O$	Monoclinic prism	" *b* " axis vertical	(001) plane nearly along field and (10$\bar{1}$) at 73½° to it	28	$\chi_1 - \chi_2 =$ 28
		a : *b* : *c*				$\chi_1 - \chi_3 =$ 77
		= 0·992 : 1 : 0·390				
		β = 94° 15′	(10$\bar{1}$) plane horizontal	" *b* " axis normal to field	51	$\psi = -$ 1°
			both (10$\bar{1}$) and (010) planes vertical	" *b* " ,, ,,	74	Cal. $\Delta\chi$ = 75
10	$Na_3Fe(C_2O_4)_3 . 5H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +12°$	31	$\chi_1 - \chi_2 =$ 31
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	6	$\chi_1 - \chi_3 =$ 24
		= 1·369 : 1 : 1·201				$\psi = -$ 2°
		β = 100° 15′	" *a* " axis vertical	" *b* " ,, ,,	22	Cal. $\Delta\chi$ = 23
	Diamagnetic crystals					
11	$Mg(NH_4)_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +22°$	1·1	$\chi_1 - \chi_2 =$ 1·1
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·3	$\chi_1 - \chi_3 =$ 0·6
		= 0·740 : 1 : 0·492				$\psi = -$ 5°
		β = 107° 6′	" *a* " axis vertical	" *b* " ,, ,,	0·6	Cal. $\Delta\chi$ = 0·4
12	$Zn(NH_4)_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +11°$	1·2	$\chi_1 - \chi_2 =$ 1·2
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·4	$\chi_1 - \chi_3 =$ 0·8
		= 0·737 : 1 : 0·500				$\psi = +$ 6°
		β = 106° 52′	" *a* " axis vertical	" *b* " ,, ,,	0·7	Cal. $\Delta\chi$ = 0·8

TABLE I—(continued)

Serial number 1	Crystal 2	Crystallographic data 3	Mode of suspension 4	Orientation in the field 5	$\lvert\Delta\chi\rvert$ 6	Magnetic anisotropy 7
13	$MgRb_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +3°$	0·9	$\chi_1 - \chi_2 =$ 0·9
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·2	$\chi_1 - \chi_3 =$ 0·7
		= 0·740 : 1 : 0·498				$\psi = +13°$
		$\beta = 105° 59'$	" *a* " axis vertical	" *b* " ,, ,,	0·7	Cal. $\Delta\chi$ = 0·7
14	$ZnRb_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = -7\frac{1}{2}°$	0·9	$\chi_1 - \chi_2 =$ 0·9
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·3	$\chi_1 - \chi_3 =$ 0·6
		= 0·737 : 1 : 0·501				$\psi = +23\frac{1}{2}°$
		$\beta = 105° 53'$	" *a* " axis vertical	" *b* " ,, ,,	0·6	Cal. $\Delta\chi$ = 0·6
15	$MgCs_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = -34°$	1·3	$\chi_1 - \chi_2 =$ 1·3
		a : *b* : *c*	(001) plane horizontal	" *b* " axis normal to field	0·1	$\chi_1 - \chi_3 =$ 1·0
		= 0·728 : 1 : 0·495				$\psi = +51°$
		$\beta = 107° 6'$	" *a* " axis vertical	" *b* " ,, ,,	0·5	Cal. $\Delta\chi$ = 0·6
16	$MgTl_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +10\frac{1}{2}°$	0·8	$\chi_1 - \chi_2 =$ 0·8
		a : *b* : *c*	(001) plane horizontal	" *b* " axis normal to field	0·5	$\chi_1 - \chi_3 =$ 1·3
		= 0·744 : 1 : 0·500				$\psi = +6°$
		$\beta = 106° 30'$	" *a* " axis vertical	" *b* " ,, ,,	1·2	Cal. $\Delta\chi$ = 1·3
			" *c* " ,,	" *b* " ,, ,,	0·5	Cal. $\Delta\chi$ = 0·5
17	$MgK_2(SO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\psi = -2°$	1·2	$\chi_1 - \chi_2 =$ 1·2
		a : *b* : *c*	(001) plane horizontal	" *b* " axis along field	0·4	$\chi_1 = \chi_3 =$ 0·7
		= 0·741 : 1 : 0·499				$\psi = -2°$
		$\beta = 104° 48'$	(100) ,,	" *c* " ,, ,,	0·7	Cal. $\Delta\chi$ = 0·7
18	$MgNa_2(SO_4)_2 . 4H_2O$ (Bloedite)	Monoclinic prism	" *b* " axis vertical	$\theta = -55°$	0·5	$\chi_1 - \chi_2 =$ 0·5
		a : *b* : *c*	" *a* " ,,	" *b* " axis normal to field	0·4	$\chi_1 - \chi_3 =$ 0·7
		= 1·349 : 1 : 0·672				$\psi = +66°$
		$\beta = 100° 48'$ (does not belong to the Tutton series: isomorphous with $MnK_2(SO_4)_2 . 4H_2O$)	(001) plane horizontal	" *b* " ,, ,,	0·6	Cal. $\Delta\chi$ = 0·5

TABLE I—(continued)

Serial number 1	Crystal 2	Crystallographic data 3	Mode of suspension 4	Orientation in the field 5	$\lvert\Delta\chi\rvert$ 6	Magnetic anisotropy 7
19	$Mg(NH_4)_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " vertical	$\theta = +19\frac{1}{2}°$	1·5	$\chi_1 - \chi_2 =$ 1·5
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·3	$\chi_1 - \chi_3 =$ 1·0
		= 0·742 : 1 : 0·497				$\psi = -$ 3°
		β = 106° 27′	" *a* " axis vertical	" *b* " ,, ,,	0·8	Cal. $\Delta\chi$ = 0·8
20	$MgRb_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +11°$	1·3	$\chi_1 - \chi_2 =$ 1·3
		a : *b* : *c*	(001) plane horizontal	" *a* " axis normal to field	0·2	$\chi_1 - \chi_3 =$ 1·1
		= 0·742 : 1 : 0·501				$\psi = +$ 4°
		β = 105° 14′	" *a* " axis vertical	" *b* " ,, ,,	1·0	Cal. $\Delta\chi$ = 1·1
21	$MgTl_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +16°$	2·0	$\chi_1 - \chi_2 =$ 2·0
		a: *b* : *c*	" *a* " ,,	" *b* " axis normal to field	2·4	$\chi_1 - \chi_3 =$ 2·6
		= 0·749 : 1 : 0·499				$\psi =$ 0
		β = 105° 36′	(001) plane horizontal	" *b* " ,, ,,	0·8	Cal. $\Delta\chi$ = 0·8
22	$K_3Al(C_2O_4)_3 . 3H_2O$	Monoclinic prism	" *b* " axis vertical	$\psi = +19°$	6·9	$\chi_1 - \chi_2 =$ 6·9
		a : *b* : *c*	(100) plane horizontal	" *b* " axis normal to field	12·4	$\chi_1 - \chi_3 =$ 13·1
		= 0·999 : 1 : 0·395				$\psi = +$ 19°
		β = 92° 51′	" *c* " axis vertical	" *b* " ,, ,,	6·9	Cal. $\Delta\chi$ = 6·9
23	$Na_3Al(C_2O_4)_3 . 5H_2O$	Monoclinic prism	" *b* " axis vertical	$\theta = +\frac{1}{2}°$	4·9	$\chi_1 - \chi_2 =$ 4·9
		a : *b* : *c*	" *a* " ,,	" *b* " axis normal to field	8·5	$\chi_1 - \chi_3 =$ 8·5
		= 1·399 : 1 : 1·198				$\psi = +$ 9°
		β = 99° 28′	(001) plane horizontal	" *b* " ,, ,,	3·6	Cal. $\Delta\chi$ = 3·6

TABLE II

Serial number	Crystal	Direction along which susceptibility was measured	Temp °C	Density of crystal	Vol. susceptibility	Corresponding gm mol susceptibility	Mean gm mol susceptibility at 30° C	Magnetic moment of Mn^{++} or Fe^{+++} in Weiss Magnetons
1	2	3	4	5	6	7	8	9
1	$Mn(NH_4)_2(SO_4)_2 . 6H_2O$	Along χ_1-axis	30·8	1·834	64·7	13,800	13,830	29·0
2	$MnRb_2(SO_4)_2 . 6H_2O$	,, χ_1-axis	30·6	2·456	65·8	14,090	14,030	29·2
		,, χ_1-axis	28·4	2·473	66·0	14,040		
3	$MnCs_2(SO_4)_2 . 6H_2O$	,, χ_1-axis	24·0	2·762	62·5	14,050	13,820	29·0
		,, χ_1-axis	21·6	2·734	62·8	14,270		
4	$MnTl_2(SO_4)_2 . 6H_2O$	,, " *a* "-axis	32·3	3·42	61·8	13,800	13,910	29·1
5	$MnK_2(SO_4)_2 . 4H_2O$	,, " *b* "-axis	29·6	2·330	81·1	13,820	13,830	29·0
6	$Mn(NH_4)_2(SeO_4)_2 . 6H_2O$	,, χ_1-axis	30·9	2·123	60·4	13,800	13,840	29·0
7	$MnRb_2(SeO_4)_2 . 6H_2O$	,, χ_1-axis	25·8	2·748	62·7	14,160	13,980	29·2
		,, χ_1-axis	27·1	2·748	62·6	14,150		
8	$MnTl_2(SeO_4)_2 . 6H_2O$	,, χ_1-axis	29·5	3·526	58·7	14,290	14,290	29·5
		,, " *b* "-axis	26·0	3·522	59·6	14,520		
9	$Na_3Fe(C_2O_4)_3 . 5H_2O$	,, " *b* "-axis	25·8	1·928	57·7	14,330	14,180	29·3
			26·1	1·919	57·6	14,370		
10	$K_3Fe(C_2O_4)_3 . 3H_2O$	,, χ_1-axis	23·8	2·134	62·3	14,330	13,960	29·1
			25·2	2·167	62·5	14,170		

is due to merely experimental errors arising from the imperfections in the crystals, or to a small negative Weiss constant Θ in the expression $\chi = C/(T - \Theta)$ arising from a feeble exchange interaction between the spin moments. The first cause seems to be more probable, especially since the magnitudes of the deviations from 29·4 are quite arbitrary.

VII—ANISOTROPY OF THE DIAMAGNETISM OF THE CRYSTALS

As is well-known, diamagnetic crystals also exhibit a feeble anisotropy, so that a part of the observed anisotropy of the manganous and ferric salts should be that of their diamagnetism. Let us denote it by $(\Delta\chi)_d$. Theoretically, it can be eliminated since it should be independent of temperature, whereas the paramagnetic part of the anisotropy should vary approximately as its inverse square. But practically, this method of separating $(\Delta\chi)_d$ is neither convenient nor accurate, and it is desirable to obtain it *indirectly* in the following manner.

Let us consider manganous Tutton salts, of the type $MnSO_4 . A_2SO_4 . 6H_2O$, or $MnSeO_4 . A_2SeO_4 . 6H_2O$, where A represents a monovalent atom. It is well known that by replacing the Mn in them by either Mg or Zn we obtain a series of diamagnetic crystals which are isomorphous with the corresponding manganous salts. We have studied the magnetic anisotropies of these diamagnetic salts as well, and the results obtained are given in Table I. They reveal the following characteristics. (1) The anisotropies of the diamagnetic Tutton salts are much smaller than those of the manganous salts, suggesting that for the latter salts $(\Delta\chi)_d$ is only a small part of the observed $\Delta\chi$. (2) The diamagnetic anisotropies show only small variations from crystal to crystal. (3) Even these small variations occur only when the monovalent atom A is changed, or when the SO_4 group is replaced by SeO_4; when, on the other hand, the divalent atom Mg is replaced by Zn, there is practically no variation in anisotropy; and it may therefore be presumed that when either of them is replaced by Mn the anisotropy of the diamagnetism of the crystal will still be the same.

Since our present purpose in estimating the diamagnetic part of the anisotropy is merely to separate it from the main anisotropy due to splitting, in which we are specially interested, we can reasonably assume that for any given manganous salt the diamagnetic anisotropy $(\Delta\chi)_d$ is the same as that of the isomorphous diamagnetic salt obtained by replacing the Mn by either Mg or Zn, the other atoms in the molecule being kept the same.

VIII—ANISOTROPY DUE TO THE MUTUAL INFLUENCE OF THE MAGNETIC MOMENTS

Had the paramagnetic ions in the crystal been arranged in a regular cubic lattice, the Poisson-Lorentz magnetic polarization field acting on any of the ions would be isotropic, and equal to $\frac{4}{3}\pi\kappa H$, where κ is the *volume* susceptibility of the crystal and

H is the field in the medium. When, however, as in a manganous ammonium sulphate crystal, the distribution of the Mn^{++} ions surrounding any given one deviates from cubic symmetry, the polarization fields will be asymmetric, and the crystal will be magnetically anisotropic in consequence. The principal susceptibilities will be given by the expressions—

$$\chi_q = \chi_0 (1 + \Phi_q \kappa), \qquad q = 1, 2, 3, \quad \ldots \ldots \quad (3)$$

where

$$\Phi_1 + \Phi_2 + \Phi_3 = 4\pi. \quad \ldots \ldots \quad (4)$$

Φ_1, Φ_2, and Φ_3 are constants characteristic of the distribution of the Mn^{++} ions in the crystal, and χ_0 is the susceptibility of the *free* ions.

The corresponding anisotropy $(\Delta\chi)_m$ due to the mutual influence of the magnetic moments would be equal to $\Delta\,\Phi\kappa\chi_0$.

The structure of the Tutton salts has been studied in detail by HOFMANN* by X-ray methods. The dimensions of the unit cell are roughly $a = 9{\cdot}2$, $b = 12{\cdot}5$, $c = 6{\cdot}2$ A, $\beta = 107°$, and the two divalent ions in the unit cell occupy the positions (000) and $(\frac{1}{2}\frac{1}{2}0)$. With these positions for the Mn^{++} ions it is possible to calculate the Φ's. The calculation is laborious; but a rough estimate can be made, and it is found that they cannot differ much from $4\pi/3$, and that the $\Delta\,\Phi$'s should be much less than unity. Since at room temperature the *volume* susceptibilities κ of the manganous Tutton salts are about 60×10^{-6}, the corresponding anisotropy is given by

$$(\Delta\chi)_m/\chi = \Delta\Phi\,.\,\kappa < 6 \times 10^{-5}\,; \quad \ldots \ldots \quad (5)$$

i.e., the anisotropy due to the mutual magnetic influence of the Mn^{++} ions in these crystals can not be greater than a tenth part of the observed anisotropy, and is probably much less. It may therefore be neglected to a first approximation.

IX—THE STARK ANISOTROPY

Thus the correction for the diamagnetic anisotropy is the only appreciable correction to be made, and applying it we obtain directly the anisotropy due to the crystalline Stark splitting of the S-levels.† In making this correction it should be remembered that the principal axes of diamagnetism are not the same as the observed principal magnetic axes, because, as will be seen from Table I, the ψ's for the manganous and the corresponding Mg (or Zn) salts are not identical.

Let OF in fig. 1 be the direction of the χ_1 axis as actually observed, OD that of the diamagnetic χ_1 axis, and OS that of the paramagnetic χ_1 axis. Let their relative inclinations be as marked in the figure. If $(\chi_1 - \chi_2)_f$ be the *observed* anisotropy in

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* 'Z. Kristallog.', vol. 78, p. 279 (1931)

† The exchange interactions between the spin moments may also have an influence on the splitting. But for such large magnetic dilutions as obtain in the Tutton salts it should be small. At any rate, we shall neglect it for the present and refer to it again in a later portion of this paper.

the (010) plane, $(\chi_1 - \chi_2)_d$ the diamagnetic part, and $(\chi_1 - \chi_2)_s$ the paramagnetic part (the Stark anisotropy), then*

$$\tan 2\sigma = P/Q, \qquad (6)$$

where

$$P = (\chi_1 - \chi_2)_d \sin 2\delta \qquad (7)$$

$$Q = (\chi_1 - \chi_2)_f - (\chi_1 - \chi_2)_d \cos 2\delta. \qquad (8)$$

Thus σ, and therefore the directions of the paramagnetic axes, are known.

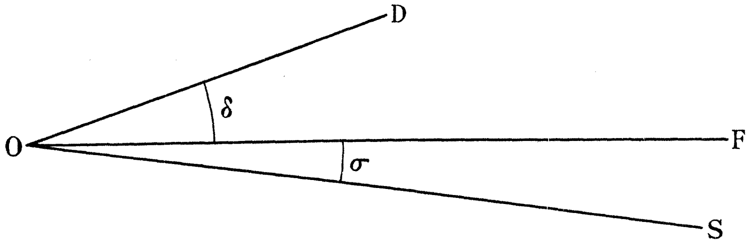

FIG. 1.

The anisotropy of the paramagnetism is given by the expressions

$$(\chi_1 - \chi_2)_s = (P^2 + Q^2)^{\frac{1}{2}}, \qquad (9)$$

and

$$(\chi_1 - \chi_3)_s = \tfrac{1}{2}\,[(\chi_1 - \chi_2)_s - (\chi_1 - \chi_2)_f + (\chi_1 - \chi_2)_d] + [(\chi_1 - \chi_3)_f - (\chi_1 - \chi_3)_d]. \qquad (10)$$

The data given in the last three columns of Table III were calculated in this manner.

X—MAGNITUDE OF THE STARK SPLITTING

We can now use the Stark anisotropies given in the last two columns of Table III to calculate the magnitude of the splitting of the S levels of Mn^{++} under the crystalline fields. The theoretical relations between the splitting and the anisotropy have been worked out in detail by VAN VLECK and PENNEY.† We shall merely quote here their final results. For a crystal whose paramagnetic ions are all in the ^6S state, the three principal susceptibilities are given by the expressions—

$$\chi_1 = C\left(\frac{1}{T} + \frac{2r}{T^2} + \ldots\right) \qquad (11A)$$

$$\chi_2 = C\left(\frac{1}{T} - \frac{r+s}{T^2} + \ldots\right) \qquad (11B)$$

$$\chi_3 = C\left(\frac{1}{T} - \frac{r-s}{T^2} + \ldots\right) \qquad (11C)$$

$$C = \frac{N\mu^2}{3k}, \qquad (12)$$

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* The derivation of these expressions for σ and for the paramagnetic anistropy is simple.

† 'Phil. Mag.,' vol. 17, p. 961 (1934).

TABLE III

Crystal	Observed anisotropy $(\Delta\chi)_f$			Anisotropy of the corresponding Mg salt $(\Delta\chi)_d$			Stark anisotropy $(\Delta\chi)_s$		
	ψ	$\chi_1-\chi_2$	$\chi_1-\chi_3$	ψ	$\chi_1-\chi_2$	$\chi_1-\chi_3$	ψ	$\chi_1-\chi_2$	$\chi_1-\chi_3$
$MnSO_4 . R_2SO_4 . 6H_2O$									
R = NH_4	−16°	8·7	6·0	− 5°	1·1	0·6	−17½°	7·7	5·5
				Zn salt : + 6°	1·2	0·8	−19°	7·8	5·4
Rb	−12°	8·9	6·2	+13°	0·9	0·7	−14½°	8·3	5·7
				Zn salt : +23½°	0·9	0·6	−15°	8·6	5·9
Cs	−12½°	7·0	5·0	+51°	1·3	1·0	−16°	7·9	5·1
Tl	−16½°	8·9	7·2	+ 6°	0·8	1·3	−18½°	8·3	6·0
$MnSeO_4 . R_2SeO_4 . 6H_2O$									
R = NH_4	−20°	8·9	6·3	− 3°	1·5	1·0	−23°	7·7	5·5
Rb	−14°	9·0	7·3	+ 4°	1·3	1·1	−17°	7·9	6·3
Tl	−14°	10·2	8·5	0	2·0	2·6	−17°	8·5	6·1
$MnSO_4 . K_2SO_4 . 4H_2O$ . . (does not belong to the Tutton series)	−61°	4·3	1·5	+66°	0·5	0·7	−58°	4·4	1·1

where μ is the magnetic moment of the ion, equal to $g\beta\sqrt{5/2 \times 7/2}$; N is the Avogadro number, k, is the Boltzmann constant, g is the Landé factor (equal to 2), β is the Bohr magneton, $eh/(4\pi mc)$ and T is the absolute temperature;

$$r = \frac{12a + 8b}{35k}, \qquad s = \frac{4\sqrt{10}\,.\,c + 12\sqrt{2}\,.\,e}{35k}, \quad . \; . \; . \; . \; . \; . \qquad (13)$$

where a, b, c, and e are the constants of the crystalline splitting, which are, of course, very small in comparison with kT at room temperature. The mean susceptibility of the crystal is equal to

$$\chi = (\chi_1 + \chi_2 + \chi_3)/3 = C/T \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (14)$$

From relations (11) we obtain for the Stark anisotropies

$$\frac{\chi_1 - \chi_2}{\chi} = \frac{3r + s}{T}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (15\text{A})$$

and

$$\frac{\chi_1 - \chi_3}{\chi} = \frac{3r - s}{T}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (15\text{B})$$

With the help of these relations we can calculate, from the experimental anisotropies given in Table III, the values of r and s characteristic of the crystalline Stark splitting. Thus, for manganous ammonium sulphate at T = 303° K,

$$\frac{\chi_1 - \chi_2}{\chi} = \frac{7\cdot8}{13{,}830} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (16\text{A})$$

$$\frac{\chi_1 - \chi_3}{\chi} = \frac{5\cdot5}{13{,}830}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (16\text{B})$$

whence,

$$r = 0\cdot049°,\ s = 0\cdot025°. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (17)$$

Substituting these values in (13), we obtain

$$\frac{a + 2b/3}{k} = 0\cdot142° \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (18\text{A})$$

$$\frac{c + 3e/\sqrt{5}}{k} = 0\cdot070°. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (18\text{B})$$

It is not possible from the magnetic data alone to obtain a and b separately, or c and e. We can see, however, that the energy separations of the Stark components should be of the order of $k \times 0\cdot1°$.

XI—Some Simplifying Assumptions

To obtain a closer estimate of the crystalline separations of the S-levels, we have to make some simplifying assumptions. Kramers has shown that when the number of electrons in the incomplete shell of the ion is odd, as with Mn^{++}, the (2J + 1)-fold degeneracy is not completely removed by the crystalline field, however little symmetry there may be in the field ; a two-fold degeneracy is left over. There would thus be only three split levels for the Mn^{++} ion. Let us, however, assume for simplicity, following Kürti and Simon* in their recent discussions on entropies of paramagnetic crystals at very low temperatures, that the degeneracy has been completely removed, and further, that the six Stark levels so produced are equally spaced, at energy intervals of $k\theta_s$, where θ_s is a temperature characteristic of the crystalline splitting.

The effect of the crystalline *electric* fields in splitting the ^6S levels would then be equivalent to that of a *magnetic* field H_s given by the relation

$$g\beta H_s = k\theta_s. \qquad (19)$$

If we can determine this equivalent magnetic field H_s, we obtain directly the characteristic temperature θ_s.

XII—Stark Splitting and the Weiss Field

Returning to our expressions (11) for the principal susceptibilities, since r and s ($\sim 0\cdot05°$) are very small in comparison with the room temperature T (303°), we can rewrite the expressions in the form

$$\chi_1 = \frac{C}{T - \Theta_1}, \quad \chi_2 = \frac{C}{T - \Theta_2}, \quad \chi_3 = \frac{C}{T - \Theta_3}, \qquad (20)$$

where

$$\Theta_1 = 2r, \quad \Theta_2 = -(r+s), \quad \Theta_3 = -(r-s), \qquad (21)$$

$$\Theta_1 + \Theta_2 + \Theta_3 = 0. \qquad (22)$$

The new expressions (20) are of the Weiss type, and in the usual treatment the Curie temperatures Θ_1, Θ_2, and Θ_3, occurring in them, which in the present crystals really arise from the crystalline fields, would be considered as due to certain internal *magnetic* fields. Let us now enquire what relation our H_s bears to this internal field of the Weiss theory, since both of them are magnetic fields intended to replace effectively the crystalline fields.

The Weiss field, as is well known, is an internal field, which is superposed on the externally applied magnetic field, and is of magnitude αI, where I is the intensity of magnetization per unit volume and α is a constant connexion with the Curie temperature Θ by the relation†

$$\alpha = \frac{3k\Theta}{\mu I_0}, \qquad (23)$$

in which I_0 is the saturation intensity of magnetization, and μ is the moment of the magnetic ion. It would, therefore, vary with I, and would not be constant as our H_s should be.

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[*] 'Proc. Roy. Soc.,' A, vol. 149, p. 152 (1935).

[†] *See* Stoner, " Magnetism and Matter " (London, 1934), chap. iv.

This difference between the Weiss field and H_s is due to the following circumstance, which, incidentally, gives also the relation between the two. The Weiss field is the magnetic equivalent of the crystalline field so far as its influence on the magnetization is concerned, where as H_s is the appropriate magnetic equivalent of the crystalline field as regards its effect on the splitting of the ^6S levels. The two fields would be identical only if the crystalline splitting of ^6S were *actually* into six equally spaced levels, which, as we have already mentioned, is not so ; the actual splitting is into three doubly degenerate levels.

Owing to this two-fold degeneracy, which does not differentiate change in the signs of the spin moments, the crystalline splitting does not produce any magnetization by itself. If, however, by the application of an external magnetic field the degeneracy is removed, the crystalline splitting will exert an influence on the magnetization, which will increase continually with the increase in the latter ; when saturation is reached and the spin moments are all aligned along the same direction, the crystalline splitting will contribute its full share to the magnetization. This can be visualized in the following manner. Whereas the crystalline field alone would prefer orientations corresponding to $m = \pm 5/2$, *i.e.*, the maximum numerical value of m, the magnetization field would progressively increase the population corresponding to the positive value of m in strong preference to the negative, and when saturation is reached, and all the ions are in the $m = +5/2$ state, the contribution to the magnetization field as arising from the crystalline splitting would have reached its maximum value, which should naturally be our H_s. We thus obtain

$$H_s = \alpha I_0, \qquad (24)$$

which, in view of (23), gives

$$H_s = 3k\Theta/\mu. \qquad (25)$$

In applying this formula to *crystals*, there are three Curie temperatures to be considered. For example, for manganous ammonium sulphate the temperatures are

$$\Theta_1 = 0\cdot 10^\circ, \qquad \Theta_2 = -0\cdot 07^\circ, \qquad \Theta_3 = -0\cdot 03^\circ \text{ K}. \qquad (26)$$

But when we are dealing with phenomena that occur at temperatures not much lower than 0·1° K, as we should be in the next section, the field corresponding to Θ_1 would be the predominant field, and we may put

$$H_s = 3k\Theta_1/\mu. \qquad (27)$$

Since for Mn^{++}

$$\mu = g\beta\sqrt{5/2 \times 7/2}, \qquad (28)$$

we obtain, using (19), or, in view of relations (19) and (24),

$$\theta_s = 3g\beta\Theta_1/\mu = 3\Theta_1/\sqrt{5/2 \times 7/2}, \qquad (29)$$

which, on substituting for Θ_1, yields

$$\theta_s = 0\cdot10^\circ \text{ K}. \qquad (30)$$

This would correspond to a separation of the Stark components of

$$\Delta\nu = 0\cdot07 \text{ cm}^{-1}. \qquad (31)$$

This value of θ_s for manganous ammonium sulphate agrees well with the value 0·11° K obtained by Kürti and Simon from adiabatic demagnetization measurements on this salt at very low temperatures (*see* § XIII).

From (19), the value of the inner field H_s in manganous ammonium sulphate comes out as 750 gauss.

The characteristic temperatures for the other salts can be calculated in the same manner, and are given in Table IV.

Table IV

Crystal	Curie temperatures Θ_1	Θ_2	Θ_3	Characteristic temperature θ_s
$MnSO_4 . R_2SO_4 . 6H_2O$				
R = NH_4	0·10° K	−0·07° K	−0·03° K	0·10° K
Rb	0·10	−0·08	−0·02	0·10
Cs	0·09	−0·07	−0·02	0·09
Tl	0·10	−0·08	−0·02	0·10
$MnSeO_4 . R_2SeO_4 . 6H_2O$				
R = NH_4	0·10	−0·07	−0·03	0·10
Rb	0·10	−0·07	−0·03	0·10
Tl	0·10	−0·08	−0·02	0·10
$MnSO_4 . K_2SO_4 . 4H_2O$	0·04	−0·06	0·02	0·04

All the manganous Tutton salts have thus practically the same characteristic temperature, namely, 0·10° K. Manganous potassium sulphate has a considerably lower temperature.

[*Added in proof*, *May* 18, 1936—In connexion with the calculation of the characteristic temperatures of crystals from their magnetic anisotropies we should make the following remark. In equations (11) we have neglected all the terms higher than those involving T^{-2}, and this is justifiable for the particular crystals that we have been considering. When, however, we are dealing with crystals which are cubic or nearly cubic, the terms involving T^{-2} become small, and the T^{-3} terms may become comparable with them.]

XIII—STARK SPLITTING IN RELATION TO ENTROPY AT VERY LOW TEMPERATURES

The Stark splitting of paramagnetic S-levels plays an important part in very low temperature phenomena. For example, as KÜRTI and SIMON have shown, at temperatures in the neighbourhood of 0·1° K the entropy temperature curves for these paramagnetic salts are almost wholly determined by it, and consequently also their specific heats at these temperatures. Even the rough model of the splitting of the levels that has been adopted, viz., into six equally spaced ones, having a constant energy difference of $k\theta_s$, enables us to calculate these quantities to a close approximation. We shall merely quote here some of the results obtained by KÜRTI and SIMON.

(1) *Entropy at Very Low Temperatures*—For temperatures in the neighbourhood of 0·1° absolute, practically the whole of the entropy of these manganous Tutton salts is due to the orientative effect of the crystalline field on the magnetic moments, that due to the lattice oscillations being quite small in comparison. With the assumed constant energy differences between successive Stark levels, viz., $k\theta_s$, the calculation of the entropy can be done in two ways, which are, of course, analytically equivalent.

(*a*) The entropy S can be treated as that of *free* magnetic moments, placed in a magnetic field H_s. The entropy per gram ion is then given by

$$S = S_0 + \int_0^{H_s} \left(\frac{\partial \chi}{\partial T}\right)_H dH, \quad \ldots \ldots \ldots \ldots \quad (32)$$

where S_0 is the entropy when the crystalline fields are absent;

$$S_0 = R \log_e (2J + 1), \quad \ldots \ldots \ldots \ldots \quad (33)$$

and is therefore known. $(\partial\chi/\partial T)_H$ is also easily calculated, since the susceptibility χ in this expression refers to *free* ions.

(*b*) S can also be calculated, as shown by KÜRTI and SIMON, directly from the Stark pattern assumed;

$$S = R\left[T\frac{d \log_e Q_{(2J+1),\theta_s}}{dT} + \log_e Q_{(2J+1),\theta_s}\right], \quad \ldots \ldots \quad (34)$$

where

$$Q_{(2J+1),\theta_s} = 1 + e^{-\theta_s/T} + e^{-2\theta_s/T} + \ldots + e^{-2J\theta_s/T}. \quad \ldots \ldots \quad (35)$$

Thus the entropy-temperature curve at these low temperatures can be readily plotted from the known values of θ_s.

(2) *Specific Heats*—The calculation of the specific heats at these temperatures from the entropy-temperature curve is also easy. Denoting by C the heat capacity of the salt per gram ion of its Mn^{++} content.

$$C = T\frac{dS}{dT}. \quad \ldots \ldots \ldots \ldots \ldots \quad (36)$$

The specific heat curve has a pronounced maximum at a temperature slightly lower than θ_s.

Thus, *purely from measurements at room temperature, from which we obtained the characteristic temperatures* θ_s *given in Table IV, we can predict the entropy-temperature curve and the specific-heat-temperature curve of these crystals in the neighbourhood of* 0·1° *absolute.* This is of interest, since at present, short of actual measurements at these low temperatures, we have no other means of predicting these curves.

We should refer in this place to one other phenomenon in which θ_s plays a prominent part. It determines, as has been shown by KÜRTI and SIMON, the low temperature that can be obtained by the adiabatic demagnetization method of DEBYE* and GIAUQUE.†

Let the salt be magnetized isothermally at a temperature T_i by a magnetic field H_i, and then demagnetized *adiabatically* by suddenly removing it from the field and let T_f be the final temperature attained by the salt. At the initial temperature, which usually is of the order of 1° K, the crystalline field has little influence, so that the entropy is that of free magnetic ions placed in a field H_i, while at the final temperature it should be equivalent to that of the same *free* magnetic ions under the inner field H_s. Since the two entropies should be equal,

$$\frac{H_i}{T_i} = \frac{H_s}{T_f}, \quad \ldots\ldots\ldots\ldots \quad (37)$$

which, on substituting for H_s from (19), gives

$$\frac{T_f}{T_i} = \frac{k\theta_s}{g\beta H_i}. \quad \ldots\ldots\ldots\ldots \quad (38)$$

This relation, obtained by KÜRTI and SIMON, has been experimentally verified by them and they have determined on the basis of it the characteristic temperatures of some paramagnetic salts, from the demagnetization experiments made on them. Only one manganous salt has been experimented by them, namely, manganous ammonium sulphate, for which, as we have seen, the value of θ_s thus obtained agrees well with that deduced by us from the magnetic anisotropy of the crystal at room temperatures.

XIV—STARK SPLITTING IN OTHER PHYSICAL PHENOMENA

Among the other phenomena that depend on the crystalline splitting are Faraday rotation, and absorption. Both of them involve, in addition to the splitting of the ground levels, that of the higher levels also, which makes the interpretation more difficult than that of simple susceptibility phenomena. For the manganous salts, however, since the higher level involved would be a P level, whose splitting under the crystalline fields would not be large, we should expect: (1) the paramagnetic Faraday rotation in manganous salts to be small, and vary nearly as the inverse temperature; (2) the absorption frequencies and the absorption coefficients of single crystals

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* 'Ann. Physik,' vol. 81, p. 1154 (1926).

† 'J. Amer. Chem. Soc.,' vol. 49, p. 1864 (1927).

of manganous salts to be independent of (*a*) the direction of vibration of the light, unlike in cobalt salts, for example, which should show strong pleochroism, and (*b*) the state of aggregation, and the nature of the anions, again unlike the cobalt salts.

These results have been verified experimentally.*†

XV—Interaction Between the Spins

Till now we had neglected, for simplicity, the influence of the interactions between the spin moments, and assumed that the whole of the paramagnetic anisotropy is due to the splitting of the S-levels under the crystalline fields alone. It should be mentioned here that the general results that we have obtained regarding the magnitude of the splitting do not depend on the validity of this assumption. If the interaction is not negligible, it would merely mean that the actual splitting is under the combined action of the crystalline and the interaction fields, and with the assumption of equal spacing of the split levels, the temperatures θ_s that we have calculated (*see* Table IV) would still characterize the splitting of the S-levels in the crystal; only it is not now due to the crystalline field alone. The calculation of the entropy, specific heat, etc., would therefore remain unaffected.

It would, however, be of interest to know how much of the splitting is due to the crystalline field, and how much to the spin interactions. Rough estimates of their relative contributions can be made in the following manner. We have already mentioned that $MnSO_4 . (NH_4)_2 SO_4 . 6H_2O$ and the corresponding diamagnetic salt $MgSO_4 . (NH_4)_2 SO_4 . 6H_2O$ are isomorphous. They readily form mixed crystals, and crystals of any desired composition can be easily grown from aqueous solutions of a suitable mixture of the two. Since the crystalline electric fields which are responsible for the Stark anisotropy are determined by the atoms immediately surrounding the Mn^{++} ions, and since their distributions are presumably independent of the concentration of Mn^{++} in the mixed crystal, we should expect the Stark anisotropy to be independent of the concentration of Mn. The interaction anisotropy, on the other hand, should rapidly fall down as the concentration of Mn in the crystal diminishes.

Let us, for brevity, denote by A the molecule of $MnSO_4 . (NH_4)_2 SO_4 . 6H_2O$ and by B that of $MgSO_4 . (NH_4)_2 SO_4 . 6H_2O$. Consider now a molecule A + nB of the mixed crystal. Its diamagnetic anisotropy may, to a first approximation, be taken to be equal to $(n + 1)$ times that of B, and may be corrected for, as in § IX. The remaining part of the anisotropy would then represent the sum of the Stark and the interaction anisotropies $(\Delta(\chi)_s$ and $(\Delta\chi)_i$, say. We can now use the fact that $(\Delta\chi)_s$ should be independent of magnetic dilution of the kind considered, while $(\Delta\chi)_i$ should rapidly diminish with dilution, in order to separate the two.

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* Becquerel, de Haas, and van den Handel, ' Proc. Acad. Sci. Amst.,' vol. 34, p. 1231 (1931).

† Gielessen, ' Ann. Physik,' vol. 22, p. 537 (1935).

Some preliminary measurements have been made by us on the magnetic anisotropies of a number of such mixed crystals, and the results obtained are given in Table V.

The measurements were restricted to finding the directions of the χ_1 and χ_2 axes in the (010) plane, and the anisotropy, χ_1 and χ_2, in this plane. The first column in the table gives the composition of the crystal, assumed to be of the form A + nB; the value of n for each crystal was determined by analysing it chemically for its Mn constant. Columns 2 and 3 give the observed anisotropy *for a mass consisting of* 1 *gram molecule of A and n* gram molecules of B. Assuming the diamagnetic part of the anisotropy to be equal to $(n+1) \times 1 \cdot 1$—$1 \cdot 1$ being the value of $\chi_1 - \chi_2$ for magnesium ammonium sulphate—, and the diamagnetic ψ to be $-5°$—again that of the magnesium salt—, the values of ψ and $\chi_1 - \chi_2$ for the *paramagnetic* part can be calculated in the same manner as in § IX; the calculated values are given in the last two columns of Table V.

TABLE V—$\begin{matrix} A = \mathrm{Mn} \\ B = \mathrm{Mg} \end{matrix} (\mathrm{NH_4})_2(\mathrm{SO_4})_2 \cdot 6\mathrm{H_2O}$

Composition of the crystal	Magnetic anisotropy			
	Observed		After correcting for diamagnetism	
	ψ	$\chi_1 - \chi_2$	ψ	$\chi_1 - \chi_2$
A + nB				
n = 0	−16°	8·7	−17½°	7·7
0·36	−17°	8·3(?)	−20°	6·9(?)
1·36	−18°	8·6	−23°	6·4
1·75	−18°	8·4	−24½°	5·9
3·25	−16°	9·5	−25°	5·5
5·12	−15°	11·2	−27½°	5·4
B	− 5°	1·1		

Similar data for mixed crystals for manganous and zinc ammonium sulphates are given in Table VI.

TABLE VI—$\begin{matrix} A = \mathrm{Mn} \\ B = \mathrm{Zn} \end{matrix} (\mathrm{NH_4})_2(\mathrm{SO_4})_2 \cdot 6\mathrm{H_2O}$

Composition of the crystal	Magnetic anisotropy			
	Observed		After correcting for diamagnetism	
	ψ	$\chi_1 - \chi_2$	ψ	$\chi_1 - \chi_2$
A + nB				
n = 0	−16°	8·7	−19°	7·8
0·41	−16°	8·3	−21°	7·2
1·05	−16°	8·2	−24°	6·6
3·45	−13°	8·3	−32°	5·3
4·62	−12°	9·0	−36°	5·3
B	+ 6°	1·2		

Since the diamagnetic corrections are large—for example, for the largest magnetic dilution, namely, that corresponding to $n = 5$, $(\Delta\chi)_d$ is as high as 60 to 70% of the observed anisotropy—the values given in the last column of the Tables V and VI can be taken to represent only the *order of magnitude* of the paramagnetic anisotropy. They indicate, however, a definite fall in the paramagnetic anisotropy with magnetic dilution, from a value 7·8 for pure manganous ammonium sulphate, to 5·3 when it is diluted with 5 molecules of the diamagnetic salt.

Thus, in manganous ammonium sulphate the interactions between the spin moments of Mn^{++} are quite appreciable, and may account for as much as 30% of the observed anisotropy, the remaining 70% being due to crystalline electric fields. This estimate of the relative influences of the interaction and crystalline fields on the splitting of the S levels of Mn^{++} agrees with the results of low temperature demagnetization experiments with these mixed crystals by KÜRTI and SIMON.*

XVI—FERRIC SALTS

Most of the inorganic ferric crystals are hygroscopic, and their anisotropies were difficult to measure. We therefore chose for measurement two organic compounds of iron, namely, $K_3Fe(C_2O_4)_3 . 3H_2O$, and $Na_3Fe(C_2O_4)_3 . 5H_2O$, and the corresponding double oxalates of aluminium, which are diamagnetic. The magnetic data for these crystals are given in Tables I and II. The magnitude of the Stark splitting in the ferric salts can be calculated in the same manner as for the manganous salts. To quote here only the final results, the characteristic temperatures θ_s for the potassium and sodium iron oxalates were found to be about 0·7° and 0·3° K respectively. These values are much higher than those for the manganous salts.

Some preliminary measurements on ferric ammonium oxalate show that its characteristic temperature is nearly the same as for the sodium salt, though in its water of crystallization ($3H_2O$), and in its crystal structure, it resembles strongly the potassium salt.

We desire to express our thanks to Professor P. C. MAHALANOBIS of the Presidency College, Calcutta, for the loan of the electro-magnet.

XVII—SUMMARY

The paper gives an account of measurements on the magnetic anisotropies of single crystals of manganous and ferric salts. Both the Mn^{++} and Fe^{+++} ions being in the S-state (${}^6S_{5/2}$), the anisotropies are naturally very feeble, of the order of one part in a thousand; a special experimental technique is described suitable for the measurement of such feeble anisotropies.

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* 'Proc. Roy. Soc.,' A, vol. 149, p. 172 (1935).

The various causes contributing to the anisotropy are discussed. Part of the anisotropy is shown to be that of the diamagnetism of the crystal, and part, much smaller, is that arising from the mutual influence of the magnetic moments and their non-cubic arrangement in the crystal lattice.

The bulk of the anisotropy that is left over after allowing for the above two, arises from the Stark splitting of the ^6S levels under the influence of the crystalline electric fields. A method is described for calculating the magnitude of the Stark separation from the anisotropy, and for calculating the "characteristic temperatures". The part played by the Stark splitting in various low temperature phenomena is reviewed, and it is shown how from magnetic measurements alone at room temperature it is possible to predict the entropy-temperature and specific heat temperature curves of these crystals in the neighbourhood of 0·1° absolute.

From measurements on the progressive variation of the anisotropy of mixed crystals of $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O + Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and of $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O + Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, with the concentration of Mn, the effects of the interactions between the spin moments in the crystal are estimated.