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Investigations on Magne-Crystallic Action. V. Paramagnetic Salts of the Rare Earth and the Iron Groups

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INVESTIGATIONS ON MAGNE-CRYSTALLIC ACTION

V. PARAMAGNETIC SALTS OF THE RARE EARTH. AND THE IRON GROUPS

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CONTENTS

I. Introduction

In Part II of this series (Krishnan, Chakravorty and Banerjee 1933) we gave an account of magnetic measurements on single crystals of several sulphates and double sulphates of the iron group, and in Part IV (Krishnan and Banerjee 1936) on crystals whose paramagnetic ions are all in the S-state, which are of special interest. The present Part describes further measurements, on a large number of paramagnetic crystals, among which are many rare earth salts, several double sulphates, double selenates, selenates, sulphato-selenates and fluoberyllates of the iron group, and a few feebly paramagnetic crystals like the chromates, dichromates and ferricyanides. The magnetic data are discussed on the basis of the theory developed by Van Vleck, Penney and Schlapp (1932).

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II. Experimental

The experimental method used in these measurements was the same as was described in our previous papers. The magnetic anisotropy of the crystal was measured by both the oscillational and the rotational methods described in Part III (Krishnan and Banerjee 1935) in connexion with the measurements on organic crystals. The values obtained by the two methods were practically the same, the latter method being slightly more convenient. The absolute susceptibility along some convenient direction in the crystal was measured by the modified Rabi method described in Part II.

The double sulphates, double selenates, and sulphato-selenates were prepared by mixing aqueous solutions of the two components in suitable molecular proportions. The fluoberyllates were prepared by the method described by Ray in a recent paper (1932). The fluoberyllate of cobalt ($CoBeF_4$), for example, was prepared in the following manner. First, cobalt nitrite was obtained by the double decomposition of barium nitrite and cobalt sulphate. It was mixed in solution with the required amount of ammonium fluoride. The solution was evaporated, and further heated to decomposition. Cobalt fluoride was left over, which when treated with beryllium fluoride yielded $CoBeF_4$. The double fluoberyllates were obtained by mixing aqueous solutions of the two component fluoberyllates in equimolecular proportions.

The ethyl sulphates of the rare earths were prepared by treating the corresponding hydroxides (obtained by adding ammonia to a solution of any of its salts) with ethyl sulphuric acid. Cerous ethyl sulphate, however, was prepared by the double decomposition of cerous sulphate and barium ethyl sulphate, since the hydroxide is readily oxidized in air.

Praseodymium sulphate was prepared from a specimen of the chloride, of known purity, kindly supplied by Dr P. B. Sircar, to whom we take this opportunity to express our thanks. The salts of samarium, cerium and neodymium were also fairly pure. Those of erbium were not so pure. But judged by the magnetic susceptibility, which was measured for one of these salts in solution, the amount of other rare earths present as impurity should be small.

III. Results

The results of the measurements are collected together in Tables I and II. The different columns in the tables have the same significance as in Part II. The notation adopted is also the same. For the trigonal, tetragonal and hexagonal crystals, which have an axis of magnetic symmetry, the gram-molecular susceptibility along the axis is denoted by $\chi_{\parallel}$, and that along perpendicular directions by $\chi_{\perp}$. For the orthorhombic crystals the principal susceptibilities along the "*a*", "*b*" and "*c*" axes are denoted by χ_a, χ_b and χ_c respectively. For the monoclinic crystals, the two principal susceptibilities in the (010) plane are denoted by χ_1 and χ_2, χ_1 being the greater of the two. The χ_1 axis is inclined at an angle ψ to the "c" axis, and at $\beta-\psi$ to "a", β being the obtuse angle between "c" and "a". The inclination of the χ_2 axis to "a", which in many of our experiments was directly measured, is denoted by θ, where $\theta=\beta-\pi/2-\psi$.

The measurements were all made at room temperature. During the measurements on the salts of the iron group the room temperature was about 26° C., and for the sake of uniformity the magnetic data for these crystals have been corrected so as to make them all correspond to 26° C. During the measurements on the rare earth salts and the complex salts the room temperature was about 30° C., and the values for these crystals have accordingly been reduced to 30° C.

IV. Magnetic behaviour of paramagnetic crystals: the theory of Van Vleck, Penney and Schlapp

The three outstanding features in the magnetic behaviour of paramagnetic crystals, which till recently had not been explained satisfactorily, are (1) the magnetic anisotropy of the crystals; (2) the contributions from the orbital and the spin moments of the paramagnetic ions to the susceptibility; (3) the temperature variation of the susceptibility, which, in general, deviates considerably from the Curie law. All of them receive a natural explanation on the basis of the theory developed recently by Van Vleck, Penney and Schlapp (1932).

Let us first consider a gaseous assemblage of paramagnetic atoms (or ions), and assume for simplicity that the coupling between the orbital and the spin moments of the atom is so strong that the multiplet separation is large compared with kT. The magnetic moment of the atom will then be that corresponding to the ground state, and will be given by the simple Hund rule; and the susceptibility of the gas will follow the Curie law. If, however, the multiplet separations are not large in comparison with kT, the "effective" magnetic moment of the particle will not be determined by the ground state alone, but by the immediately higher states as well, which also will be populated to some extent. The effective moment will thus vary with temperature, and the temperature variation of susceptibility will deviate from the Curie law, but in a manner that may be readily predicted.

When we come to the crystal state the problem becomes naturally more complicated, owing to the strong electric fields which are brought to play on the paramagnetic ion in the crystal, as a result of the close proximity of the neighbouring atoms or ions. This will introduce a large constraint on the freedom of rotation of the orbital moment of the paramagnetic ion, and indirectly, through the coupling of the orbital moment with the spin moment, a constraint on the spin moment as well. The effect of the first will be to quench, either partially or wholly, the orbital contribution to the effective magnetic moment of the ion, and of the second to impose on the spin moment what in

TABLE I

Serial no.	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$\lvert\Delta\chi\rvert$	Magnetic anisotropy	ψ Measured	ψ Calculated
			Rare earth salts (the data refer to 30° C.)					
	Sulphates							
1	$Pr_2(SO_4)_3.8H_2O$	Monoclinic prism	“b” axis vertical	$\theta=+2°\cdot1$	783	$\chi_1-\chi_2=$ 783	+26°	+26°·5
		$a:b:c$						
		$=2\cdot986:1:1\cdot999$	“a” ”	“b” axis along field	975	$\chi_1-\chi_3=-$ 975		
		$\beta=118°$	(001) plane horizontal	“b” ” ”	1757			
2	$Nd_2(SO_4)_3.8H_2O$	Monoclinic prism	“b” axis vertical	$\theta=+14°\cdot5$	806	$\chi_1-\chi_2=$ 806	+13°·6	+14°·0
		$a:b:c$						
		$=2\cdot983:1:1\cdot997$	“a” ”	“b” axis along field	235	$\chi_1-\chi_3=-$ 187		
		$\beta=118°\ 8'$	(001) plane horizontal	“b” ” ”	945			
3	$Sm_2(SO_4)_3.8H_2O$	Monoclinic prism	“b” axis vertical	$\theta=-24°\cdot4$	433	$\chi_1-\chi_2=$ 433	+52°·7	+52°·6
		$a:b:c$						
		$=3\cdot003:1:2\cdot002$	“a” ”	“b” axis along field	22	$\chi_1-\chi_3=$ 52		
		$\beta=118°\ 16'$	(001) plane horizontal	“b” ” ”	308			
4	$Er_2(SO_4)_3.8H_2O$	Monoclinic prism	“b” axis vertical	$\lvert\psi\rvert=77°\cdot2$	8870	$\chi_1-\chi_2=$ 8870	±77°·2	±77°·3
		$a:b:c$						
		$=3\cdot012:1:2\cdot004$	“c” ”	“b” axis normal to field	7250	$\chi_1-\chi_3=$ 7680		
		$\beta=118°\ 27'$	(100) plane horizontal	“c” ” ”	764			
5	$CeNH_4(SO_4)_2.4H_2O$	Monoclinic prism	“b” axis vertical	$\psi=+77°\cdot3$	136	$\chi_1-\chi_2=$ 136	+77°·3	+78°·4
		$a:b:c$						
		$=0\cdot360:1:0\cdot934$	“c” ”	“b” axis normal to field	77	$\chi_1-\chi_3=$ 83		
		$\beta=97°\ 15'$	(100) plane horizontal	“c” ” ”	48			
	Nitrates							
6	$Ce_2Mg_3(NO_3)_{12}.24H_2O$	Trigonal	Trigonal axis horizontal	Trigonal axis normal to field	637	$\chi_\parallel-\chi_\perp=-$ 637		
7	$Ce_2Zn_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	650	− 650		
8	$Pr_2Mg_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	632	− 632		
9	$Pr_2Zn_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	653	− 653		
10	$Nd_2Mg_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	639	− 639		
11	$Nd_2Zn_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	611	− 611		
12	$Sm_2Mg_3(NO_3)_{12}.24H_2O$	”	” ”	” ”	176	− 176		

	Ethyl sulphates							
13	$Ce_2(C_2H_5SO_4)_6 . 18H_2O$	Hexagonal	Hexagonal axis horizontal	Hexagonal axis along field	294	$\chi_{\parallel}-\chi_{\perp}=$ 294		
14	$Pr_2(C_2H_5SO_4)_6 . 18H_2O$	,,	,, ,,	,, ,,	241	241		
15	$Nd_2(C_2H_5SO_4)_6 . 18H_2O$	,,	,, ,,	,, ,,	600	600		
16	$Sm_2(C_2H_5SO_4)_6 . 18H_2O$	,,	,, ,,	,, ,,	172	172		
17	$Er_2(C_2H_5SO_4)_6 . 18H_2O$	,,	,, ,,	Hexagonal axis normal to field	6590	−6590		
	Tutton salts of the iron group of metals (the data refer to 26° C.)							
18	$FeRb_2(SO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+43°·0$	2270	$\chi_1-\chi_2=$ 2270	−27°·3	−27°·5
		$a:b:c$ = 0·738 : 1 : 0·500	"*a*" ,,	"*b*" axis along field	917	$\chi_1-\chi_3=$ 150		
		β = 105° 44′	(001) plane horizontal	"*b*" ,, ,,	1062			
19	$FeCs_2(SO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+40°·8$	2540	$\chi_1-\chi_2=$ 2540	−23°·9	−23°·6
		$a:b:c$ = 0·726 : 1 : 0·495	"*a*" ,,	"*b*" axis along field	502	$\chi_1-\chi_3=$ 570		
		β = 106° 52′	(001) plane horizontal	"*b*" ,, ,,	901			
20	$FeTl_2(SO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+42°·5$	2220	$\chi_1-\chi_2=$ 2220	−26°·2	−26°·9
		$a:b:c$ = 0·743 : 1 : 0·500	"*a*" ,,	"*b*" axis along field	1010	$\chi_1-\chi_3=$ 30		
		β = 106° 16′	(001) plane horizontal	"*b*" ,, ,,	1150			
21	$FeTl_2(SeO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+44°·0$	2230	$\chi_1-\chi_2=$ 2230	−28°·5	−28°·6
		$a:b:c$ = 0·745 : 1 : 0·501	"*a*" ,,	"*b*" axis along field	722	$\chi_1-\chi_3=$ 360		
		β = 105° 27′	(001) plane horizontal	"*b*" ,, ,,	792			
22	$CoSeO_4 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=-52°·3$	4030	$\chi_1-\chi_2=$ 4030	+60°·5	+60°·9
		$a:b:c$ = 1·571 : 1 : 1·682	"*a*" ,,	"*b*" axis along field	108	$\chi_1-\chi_3=$ 2440		
		β = 98° 14′	(001) plane horizontal	"*a*" ,, ,,	967			
23	$CoRb_2(SO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+40°·5$	2440	$\chi_1-\chi_2=$ 2440	−24°·5	−25°·1
		$a:b:c$ = 0·739 : 1 : 0·501	"*a*" ,,	"*b*" axis normal to field	163	$\chi_1-\chi_3=$ 1220		
		β = 106° 1′	(001) plane horizontal	"*a*" ,, ,,	164			
24	$CoCs_2(SO_4)_2 . 6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta=+62°·0$	2600	$\chi_1-\chi_2=$ 2600	−44°·9	−44°·6
		$a:b:c$ = 0·727 : 1 : 0·497	"*a*" ,,	"*b*" axis along field	1515	$\chi_1-\chi_3=$ 500		
		β = 107° 8′	(001) plane horizontal	"*b*" ,, ,,	80			

TABLE I (*continued*)

Serial no.	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$\lvert\Delta\chi\rvert$	Magnetic anisotropy	ψ	
							Measured	Calculated
25	$CoTl_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +54°\cdot2$	2010	$\chi_1-\chi_2 = 2010$	$-37°\cdot8$	$-37°\cdot0$
		$= 0\cdot741 : 1 : 0\cdot500$	"*a*" ,,	"*b*" axis along field	337	$\chi_1-\chi_3 = 960$		
		$\beta = 106° 25'$	(001) plane horizontal	"*a*" ,, ,,	243			
26	$Co(NH_4)_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +60°\cdot8$	3120	$\chi_1-\chi_2 = 3120$	$-44°\cdot4$	$-43°\cdot6$
		$= 0\cdot745 : 1 : 0\cdot503$	"*a*" ,,	"*b*" axis along field	362	$\chi_1-\chi_3 = 1980$		
		$\beta = 106° 23'$	(001) plane horizontal	"*a*" ,, ,,	1195			
27	$CoK_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +27°\cdot9$	3130	$\chi_1-\chi_2 = 3130$	$-13°\cdot6$	$-13°\cdot4$
		$= 0\cdot752 : 1 : 0\cdot506$	"*a*" ,,	"*b*" axis normal to field	2410	$\chi_1-\chi_3 = 3090$		
		$\beta = 104° 17'$	(001) plane horizontal	"*b*" ,, ,,	633			
28	$CoRb_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +35°\cdot2$	2900	$\chi_1-\chi_2 = 2900$	$-20°\cdot0$	$-20°\cdot2$
		$= 0\cdot743 : 1 : 0\cdot502$	"*a*" ,,	"*b*" axis normal to field	1275	$\chi_1-\chi_3 = 2250$		
		$\beta = 105° 14'$	(001) plane horizontal	"*b*" ,, ,,	320			
29	$CoTl_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +47°\cdot2$	2450	$\chi_1-\chi_2 = 2450$	$-31°\cdot5$	$-30°\cdot9$
		$= 0\cdot746 : 1 : 0\cdot502$	"*a*" ,,	"*b*" axis normal to field	657	$\chi_1-\chi_3 = 1950$		
		$\beta = 105° 40'$	(001) plane horizontal	"*b*" ,, ,,	794			
30	$CoK_2SO_4SeO_4.6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta = +29°\cdot0$	2960	$\chi_1-\chi_2 = 2960$	$-14°$	$-13°$
			"*a*" ,,	"*b*" axis normal to field	1904	$\chi_1-\chi_3 = 2560$		
		$\beta = 105°$	(001) plane horizontal	"*b*" ,, ,,	254			
31	$Co(NH_4)_2(BeF_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +54°\cdot9$	2930	$\chi_1-\chi_2 = 2930$	$-38°\cdot1$	$-37°\cdot3$
		$= 0\cdot740 : 1 : 0\cdot485$	"*a*" ,,	"*b*" axis along field	375	$\chi_1-\chi_3 = 1550$		
		$\beta = 106° 46'$	(001) plane horizontal	"*a*" ,, ,,	539			
32	$NiSeO_4.6H_2O$	Tetragonal $a:c = 1\cdot836$	Tetragonal axis horizontal	Tetragonal axis normal to field	90	$\chi_\perp-\chi_\parallel = 90$		
33	$NiRb_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +27°\cdot0$	144	$\chi_1-\chi_2 = 144$	$-11°\cdot0$	$-11°\cdot6$
		$= 0\cdot735 : 1 : 0\cdot502$	"*a*" ,,	"*b*" axis normal to field	106	$\chi_1-\chi_3 = 137$		
		$\beta = 106° 3'$	(001) plane horizontal	"*b*" ,, ,,	24			
34	$NiCs_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$	"*b*" axis vertical	$\theta = +27°\cdot7$	134	$\chi_1-\chi_2 = 134$	$-10°\cdot7$	$-11°\cdot2$
		$= 0\cdot727 : 1 : 0\cdot498$	"*a*" ,,	"*b*" axis normal to field	97	$\chi_1-\chi_3 = 127$		
		$\beta = 107° 2'$	(001) plane horizontal	"*b*" ,, ,,	23			

35	$NiTl_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}740 : 1 : 0{\cdot}500$ $\beta = 106°\ 23'$	“b” axis vertical	$\theta = +27°{\cdot}3$	114	$\chi_1-\chi_2 =$ 114	−10°·9	−10°·9
			“a” ”	“b” axis normal to field	84	$\chi_1-\chi_3 =$ 108		
			(001) plane horizontal	“b” ” ”	18			
36	$Ni(NH_4)_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}740 : 1 : 0{\cdot}505$ $\beta = 106°\ 17'$	“b” axis vertical	$\theta = +44°{\cdot}2$	116	$\chi_1-\chi_2 =$ 116	−27°·9	−26°·2
			“a” ”	“b” axis normal to field	43	$\chi_1-\chi_3 =$ 96		
			(001) plane horizonal	“b” ” ”	33			
37	$NiK_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}747 : 1 : 0{\cdot}506$ $\beta = 104°\ 27'$	“b” axis vertical	$\theta = +27°{\cdot}5$	146	$\chi_1-\chi_2 =$ 146	−13°·0	−13°·9
			“a” ”	“b” axis normal to field	113	$\chi_1-\chi_3 =$ 146		
			(001) plane horizontal	“b” ” ”	33			
38	$NiRb_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}740 : 1 : 0{\cdot}503$ $\beta = 105°\ 20'$	“b” axis vertical	$\theta = +28°{\cdot}2$	157	$\chi_1-\chi_2 =$ 157	−12°·9	−13°·5
			“a” ”	“b” axis normal to field	110	$\chi_1-\chi_3 =$ 147		
			(001) plane horizontal	“b” ” ”	26			
39	$NiCs_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}729 : 1 : 0{\cdot}499$ $\beta = 106°\ 11'$	“b” axis vertical	$\theta = +33°{\cdot}8$	164	$\chi_1-\chi_2 =$ 164	−17°·6	−17°·3
			“a” ”	“b” axis normal to field	85	$\chi_1-\chi_3 =$ 135		
			(001) plane horizontal	“b” ” ”	21			
40	$NiTl_2(SeO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}746 : 1 : 0{\cdot}502$ $\beta = 105°\ 36'$	“b” axis vertical	$\theta = +32°{\cdot}7$	123	$\chi_1-\chi_2 =$ 123	−17°·1	−15°·9
			“a” ”	“b” axis normal to field	80	$\chi_1-\chi_3 =$ 113		
			(001) plane horizontal	“b” ” ”	24			
41	$Ni(NH_4)_2SO_4SeO_4.6H_2O$	Monoclinic prism Belongs to the Tutton series $\beta = 106°$	“b” axis vertical	$\theta = +39°{\cdot}4$	131	$\chi_1-\chi_2 =$ 131	−23°	−22°
			“a” ”	“b” axis normal to field	63	$\chi_1-\chi_3 =$ 113		
			(001) plane horizontal	“b” ” ”	31			
42	$Ni(NH_4)_2(BeF_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}737 : 1 : 0{\cdot}491$ $\beta = 106°\ 40'$	“b” axis vertical	$\theta = +31°{\cdot}0$	107	$\chi_1-\chi_2 =$ 107	−14°·3	−15°·6
			“a” ”	“b” axis normal to field	75	$\chi_1-\chi_3 =$ 106		
			(001) plane horizontal	“b” ” ”	29			
43	$CuRb_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}749 : 1 : 0{\cdot}503$ $\beta = 105°\ 18'$	“b” axis vertical	$\theta = +86°{\cdot}0$	350	$\chi_1-\chi_2 =$ 350	−70°·7	−70°·4
			“a” ”	“b” axis along field	248	$\chi_1-\chi_3 =$ 100		
			(001) plane horizontal	“a” ” ”	98			
44	$CuCs_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}743 : 1 : 0{\cdot}495$ $\beta = 106°\ 10'$	“b” axis vertical	$\theta = +88°{\cdot}1$	339	$\chi_1-\chi_2 =$ 339	−71°·9	−71°·6
			“a” ”	“b” axis along field	225	$\chi_1-\chi_3 =$ 114		
			(001) plane horizontal	“a” ” ”	113			
45	$CuTl_2(SO_4)_2.6H_2O$	Monoclinic prism $a:b:c$ $= 0{\cdot}750 : 1 : 0{\cdot}503$ $\beta = 105°\ 33'$	“b” axis vertical	$\theta = +88°{\cdot}2$	283	$\chi_1-\chi_2 =$ 283	−72°·6	−72°·0
			“a” ”	“b” axis along field	212	$\chi_1-\chi_3 =$ 71		
			(001) plane horizontal	“a” ” ”	70			

TABLE I (*continued*)

Serial no.	Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$\lvert \Delta\chi \rvert$	Magnetic anisotropy	ψ Measured	ψ Calculated
46	$Cu(NH_4)_2(SeO_4)_2.6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta = -51°{\cdot}2$	353	$\chi_1 - \chi_2 =$ 353	$+66°{\cdot}7$	$+66°{\cdot}6$
		$a : b : c$						
		$= 0{\cdot}748 : 1 : 0{\cdot}515$	"*a*" ,,	"*b*" axis along field	96	$\chi_1 - \chi_3 =$ 118		
		$\beta = 105° \ 30'$	(001) plane horizontal	"*b*" ,, ,,	21			
47	$CuK_2(SeO_4)_2.6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta = +66°{\cdot}9$	367	$\chi_1 - \chi_2 =$ 367	$-53°{\cdot}5$	$-54°{\cdot}5$
		$a : b : c$						
		$= 0{\cdot}751 : 1 : 0{\cdot}514$	"*a*" ,,	"*b*" axis along field	220	$\chi_1 - \chi_3 =$ 95		
		$\beta = 103° \ 25'$	(001) plane horizontal	"*a*" ,, ,,	43			
48	$CuRb_2(SeO_4)_2.6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta = +88°{\cdot}0$	354	$\chi_1 - \chi_2 =$ 354	$-73°{\cdot}3$	$-75°$
		$a : b : c$						
		$= 0{\cdot}750 : 1 : 0{\cdot}507$	"*a*" ,,	"*b*" axis along field	276	$\chi_1 - \chi_3 =$ 78		
		$\beta = 104° \ 44'$	(001) plane horizontal	"*a*" ,, ,,	78			
49	$CuTl_2(SeO_4)_2.6H_2O$	Monoclinic prism	"*b*" axis vertical	$\theta = +87°{\cdot}3$	328	$\chi_1 - \chi_2 =$ 328	$-72°{\cdot}3$	$-72°$
		$a : b : c$						
		$= 0{\cdot}753 : 1 : 0{\cdot}505$	"*a*" ,,	"*b*" axis along field	255	$\chi_1 - \chi_3 =$ 72		
		$\beta = 104° \ 59'$	(001) plane horizontal	"*a*" ,, ,,	71			
			Complex salts (the data refer to 30° C.)					
50	$K_3Fe(CN)_6$	Monoclinic prism	"*b*" axis vertical	$\lvert \psi \rvert = 88°{\cdot}9$	451	$\chi_1 - \chi_2 =$ 451	$\pm 88°{\cdot}9$	90°
		$a : b : c$						
		$= 1{\cdot}288 : 1 : 0{\cdot}801$	"*c*" ,,	"*b*" axis normal to field	123	$\chi_1 - \chi_3 =$ 123		
		$\beta = 90° \ 6'$	(100) plane horizontal	"*c*" ,, ,,	328			
51	$(NH_4)_2Cr_2O_7$	Monoclinic	"*b*" axis vertical	$\theta = +60°{\cdot}9$	19·6	$\chi_1 - \chi_2 =$ 19·6	$-57°{\cdot}2$	$-58°$
		$a : b : c$						
		$= 1{\cdot}027 : 1 : 1{\cdot}766$	"*a*" ,,	"*b*" axis along field	7·3	$\chi_1 - \chi_3 =$ 8·0		
		$\beta = 93° \ 42'$	(001) plane horizontal	"*a*" ,, ,,	3·6			
52	K_2CrO_4	Orthorhombic	"*b*" axis vertical	"*a*" axis along field	0·6	$\chi_a - \chi_b =$ 1·5		
		$a : b : c$						
		$= 0{\cdot}569 : 1 : 0{\cdot}730$	"*a*" ,,	"*c*" ,, ,,	0·9	$\chi_a - \chi_c =$ 0·6		
			"*c*" ,,	"*a*" ,, ,,	1·5			
53	$(NH_4)_2CrO_4$	Monoclinic prism	"*b*" axis vertical	$\theta = +65°{\cdot}0$	2·6	$\chi_1 - \chi_2 =$ 2·6	$-40°$	$-39°$
		$a : b : c$						
		$= 1{\cdot}960 : 1 : 1{\cdot}226$	"*a*" ,,	"*b*" axis along field	2·5	$\chi_1 - \chi_3 =$ −0·4		
		$\beta = 115° \ 13'$	(001) plane horizontal	"*b*" axis along field	0·9			

TABLE II

Serial no. 1	Crystal 2	Direction along which susceptibility was measured 3	Temp. ° C. 4	Density of crystal 5	Volume susceptibility 6	Corresponding g.-mol. susceptibility 7	Mean susceptibility at 30° C. 8
1	$Pr_2(SO_4)_3.8H_2O$	Along χ_1 axis	31·1	2·834	35·2	8,870	8,970
			32·5	2·884	35·5	8,790	8,930
2	$Nd_2(SO_4)_3.8H_2O$	,,	32·9	2·851	37·0	9,350	9,240
			30·5	2·831	37·1	9,440	9,250
3	$Sm_2(SO_4)_3.8H_2O$	,,	31·3	2·978	9·02	2,220	2,070
			31·0	2·990	9·06	2,220	2,070
4	$Ce(NH_4)(SO_4)_2.4H_2O$	,,	31·5	2·589	12·13	1,980	1,920
			31·0	2·525	12·03	2,010	1,940
5	$Ce_2Mg_3(NO_3)_{12}.24H_2O$	Normal to trigonal axis	32·0	1·914	4·83	3,860	3,670
			31·0	2·010	5·11	3,890	3,690
6	$Ce_2Zn_3(NO_3)_{12}.24H_2O$	,, ,,	32·1	2·222	5·50	4,090	3,900
			32·0	2·222	5·52	4,110	3,920
7	$Nd_2Mg_3(NO_3)_{12}.24H_2O$	,, ,,	32·8	2·090	10·88	8,010	7,870
			33·2	2·076	10·78	7,990	7,860
8	$Nd_2Zn_3(NO_3)_{12}.24H_2O$	,, ,,	32·0	2·279	10·99	8,010	7,860
			33·0	2·214	10·60	7,950	7,830
9	$Sm_2Mg_3(NO_3)_{12}.24H_2O$	,, ,,	30·1	2·164	3·16	2,260	2,200
			31·9	2·163	3·10	2,220	2,180
10	$Ce_2(C_2H_5SO_4)_6.18H_2O$	Along hexagonal axis	30·2	1·839	5·44	4,010	3,820
			30·3	1·841	5·47	4,030	3,840
11	$Nd_2(C_2H_5SO_4)_6.18H_2O$	,, ,,	31·0	1·924	13·47	9,540	9,170
			31·8	1·910	13·38	9,550	9,210
12	$Sm_2(C_2H_5SO_4)_6.18H_2O$	,, ,,	32·0	1·895	2·83	2,050	1,950
			32·1	1·895	2·82	2,050	1,950
13	$Er_2(C_2H_5SO_4)_6.18H_2O$	Measured in state of solution in water					73,400
							Mean susceptibility at 26° C.
14	$FeRb_2(SO_4)_2.6H_2O$	Along χ_1 axis	25·0	2·511	61·9	12,990	12,140
			24·9	2·506	61·9	13,020	12,160
15	$FeCs_2(SO_4)_2.6H_2O$	,,	34·4	2·700	54·8	12,620	11,930
			32·8	2·670	55·6	12,950	12,200

TABLE II. (*continued*)

Serial no. 1	Crystal 2	Direction along which susceptibility was measured 3	Temp. ° C. 4	Density of crystal 5	Volume susceptibility 6	Corresponding g.-mol. susceptibility 7	Mean susceptibility at 26° C. 8
16	$FeTl_2(SO_4)_2.6H_2O$	Along χ_1 axis	24·2 24·7	3·653 3·630	63·0 62·4	13,190 13,150	12,360 12,340
17	$FeTl_2(SeO_4)_2.6H_2O$	,,	30·8 31·0	3·626 3·623	52·2 52·4	12,370 12,430	11,700 11,780
18	$CoSeO_4.6H_2O$	,,	25·5 25·0	2·236 2·247	81·5 83·4	11,310 11,520	9,130 9,320
19	$CoRb_2(SO_4)_2.6H_2O$	,,	24·6 24·8	2·515 2·507	52·4 52·3	11,040 11,060	9,770 9,800
20	$CoCs_2(SO_4)_2.6H_2O$	,,	21·7 22·2	2·851 2·829	51·0 50·5	11,180 11,150	9,990 9,980
21	$CoTl_2(SO_4)_2.6H_2O$	,,	25·7 25·3	3·674 3·566	50·3 48·9	10,520 10,530	9,520 9,520
22	$Co(NH_4)_2(SeO_4)_2.6H_2O$	,,	23·6 23·5	2·217 2·190	55·2 53·8	12,180 12,020	10,380 10,220
23	$CoK_2(SeO_4)_2.6H_2O$	,,	25·0 24·3	2·521 2·525	58·2 58·4	12,280 12,290	10,170 10,150
24	$CoRb_2(SeO_4)_2.6H_2O$	,,	22·5 22·4	2·880 2·880	54·3 54·4	11,770 11,800	9,910 9,940
25	$CoTl_2(SeO_4)_2.6H_2O$	,,	22·7 23·7	3·710 3·762	53·2 53·3	12,360 12,220	10,750 10,660
26	$CoK_2SO_4SeO_4.6H_2O$	,,	23·7 21·0	2·336 2·315	59·2 59·2	12,270 12,390	10,330 10,340
27	$Co(NH_4)_2(BeF_4)_2.6H_2O$	,,	32·0 31·9	1·822 1·831	52·5 52·7	10,750 10,740	9,470 9,460
28	$NiSeO_4.6H_2O$	Normal to tetragonal axis	25·5 26·5	2·328 2·329	32·2 32·2	4,290 4,290	4,250 4,270
29	$NiRb_2(SO_4)_2.6H_2O$	Along χ_1 axis	26·8 27·0	2·601 2·588	20·4 20·3	4,160 4,160	4,080 4,080
30	$NiCs_2(SO_4)_2.6H_2O$	,,	22·0 21·4	2·858 2·846	19·30 19·27	4,220 4,230	4,080 4,080
31	$NiTl_2(SO_4)_2.6H_2O$	,,	25·7 24·1	3·706 3·765	19·92 20·21	4,130 4,120	4,050 4,020
32	$Ni(NH_4)_2(SeO_4)_2.6H_2O$	,,	25·5 24·0	2·262 2·256	19·41 19·46	4,200 4,220	4,120 4,120

33	$NiK_2(SeO_4)_2 . 6H_2O$	,,	25·7 24·5	2·496 2·559	19·98 20·64	4,250 4,290	4,150 4,170
34	$NiRb_2(SeO_4)_2 . 6H_2O$	,,	22·0 22·8	2·843 2·826	19·63 19·55	4,310 4,320	4,150 4,170
35	$NiCs_2(SeO_4)_2 . 6H_2O$	,,	30·5 31·3	3·129 3·047	18·21 17·90	4,180 4,220	4,140 4,190
36	$NiTl_2(SeO_4)_2 . 6H_2O$	,,	24·2 24·8	3.912 3·937	19·06 19·25	4,200 4,210	4,100 4,120
37	$Ni(NH_4)_2SO_4SeO_4 . 6H_2O$	,,	32·0 33·0	2·064 2·086	19·53 19·49	4,180 4,130	4,180 4,150
38	$Ni(NH_4)_2(BeF_4)_2 . 6H_2O$	,,	31·1 31·8	1·833 1·839	19·97 19·97	4,060 4,050	4,060 4,060
39	$CuRb_2(SO_4)_2 . 6H_2O$	,,	27·4 25·8	2·500 2·502	6·77 6·77	1,450 1,450	1,310 1,300
40	$CuCs_2(SO_4)_2 . 6H_2O$	,,	21·2 22·1	2·86 2·84	6·91 6·83	1,520 1,510	1,340 1,340
41	$CuTl_2(SO_4)_2 . 6H_2O$	,,	29·0 28·8	3·579 3·634	6·69 6·80	1,440 1,440	1,340 1,340
42	$Cu(NH_4)_2(SeO_4)_2 . 6H_2O$	,,	26·0 26·2	2·202 2·190	6·75 6·73	1,520 1,520	1,360 1,360
43	$CuK_2(SeO_4)_2 . 6H_2O$	,,	24·8 24·0	2·286 2·408	6·93 7·20	1,630 1,600	1,470 1,440
44	$CuRb_2(SeO_4)_2 . 6H_2O$	,,	26·2 24·7	2·801 2·810	6·50 6·56	1,460 1,470	1,320 1,320
45	$CuTl_2(SeO_4)_2 . 6H_2O$	,,	25·6 24·5	3·761 3·713	6·92 6·94	1,600 1,620	1,470 1,480
							Mean χ at 30° C.
46	$K_3Fe(CN)_6$	,,	31·8 32·1	2·117 2·366	13·61 15·25	2,120 2,120	1,940 1,940
47	$(NH_4)_2Cr_2O_7$	,,	31·8	2·062	0·509	62	53
48	K_2CrO_4	Along "*a*" axis	31·0	2·726	0·112	8·0	7·3
49	$(NH_4)_2CrO_4$	Along χ_1 axis	31·2	1·884	0·098	7·9	7·2

effect will be equivalent to a local orienting field; this local field will naturally share with the crystalline electric field which it is intended to replace, a certain amount of asymmetry. The results will be (1) a magnetic anisotropy for the crystal, (2) a value for the effective magnetic moment of the ion which will bear no simple relation to its spin and orbital moments, and (3) a complicated deviation from the Curie law.

V. Experimental support for the theory

The theory has received experimental support from various directions. When all the paramagnetic ions in the crystal are in the S-state, and have no orbital moments to be quenched by the crystalline fields, the results are particularly simple. Such crystals should be nearly isotropic magnetically, and should obey the Curie law. Both of these results have been verified experimentally. Indeed even the second order effects, due to a very feeble splitting of the spin levels by the crystal fields, predicted by the theory, have been confirmed. For a detailed discussion of this special class of crystals the reader may be referred to Part IV of this paper (1936).

Van Vleck (1932), Schlapp and Penney (1932), Jordahl (1934), and Janes (1935) have discussed the observed anisotropy and temperature variation of susceptibility of some of the salts of the iron group. They find that the intensity and the degree of asymmetry of the crystal fields required to explain these magnetic properties are of reasonable magnitude.

In particular we may mention that from a theoretical study of the mean susceptibility of the crystal $CuSO_4.5H_2O$ at different temperatures Jordahl predicted that the crystal field acting on the Cu^{++} ion in the crystal should be predominantly cubic in symmetry, and further, from the positive sign of the potential due to this cubic field, that the field should correspond to an octohedral distribution of six equal negative charges around the Cu^{++} ion. This result is not at all obvious from general structural considerations, as the crystal is triclinic, and there are five molecules of water and one SO_4 group associated with each Cu^{++} ion. The result, however, has recently been confirmed by the X-ray studies on the fine structure of the crystal by Beevers and Lipson (1934). It is actually found that each Cu^{++} ion is surrounded by six negatively charged oxygen atoms, which form a nearly regular octohedron. Four of them belong to four water molecules, and they form a square with the Cu^{++} ion at the centre. The other two, which are contributed by the two sulphate groups, are located centrally above and below this square.

As we mentioned just now, this octohedron is only approximately regular, as the oxygens of the water molecules are much closer to the central Cu^{++} ion than the other two. The crystal field acting on the Cu^{++} ion will therefore deviate from cubic symmetry, its magnitude for directions in the plane of the square being greater than along the normal to the square. Now there are two such Cu^{++} ions in the unit cell of the crystal, and the two corresponding squares of water molecules are inclined to each other at an angle of about 82°. One should therefore expect (1) that the crystal should be magnetically anisotropic, which is of course a trivial result, as the crystal is triclinic; (2) that it should be nearly uniaxial; and (3) that the axis of magnetic symmetry should lie along the line of intersection of the planes of the two squares. All these conclusions are verified by experiment (Krishnan and Mookherji 1936).

Finally, we may mention some recent measurements by Mr Joglekar on the magnetic anisotropies of mixed Tutton salts, in which the concentration of the paramagnetic ions in the crystal is varied, over a wide range, by growing mixed crystals with varying amounts of a suitable diamagnetic Tutton salt. The results of these experiments, which are in course of publication, lend strong support to the view underlying Van Vleck's theory that the magnetic anisotropy of the crystal arises from the asymmetric crystalline electric fields acting on the paramagnetic ions.

VI. Classification of paramagnetic crystals

Following Van Vleck (1935) we may divide paramagnetic crystals into the following three groups, according to the strengths of the crystalline electric fields acting on the paramagnetic ions: (1) Crystals in which the electric fields are so feeble that the coupling between the orbital and the spin moments remains practically unaffected, e.g. the rare earth salts. The magnetic moments of these ions should approximate to the Hund value. (2) Crystals in which the fields are sufficiently strong to break the spin-orbital coupling, but not strong enough to affect the Russel-Saunders coupling between the moments of the different electrons in the ion; e.g. the sulphates and selenates of the iron group of metals. The magnetic moment of the ion in these crystals should be nearly that due to the spins only. (3) Crystals in which the fields are large enough to break even the Russel-Saunders coupling; e.g. ferricyanide, chromate, etc. The magnetic susceptibilities of these crystals should be very low.

The above conclusions regarding the effective magnetic moments of the ions in the three groups of crystals are verified by experiment.

The magnetic anisotropies of these three groups of crystals, however, may not show such clearly marked differences; because the anisotropy, besides depending on the term-level of the ion, is also sensitive to the asymmetry of the crystalline field, which varies from crystal to crystal more widely than the absolute magnitude of the field (on which the effective magnetic moment depends). But roughly we may expect the crystals of the third group to exhibit the largest anisotropy, and those of the first group the smallest. This is more or less true. Taking $\Delta\chi/\chi$ as a measure of the anisotropy, we find that, among the crystals studied by us, ammonium chromate and dichromate have the highest anisotropies, namely 0·42 and 0·37 respectively, and they belong to the third group. The two other crystals in our list that belong to this group, namely potassium chromate and potassium ferricyanide, have also a large anisotropy. Among the other crystals, the salts of the iron group (except those of nickel) have in general a higher anisotropy than the rare earth salts.

VII. Mutual inversion of the Stark-levels of six-coordinated and four-coordinated Co^{++} ions in crystals: their magnetic anisotropies contrasted

The feeble anisotropy of the nickel salts has just been referred to: $\Delta\chi/\chi$ ranges from 0·02 to 0·04, which is only one-tenth of the anisotropy of the corresponding cobalt salts, for which $\Delta\chi/\chi$ varies from about 0·2 to 0·4. This striking contrast between the anisotropies of the cobalt and the nickel ions, which are both in the F state and are adjacent in the periodic table, requires explanation. An elegant one has been supplied by Van Vleck (1932), which is as follows. For a given crystalline electric field which is predominantly cubic in symmetry and has also a feeble rhombic component, the Stark patterns of Co^{++} and Ni^{++}, whose ground states are $d^7\,{}^4\mathrm{F}$ and $d^7\,{}^3\mathrm{F}$ respectively, are very similar, except for this important difference, namely that the pattern for ${}^4\mathrm{F}$ is inverted with respect to that for ${}^3\mathrm{F}$. Since one extreme level in the pattern is a singlet, while the other is a triplet, the inversion of the pattern will naturally make a great difference to the magnetic anisotropy, which depends on the multiplicity of the lowest level. For the type of cubic crystalline field that obtains in the hydrated sulphates, selenates, etc., the singlet level is lowest for Ni^{++}, which will accordingly be almost isotropic, whereas for Co^{++} the triplet level is lowest, and will lead to a large anisotropy; in agreement with observation.

The type of cubic field referred to above as obtaining in the hydrated sulphates corresponds to an octohedral arrangement of six water molecules around the paramagnetic ion. Since the water molecules have a large dipole moment, and will all present their negative ends towards the Co^{++} or Ni^{++} ion, as the case may be, the above arrangement will in effect be equivalent to an octohedral arrangement of six equal negative charges round each paramagnetic ion.

Following Van Vleck, let us express the potential of the crystalline field in the neighbourhood of the paramagnetic ion in the form

$$\Phi = D(x^4+y^4+z^4)+Ax^2+By^2-(A+B)\,Z^2, \tag{1}$$

where the fourth power terms refer to the cubic part of the field, and the quadratic terms to the rhombic part; the principal axes of the cubic and the rhombic fields have been assumed, for simplicity, to be coincident.

The cubic field obtaining in the above octohedral arrangement of negative charges will correspond, as Gorter (1932) has pointed out, to a positive value of D, and it is for this type of cubic field that the lowest level is a singlet for Ni^{++} and a triplet for Co^{++}. If, on the other hand, the cubic part of the field corresponds to a *negative* value of D, as it will if the paramagnetic ion were surrounded by eight equal negative charges at the corners of a cube, or four at the corners of a tetrahedron, then the disposition of the Stark pattern will be the reverse of that obtaining with the octohedral distribution;

in such a crystal the lowest level in the Stark pattern of Co^{++} will be the singlet, and not the triplet, and the crystal will in consequence be almost isotropic.

The tetrahedral type of distribution may be expected to occur in salts in which the Co^{++} ion has a coordination number four, instead of the usual six, as for example in the blue double chlorides of cobalt with the alkali metals. Indeed one such crystal, namely Cs_3CoCl_5, has recently been studied for its structure by X-ray methods by Powell and Wells (1935). The crystal is tetragonal, with the axial lengths $a = 9{\cdot}18$, $c = 14{\cdot}47$ A. It is found that each cobaltous ion in the crystal is closely associated with a group of four (negatively charged) chlorine atoms, which form an approximately regular tetrahedron with the cobalt at the centre, the fifth chlorine atom standing apart at a much greater distance; the structure thus corresponding to the coordination formula $Cs_3^{1+}[CoCl_4]^{2-}\,Cl^{1-}$. We should accordingly expect the magnetic anisotropy of this crystal to be quite small, in marked contrast with the hydrated sulphates and selenates of cobalt. This is actually so, as will be seen from the following results of our magnetic measurements on this crystal.

We find that at 30° C. $\chi_{\parallel} - \chi_{\perp} = 650$

and $\chi = (\chi_{\parallel} + 2\chi_{\perp})/3 = 9930.$

$\Delta\chi/\chi$ is thus quite small, being only 6·5 %.

We have also measured the principal susceptibilities of another double chloride of cobalt with caesium, namely $Cs_2[CoCl_4]$, in which also the $[CoCl_4]$ group has presumably a tetrahedral structure. Some well-developed deep blue crystals of this substance were grown out of an aqueous solution containing suitable amounts of the two chlorides. (An analysis of the crystals for their chlorine content gave Cl = 30·4 %, as compared with 30·39 % given by the above formula.) The crystals are orthorhombic, and from rough goniometric measurements the axial ratios were found to be

$$a : b : c = 0{\cdot}38 : 1 : 0{\cdot}65.$$

The following are the results of the magnetic measurements made on the crystal at 24° C.:

"*a*" axis vertical	"*b*" axis sets along the field	$\chi_b - \chi_c = 254$
"*b*" axis vertical	"*a*" axis sets along the field	$\chi_a - \chi_c = 397$
"*c*" axis vertical	"*a*" axis sets along the field	$\chi_a - \chi_b = 146,$

as against 143 calculated from the results for the first two directions.

The absolute gram-molecular susceptibility of the crystal (density 3·46) along its "*b*" axis was found to be 8190.

Collecting the results, we have

$$\chi_a - \chi_b = 143$$
$$\chi_a - \chi_c = 397$$
$$\text{Mean } \chi = 8150$$

The maximum anisotropy of the crystal, equal to 397/8150, is thus less than 5 %.

It is further significant that for both these crystals the mean susceptibilities are smaller than for the other cobalt salts listed in our table (in which the cobalt ions are six-coordinated), and are correspondingly nearer to the "spin-only" value. This result also follows from VAN VLECK's theory.*

We have not been able to obtain any four-coordinated nickel salt which is not diamagnetic.

VIII. CONSTANTS OF THE CRYSTAL FIELD IN NICKEL SALTS

We shall now discuss in some detail the anisotropy of nickel salts with positive D, in relation to their crystal fields. These salts lend themselves readily to a quantitative discussion. The necessary theoretical expressions have been developed by SCHLAPP and PENNEY. Assuming for simplicity, that the principal axes of the cubic and the rhombic parts of the crystal field are coincident, and that they are the same for all the paramagnetic ions in the unit cell, and that the potential of the field in the neighbourhood of the paramagnetic ion can be expressed by the relation (1) given in the previous section, namely, $\Phi = D(x^4+y^4+z^4)+Ax^2+By^2-(A+B)\,z^2$, they have calculated the three principal susceptibilities, χ_1, χ_2 and χ_3 of the crystal along the z, y and x axes respectively of the crystal field. We shall merely quote here their final results. For χ_1 they obtain the expression

$$\chi_1 = \frac{8N\beta^2}{3kT}\left[1+8\lambda\alpha_1+\frac{\theta_1}{kT}+\ \ldots\right]-8N\beta^2\alpha_1, \tag{2}$$

and for χ_2 and χ_3 two similar expressions, in which λ is the constant of the spin-orbit coupling ($=-335$ cm.$^{-1}$), β is the BOHR magneton ($=eh/4\pi mc$), and N is the Avogadro number:

$$\theta_1 = \tfrac{2}{3}\lambda^2(\alpha_2+\alpha_3-2\alpha_1); \tag{3}$$

α_1, α_2 and α_3 are constants which depend on the crystal field in the manner to be described below.

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* It should be mentioned here that the feeble anisotropies of these two crystals may be imagined to arise alternatively in the following manner: (*a*) the [$CoCl_4$] groups may have a perfectly regular tetrahedral structure, and the rhombic component of the field may be totally absent; this is highly improbable; (*b*) the different [$CoCl_4$] groups that are present in the unit cell may be oriented relatively to one another in such a manner as to form a more or less isotropic combination; the low mean susceptibilities of these crystals as compared with those of the six-coordinated compounds, do not support this possibility.

Instead of the constants D, A and B appearing in (1), Schlapp and Penney introduce the new constants* Dq_0, aA and aB, where $q_0/12$ and a are the ratios of the matrix elements of the actual system with 8 electrons to those for a one-electron system, for the cubic and the rhombic fields respectively.

Denoting $a(A+B)/2$ by σ, and $a(A-B)/2$ by δ, the α's are given by the expressions

$$\left.\begin{aligned} \alpha_1 &= \frac{p^2}{r_2-r_{-2}}+\frac{q^2}{r_2-r_0}, \\ \alpha_2 &= \frac{r^2}{r_2-r_{-1}}+\frac{s^2}{r_2-r_{-3}}, \\ \alpha_3 &= \frac{t^2}{r_2-r_1}+\frac{u^2}{r_2-r_3}, \end{aligned}\right\} \tag{4}$$

in which

$$\left.\begin{aligned} (r,\, s) &= (\cos\theta_1,\, \sin\theta_1), \text{ where } \tan 2\theta_1 = \frac{-2\times 15^{\frac{1}{2}}(3\sigma+\delta)}{6(\sigma-\delta)+8Dq_0}, \\ (t,\, u) &= (\cos\theta_2,\, \sin\theta_2), \text{ where } \tan 2\theta_2 = \frac{-2\times 15^{\frac{1}{2}}(3\sigma-\delta)}{8Dq_0+6(\sigma+\delta)}, \\ (p,\, q) &= (\cos\theta_3,\, \sin\theta_3), \text{ where } \tan 2\theta_3 = \frac{4\times 15^{\frac{1}{2}}.\delta}{8Dq_0-12\sigma}, \end{aligned}\right\} \tag{5}$$

$$\left.\begin{aligned} r_2 &= -18Dq_0, \\ r_{-3} &= r^2\times 6(\sigma-\delta)+s^2\times -8Dq_0+2rs\times -15^{\frac{1}{2}}(3\sigma+\delta), \\ r_{-1} &= r^2\times -8Dq_0+s^2\times 6(\sigma-\delta)-2rs\times -15^{\frac{1}{2}}(3\sigma+\delta), \\ r_1 &= t^2\times -8Dq_0+u^2\times 6(\sigma+\delta)+2tu\times 15^{\frac{1}{2}}(3\sigma-\delta), \\ r_3 &= t^2\times 6(\sigma+\delta)+u^2\times -8Dq_0-2tu\times 15^{\frac{1}{2}}(3\sigma-\delta), \\ r_{-2} &= p^2\times -8Dq_0+q^2\times -12\sigma+2pq\times -2\times 15^{\frac{1}{2}}.\delta, \\ r_0 &= p^2\times -12\sigma+q^2\times -8Dq_0-2pq\times -2\times 15^{\frac{1}{2}}.\delta. \end{aligned}\right\} \tag{6}$$

Thus from the known values of χ_1, χ_2 and χ_3 at any given temperature, it is possible to calculate the three α's, and thence the constants Dq_0, σ and δ of the crystal field. We have made the calculation for all the nickel salts whose susceptibilities we have measured.

The first part of the calculation, namely the evaluation of the α's from the χ's, is easily done with the help of the following relations. The expression for the mean susceptibility,

$$\chi = \tfrac{1}{3}(\chi_1+\chi_2+\chi_3) = \frac{8N\beta^2}{3kT}\left[1+(\alpha_1+\alpha_2+\alpha_3)\left(\frac{8\lambda}{3}-kT\right)\right] \tag{7}$$

may be put equal to

$$\frac{p_B^2 N\beta^2}{3kT}, \tag{8}$$

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* We use the letter q_0 in place of Schlapp and Penney's q, so as to avoid confusion with another q which also appears in the expression, and has a different significance.

where p_B is the "effective Bohr magneton value" of the magnetic moment of Ni^{++} in the crystal, and we thus obtain

$$\alpha_1+\alpha_2+\alpha_3=\frac{3(p_B^2-8)}{8(8\lambda-3kT)}. \tag{9}$$

Further, from (2) and (3)

$$\frac{\alpha_1-\alpha_2}{\chi_1-\chi_2}=\frac{\alpha_1-\alpha_3}{\chi_1-\chi_3}=\frac{3kT}{8N\beta^2(8\lambda-2\lambda^2/kT-3kT)}. \tag{10}$$

With the help of (8), (9) and (10) the three α's are readily calculated from the χ's.

The second part of the calculation, namely the evaluation of Dq_0, σ and δ from the three α's, is more laborious; it requires the solving of equations which involve these quantities in a very complicated manner, and the solving has therefore to be done by the trial and error method. We give below the results of the calculations.

As already mentioned, the axes x, y and z of the crystal field have been chosen to be respectively along the χ_3, χ_2 and χ_1 magnetic axes of the crystal. In order to make this definition of the choice of the crystal field axes applicable to the orthorhombic and tetragonal crystals also (in which the χ's along the different magnetic axes have been differentiated, in our notation, by the subscripts a, b, c, or $\parallel$ and $\perp$, instead of by 1, 2 and 3), we have adopted the following convention: χ_1, χ_2 and χ_3 are taken to correspond in orthorhombic crystals with χ_a, χ_b and χ_c respectively, and in tetragonal crystals with $\chi_\parallel$, $\chi_\perp$ and $\chi_\perp$ respectively.

It is clear from Table III that the value of Dq_0 is of nearly the same magnitude in all the crystals. In other words, the cubic part of the field acting on the Ni^{++} ion, which is also the predominant part, is more or less the same in all the crystals. This suggests that the octohedron of water molecules surrounding the Ni^{++} ion has nearly the same size in all the crystals.

The values of aA and aB, on the other hand, do depend on the structure of the crystal. This may indicate a real dependence of the rhombic part of the field on the structure of the crystal, or it may be merely a consequence of the simplifying assumption that we made, namely, that the axes of the crystalline fields acting on all the Ni^{++} ions in the crystal are coincident. Speaking in relation to the group of atoms associated with each Ni^{++} ion, this is equivalent to assuming that all such groups present in the unit cell of the crystal are oriented parallel to one another, and that consequently the observed magnetic anisotropy of the crystal represents that of each such group contained in it. But actually these groups will not in general be oriented parallel, and the anisotropy of the group will therefore be greater than the observed anisotropy of the crystal by an amount which will be determined by the orientations of these groups relative to one another, and therefore indirectly by the symmetry of the crystal. Thus the rhombic part of the field calculated from the crystal anisotropy on the assumption of parallelism of the constituent groups will naturally differ from the real field to an extent which will depend on the crystal symmetry. The dependence of the values of *aA* and *aB* in Table III on the nature of the crystal may, at least partly, arise from this cause, and to that extent the dependence is only apparent.

TABLE III. CONSTANTS OF THE CRYSTAL FIELD IN NICKEL SALTS

Crystal	Dq_0	$aA = \sigma + \delta$	$aB = \sigma - \delta$
$NiSO_4.6H_2O$	1328	492	492
$NiSeO_4.6H_2O$	1096	333	333
$NiSO_4.7H_2O$	1333	675	−1137
Double sulphates			
$NiSO_4.A_2SO_4.6H_2O$:			
A = K	1356	909	−995
NH_4	1314	744	−812
Rb	1231	748	−830
Cs	1183	687	−755
Tl	1218	666	−732
Double Selenates			
$NiSeO_4.A_2SeO_4.6H_2O$:			
A = K	1129	680	−732
NH_4	1152	590	−690
Rb	1118	674	−750
Cs	1079	620	−738
Tl	1110	597	−667
$Ni(NH_4)_2SO_4SeO_4.6H_2O$	1112	599	−689
$Ni(NH_4)_2(BeF_4)_2.6H_2O$	1250	687	−739

IX. AN INTERESTING FEATURE OF THE MAGNETIC ANISOTROPY OF THE SALTS OF THE IRON GROUP

Before leaving the salts of the iron group, we may notice one interesting feature of the magnetic anisotropy of these crystals. As will be seen from Table I, and also from the data given in an earlier paper in this series (Part II, 1933), there seems to be a general tendency, except in the cobalt salts, for the magnetic ellipsoid to approximate to a spheroid; the spheroid being oblate (susceptibility along the axis being minimum) for the ferrous and the cupric Tutton salts, and for the hydrated sulphates and selenates of nickel and copper; and prolate (susceptibility along the axis being a maximum) for the nickel Tutton salts and for ferrous sulphate heptahydrate.

X. SPLITTING OF THE ENERGY LEVELS OF THE RARE EARTH IONS IN CRYSTALS IN RELATION TO THEIR MAGNETIC PROPERTIES AND ABSORPTION SPECTRA

The general theory of the magnetic properties of the rare earth salts in relation to the Stark-splitting of the energy levels of the rare earth ions in the crystals has been worked out by PENNEY and SCHLAPP (1932). Let us consider first the salts of neodymium. The ground state of the Nd^{+++} ion is $^4K_{9/2}$, and since its *J* has a half integral value, a twofold (KRAMERS) degeneracy will be left over, however asymmetric the crystal field may be; and thus there will be two coincident groups, each containing five energy levels. *When the field has cubic symmetry*, the five levels are constituted as follows: a single level, which is lowermost, and two doubly degenerate levels separated from the former by $-11{\cdot}84A$ and $-40{\cdot}54A$ respectively, where A is a certain negative quantity, having the dimensions of energy, whose value depends on the magnitude of the field (and on the quantum state $^4K_{9/2}$ of the free Nd^{+++} ion).

As a result of this separation of the levels the susceptibility of the ion in the crystal will differ from that of the free ion, i.e. from the Hund value, by an amount which will be determined by this quantity A, and in a simple manner. Granting that the field is cubic, it should therefore be possible theoretically to calculate the value of A from the observed deviation of the susceptibility of the crystal from the Hund value, and thus to predict the Stark-separation of the ground levels of the rare earth ion in the crystal. But actually we are not able to do this at present, as the deviation from the Hund value is small, and the measurements on the mean susceptibility of the crystal are not sufficiently accurate. For example in the crystal of $Nd_2(SO_4)_3 . 8H_2O$, as PENNEY and SCHLAPP have pointed out, the magnetic values of GORTER and DE HAAS (1931) over a wide range of temperature correspond to $A = -20{\cdot}6$ cm.$^{-1}$, whereas CABRERA's measurements (1925) give practically the Hund value, corresponding to $A = 0$, while ZERNICKE and JAMES (1926) and ST MEYER (1925) obtain intermediate values.

SPEDDING and his co-workers (1937), on the other hand, have looked for a verification of the theory regarding the Stark-separation of the energy levels of the rare earth ions in crystals, in their absorption spectra. In a series of papers published recently in the *Journal of Chemical Physics* they have studied the absorption spectra of several rare earth salts in the crystal state at different temperatures, and deduced therefrom the low-lying energy levels of the rare earth ions in the crystals. In the crystal of $Nd_2(SO_4)_3 . 8H_2O$, for example, they obtain three levels, at 0, 77 and 260 cm.$^{-1}$ respectively, whose relative spacings are the same as those predicted by the theory for a cubic field, since $77 : 260 \approx -11{\cdot}84A : -40{\cdot}54A$. The actual separation evidently corresponds to $A = -\frac{260}{40{\cdot}54}$ cm.$^{-1}$ $= -6{\cdot}4$ cm.$^{-1}$, which is not an improbable value as it fits well with the magnetic susceptibility measurements of ZERNICKE and JAMES, which extend over a wide range of temperatures, and of ST MEYER at room temperature.

In the crystal of $NdCl_3 . 6H_2O$ they obtain similarly three levels, at 0, 62 and 250 cm.$^{-1}$ respectively, and these separations correspond to $A = -6{\cdot}2$ cm.$^{-1}$.

For the Pr^{+++} ion, the theoretical Stark-pattern in a cubic field consists of four levels, at 0, $-336A$, $-576A$, and $-1296A$ respectively. Experimentally from the absorption spectrum of the crystal of $Pr_2(SO_4)_3 . 8H_2O$ SPEDDING, HOWE and KELLER (1937) deduce the same number of levels, with their relative positions as predicted by theory. Similarly for Er^{+++} theory predicts for a cubic field a Stark-pattern consisting of five levels (SPEDDING 1937), and experimentally four levels have been observed (two of the theoretical levels being too close together to be resolved properly), which have the predicted relative spacings.

Further the actual separations of the levels of Pr^{+++}, Nd^{+++} and Er^{+++} in the respective octohydrated sulphates, as deduced from their absorption spectra, correspond to practically the same intensity of field in all the three crystals; a result which is to be expected in view of the isomorphism of the crystals,* and which is particularly satisfactory since some earlier discussions of the magnetic data of Pr and Nd sulphates seemed to give widely different fields in the two crystals.

The above results and the further observation that all the levels are single, including those which theoretically are degenerate and should be expected to split up if the field had a lower symmetry than the cubic, are taken by Spedding to indicate a practically rigorous cubic symmetry for the field. Indeed the evidence for this from the absorption spectra is apparently so strong that it has been suggested that the separation of the energy levels as deduced from the absorption data may be used for checking the observed susceptibility values for the crystal. On this criterion it is surmised, for example, that for $Nd_2(SO_4)_3 . 8H_2O$ the values of Gorter and de Haas should be too low, and of Cabrera too high, and those of Zernicke and James and of St Meyer should be nearly correct. Further since the splitting constant A is proportional to $(Z-\sigma)^4$, where Z is the atomic number and σ is the screening constant, it has been further suggested that by comparing the values of A (deduced from the absorption spectra) for any two of the rare earth ions under identical crystal fields (a condition which will practically obtain if the two ions are present in the same mixed crystal, or in two different crystals which are isomorphous), we may estimate the screening constants for the two ions.

XI. The magnetic anisotropy of the rare earth sulphates, and the asymmetry of their crystal fields

In view of these developments based on the presumed cubic symmetry of the fields acting on the rare earth ions in the crystals, and of the indirect nature of the evidence from the absorption spectra for such a cubic symmetry, it would be desirable to obtain some independent evidence regarding the symmetry.

One direct result of a cubic field would be a magnetic isotropy for the crystal, and any observed deviation from magnetic isotropy will give us some idea of the deviation of the field from cubic symmetry. Let us consider again the hydrated sulphates, and

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* That the crystal fields acting on the Pr^{+++} ion in the crystal of $Pr_2(SO_4)_3 . 8H_2O$ and on the Nd^{+++} ion in the crystal of $Nd_2(SO_4)_3 . 8H_2O$, should have practically the same intensity, is also suggested by the observation of Spedding (1937) that the absorption lines of neodymium sulphate present as a small impurity in the crystal of $Pr_2(SO_4)_3 . 8H_2O$ are in practically the same positions as in the crystal of $Nd_2(SO_4)_3 . 8H_2O$.

denote the difference between the maximum and the minimum principal susceptibilities of the crystal by $\Delta\chi_m$. The values of the anisotropy $\Delta\chi_m/\chi$ for these crystals are as given below:

TABLE IV

Crystal	$\Delta\chi_m/\chi$
$M_2(SO_4)_3.8H_2O$	
$M =$ Pr	0·20
Nd	0·11
Sm	0·21
Er	0·12

$\Delta\chi_m/\chi$ is not small, and when we remember that the group of atoms associated with each M^{+++} ion in the crystal should have at least this anisotropy, and has very probably more (as the different such groups—eight in number—present in the unit cell of the crystal, will not in general be oriented parallel to one another), and that it is the anisotropy of the above group (and not that of the crystal) that corresponds to the asymmetry of the crystalline field under consideration, it is easy to realize that the deviation from cubic symmetry should be quite marked.

Considering now those energy levels whose degeneracy has not been removed by the cubic field, but will be by a field of lower symmetry, one may safely conclude from the figures given in Table IV that the separation of these levels by the non-cubic part of the field will not be small in comparison with the separation between them and their neighbours produced by the cubic part of the field. The interpretation of the absorption spectra will naturally be more complicated, and the determination of the energy levels therefrom correspondingly difficult. A rediscussion of the valuable results on the absorption spectra of these crystals obtained by SPEDDING and his co-workers, taking into account the non-cubic nature of the crystalline fields as evidenced by the magnetic anisotropy of the crystals, is very desirable.

[*Note added on correction of proof,* 9 *December* 1937.] Mr D. C. Chakrabarty and one of us have recently studied the absorption spectra of single crystals of some of these rare earth salts, using *polarized* light. Many of the absorption lines are found to be strongly polarized, some of them being confined almost wholly to one or another of the principal directions of vibration in the crystal. We are making a preliminary classification of the absorption lines on the basis of their polarization, in the hope that such a classification may be helpful in any attempt at complete analysis of the absorption spectra of these crystals, which are rather complicated.]

We may mention here that the other rare earth salts that we have studied have also a fair degree of anisotropy; except the ethyl sulphate of praseodymium, which is almost isotropic, with $\Delta\chi_m/\chi$ only 3 %, and is in strong contrast with its octohydrated sulphate, for which $\Delta\chi_m/\chi$ is about 20 %.

XII. Further remarks on the rare earth salts

When the present measurements were started, no data were available for the magnetic anisotropy of any of the rare earth salts. Recently, however, Fereday and Wiersma (1935) have measured the anisotropy of some of the ethyl sulphates over a large range of temperature. Our results for these crystals at room temperature agree with theirs, as will be seen from the following table; except for erbium ethyl sulphate, for which our value, besides being nearly two and a half times theirs, has also the opposite sign. As we mentioned in the introduction, the specimen of erbium salt with which the present measurements were made was not quite pure; but it does not seem probable that the large discrepancy in the results can be due to this cause. We are trying to obtain a pure specimen with which to repeat the measurements.

Table V

Crystal	$\chi_{\parallel}-\chi_{\perp}$ at 30° C.	
	Fereday and Wiersma extrapolated	Present measurements
$M_2(C_2H_5SO_4)_6 . 18H_2O$		
$M =$ Ce	300	294
Pr	300?	241
Nd	600	600
Er	2590	−6590

Powder measurements have been made on the hydrated sulphates by several investigators, and the results obtained by some of them are given in the following table, for comparison with the mean of the three principal susceptibilities for single crystals obtained in the present measurements. Instead of giving the susceptibilities we have entered in the table the effective Bohr magneton values, p_B, calculated with the help of the relation

$$p_B = \sqrt{\frac{3k\chi_I T}{N\beta^2}}, \tag{11}$$

Table VI. Values of p_B for the rare earth ions

$M_2(SO_4)_3 . 8H_2O$	$M=$	Pr	Nd	Sm
Theoretical, for the free ion:				
Hund		3·58	3·62	0·84
Van Vleck and Frank		3·62	3·68	1·55 1·65
Observed, for the ion in the crystal:				
Zernicke and James (1926)	20° C.	3·48	3·54	1·56
Freed (1930)	17°·6	—	—	1·58
Gorter and de Haas (1931)	15–16°	3·43	3·38	—
Selwood (1933)	20°	—	3·56	—
Rodden (1934)	23–26°	3·63	3·72	1·69
Present measurements	30°	3·35	3·41	1·69

where χ_I is the mean susceptibility of the crystal per gram ion of the rare earth, obtained after correcting for the diamagnetism of the crystal. In making this correction we have taken the diamagnetism of the group $(SO_4^{--})_3.8H_2O$ to be -204 and that of the rare earths ions to be -28.

Summary

An account is given of measurements on the magnetic anisotropy and the mean susceptibility of a large number of paramagnetic crystals, among which are several salts of the rare earths, many of the iron group, and some feebly paramagnetic salts. The results are discussed, on the basis of the theory of Van Vleck, Penney and Schlapp, in relation to the Stark-splitting of the energy levels of the paramagnetic ions under the influence of the strong crystalline electric fields acting on the ions. A detailed calculation is given of the constants of the crystal field in the nickel salts.

The striking contrast in the magnetic behaviour of the six-coordinated and the four-coordinated cobalt compounds, predicted by the theory, is verified experimentally. The former salts are strongly anisotropic magnetically, while the latter are only feebly so. The mean susceptibilities of the former deviate more from the "spin-only" value than those of the latter.

All the salts of the iron group, except those of cobalt, have two of their principal susceptibilities nearly equal; i.e. the magnetic ellipsoids of these crystals approximate to a spheroid.

The conclusion drawn from studies on the absorption spectra of some of the rare earth salts that the fields acting on the rare earth ions in these crystals should be almost cubic in symmetry is not supported by observations on the magnetic anisotropy of these crystals.

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