

MAGNETIC STUDIES ON NICKEL IONS IN CRYSTALS

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ABSTRACT. Measurements have been made of the anisotropies and the principal magnetic susceptibilities of a number of crystalline nickel salts. With the help of these measurements and the available X-ray data for these crystals, the contributions of the constituent paramagnetic units have been worked out. The constants of the crystalline electric field have been calculated on the basis of the theory of Van Vleck, Penney and Schlapp and the relative contributions of the different terms in the theoretical expressions derived according to their theory, to the effective magnetic moments in different directions of the paramagnetic units have been discussed. Finally the magnetic anisotropy has been discussed in relation to the Stark splitting due to the crystalline electric field.

INTRODUCTION

Penney and Schlapp (1932) have explained the observed deviations from the free-ion behaviour of the effective magnetic moments of the Ni^{++} ions in crystals attributing these deviations to the influence of strong and asymmetric crystalline fields in the neighbourhood of the paramagnetic ion. Their calculations are based on the assumption that the axes of the crystalline fields acting on the Ni^{++} ions in the crystals are coincident. Speaking in relations to the paramagnetic groups in the unit cell of the crystals, this is equivalent to assuming that all such paramagnetic groups in the unit cell of the crystal are oriented parallel to each other. Consequently the observed crystal anisotropy represents the anisotropy of the individual paramagnetic units in the unit cell. But X-ray studies on the fine structure of some of the nickel salts show that it is not true. The different paramagnetic groups in the unit cell of the crystal are oriented relative to one another in such a manner as to build up the symmetry of the unit cell from those of the individual units. Hence the crystal anisotropy is only the average effect of the different groups in the unit cell although the mean of the principal susceptibilities remains unaffected by it.

In this communication, the results of magnetic measurements on single crystal of some of the nickel salts, for which fine structure study is available, are correlated with the paramagnetic groups in the unit cell of the crystal and then discussed in the light of the theory of Penney and Schlapp.

EXPERIMENTAL

Cobalt-free nickel salts of reagent quality were used and crystals were grown out of aqueous solutions.

The magnetic anisotropy was measured by the rotational method of Krishnan and Banerjee (1934) and the absolute susceptibility along some convenient direction in the crystal was measured by the balancing method of the

TABLE I
Temperature = 30°C

Crystal	Crystallographic data	Made of Suspension	Orientation in the field	$\Delta\chi$	Magnetic Anisotropy
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Tetragonal D_2^2 ; $Z=4$ $a=b=9.6 \text{ \AA}$ $c=18.3 \text{ \AA}$	Tetrag. ax. horiz.	Tetrag. ax. normal to the field	83	$\chi_1 - \chi_{11} = 83$
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	Rhombic V_4 ; $Z=4$ $a=11.8 \text{ \AA}$ $b=12.0 \text{ \AA}$ $c=6.8 \text{ \AA}$	'c' ax. vert. 'a' " " 'b' " "	'a' ax. along field 'c' " " " 'a' " " "	163 } 124 } 33.5	$\chi_a - \chi_b = 163$ $\chi_c - \chi_b = 124$ Cal. $\Delta\chi = 39$
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Moncl. prism C_2^2 ; $Z=2$ $a=8.49 \text{ \AA}$ $b=11.77$ " $c=4.87$ " $\beta=93^\circ 25'$	'b' ax. vert. 'c' " " 'b' and 'c' axes horiz.	$\psi=136.7$ 'b' ax. normal field 'b' " " "	234 } 24 } 78	$\chi_1 - \chi_2 = 234$ $\chi_1 - \chi_3 = 167$ Cal. $\psi = 38^\circ.5$
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Moncl. prism $a:b:c = 718:1:4028$ $\beta=94^\circ 23'$	'b' ax. vert. 'c' " " 'b' and 'c' axes horiz.	$\psi = -8.2$ 'b' ax. along field 'b' " " "	5,420 } 2,806 } 2,374	$\chi_1 - \chi_2 = 5,420$ $\chi_1 - \chi_3 = 2,494$ Cal. $\psi = -8^\circ.5$

TABLE II

Crystal	Direction along which sus. was measured	Temperature °C	Density of the crystal	Vol. susceptibility	Corresponding gm. mol. susceptibility	Mean susceptibility at 30°C	Square of the effective moments μ^2 at 30°C
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Along x_1 axis	30.0	2.080	32.17	4,068	4,040	$\mu_1^2 = 10.19$ $\mu_2^2 = 10.02$ $\mu_3^2 = 10.13$
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	Along 'a' axis	30.0	1.972	28.91	4,117	4,050	$\mu_a^2 = 11.53$ $\mu_b^2 = 9.997$ $\mu_c^2 = 10.30$ $\mu^2 = 10.61$
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Along x_1 axis	28.8	1.749	31.7	4,510	4,350	$\mu_1^2 = 11.04$ $\mu_2^2 = 10.74$ $\mu_3^2 = 12.88$ $\mu^2 = 10.89$
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Along 'b' axis	29.2	1.720	74.5	80,800	10,630	$\mu_1^2 = 28.37$ $\mu_2^2 = 15.11$ $\mu_3^2 = 22.26$ $\mu^2 = 21.91$

same workers. These two measurements when combined give the three principal susceptibilities in the crystal.

RESULTS

The results of measurements are collected in Tables I and II and expressed in the usual units (10^6 c.g.s. unit). χ_0 represents the gram molecular susceptibility along the axis of symmetry for tetragonal crystals and χ_1 that along directions normal to it. χ_a , χ_b and χ_c represents the gram molecular susceptibilities along the three crystallographic axes of a rhombic crystal; for monoclinic crystals χ_3 represents the gram molecular susceptibility along 'b' axis while greater of the two in the (010) plane is represented by χ_1 and the smaller by χ_2 ; ψ is the angle which the 'c' crystallographic axis makes with χ_1 -axis.

Effective magnetic moments of the crystals, μ_i , are calculated by the expression $\mu_i = 2.84 \sqrt{\chi'_i} T$, where χ'_i are the susceptibilities corrected for diamagnetism (both for cation and anion) and $i=1, 2$ and 3 or \parallel and \perp . The diamagnetism for Ni^{++} and Co^{++} ions were calculated to be -17.3×10^{-6} and -18.3×10^{-6} respectively by the method of Slater as modified by Angus (1932). The following diamagnetic corrections were adopted for different groups as given by Stoner (1935):

SO_4^-	$\text{CH}_3(\text{CHOO})_2$	H_2O
-33.6	-28.6	-13.0

MAGNETIC ANISOTROPIES OF CRYSTALS IN RELATION TO THE ANISOTROPIES OF THE CONSTITUENT PARAMAGNETIC UNITS

The results obtained in previous sections are discussed in this section in relation to X-ray data of the fine structure of the crystals.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.—This crystal has been analysed by X-ray methods by Beever and Lipson (1932). It is assigned a space group D_4^2 with four molecules in the unit cell. They find that the six water molecules group round the metal ion and lie at the corners of an octahedron. Four of them form a square about Ni^{++} ion and the remaining two lie centrally above and below the square. There are four such groups in the unit cell. The distance (NiO_1) of oxygen atoms lying centrally above and below the square from the Ni^{++} ion is 2.02 Å. While the distance (NiO_n) of oxygen atoms in the plane from the Ni^{++} ion is 2.04 Å.

Let the gram molecular susceptibility along (NiO_1) be represented by K_1 and along (NiO_n) be represented by K_n . Evidently K_1 is greater than K_n . The inclination (γ) of K_n -axis to 'c' crystallographic axis from X-ray data is 45.8.

Hence

$$K_1 - K_n = \frac{\chi_1 - \chi_n}{1 - \frac{3}{8} \sin^2 45.8}$$

using the values of $(\chi_1 - \chi_2)$ and $\bar{\chi}$ from Tables I and II, we obtain

$$\left. \begin{array}{l} K_1 - K_2 = 311 \\ K = 4,040 \end{array} \right\} \times 10^{-6} \text{ at } 30^\circ\text{C.}$$

Therefore the anisotropy of the paramagnetic unit ($\Delta K/K$) is .077. The corresponding squares of the effective magnetic moments are

$$n_1^2 = 9.68, \quad n_2^2 = 10.58, \quad \bar{n}^2 = 10.23.$$

$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.—This crystal has been studied by X-ray methods by Hull (1934). Its space group is C_{2h}^2 with two molecules in the unit cell. If the distribution of oxygen atoms about the metal ion is taken to be the same as in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, *i.e.*, four oxygens contributed by four water molecules forming a square about Ni^{++} ion and the other two contributed by two acetate groups lie centrally above and below the square, but at a smaller distance from the Ni^{++} ion than the other four oxygen atoms, one can calculate the anisotropy of the individual paramagnetic unit in the unit cell of the crystal in the following manner—

Let Z_1 and Z_2 represent the axes of the symmetry of the two units, (010) plane is the symmetry plane of the crystal, so the principal magnetic axes of one of the units is obtained from those of the other by reflection on the (010) plane. Since the paramagnetic unit possesses uniaxial magnetic symmetry, χ_1 will be the direction normal to the plane containing Z_1 and Z_2 axes and χ_2 will be the internal bisector of the angle (2ψ) between Z_1 and Z_2 .

Therefore

$$\left. \begin{array}{l} \chi_1 = K_2, \quad \chi_2 = K_2 \cos^2\psi + K_1 \sin^2\psi, \quad \chi_3 = K_2 \sin^2\psi + K_1 \cos^2\psi, \\ \cos^2\psi = \frac{\chi_3 - \chi_2}{K_1 - K_2} \end{array} \right\} \dots \quad (1)$$

and $\frac{1}{3}(\chi_1 + \chi_2 + \chi_3) = \frac{1}{3}(K_2 + 2K_1)$

Using the experimental values from Tables I and II we get

$$\left. \begin{array}{l} K_1 - K_2 = 401 \\ K = 4,350 \\ 2\psi = 80.4 \end{array} \right\} \times 10^{-6} \text{ at } 30^\circ\text{C.}$$

Thus the anisotropy of the paramagnetic unit is .092. The corresponding squares of the effective moments are

$$n_1^2 = 10.28, \quad n_2^2 = 11.27, \quad \bar{n}^2 = 10.94.$$

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.—The fine structure study of this crystal by Beevers and Schwartz (1935) assigns it the space group V_4 with four molecules in the unit cell. The disposition of water molecules about Ni^{++} ion is the same as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, *i.e.* six oxygens at the corners of an octahedron with Ni^{++} ion at the centre. The seventh water molecule does not come in contact with the metal ion. Four out of the six oxygen atoms form a square with Ni^{++} ion at the

centre, the other two are situated centrally above and below the square. The average distance (NiO_I) of oxygen atoms in the plane from the Ni^{++} ion namely 2.01\AA is smaller than the average distance (NiO_{II}) namely 2.08\AA of the other two oxygens from Ni^{++} ion. Hence K_{\parallel} , gram molecular susceptibility along the axis of symmetry of the group should be greater than K_{\perp} , gram molecular susceptibility for directions in the plane of the square.

If α , β and γ are the inclinations of K_{\parallel} axis to the a , b and c crystallographic axes then we have

$$K_{\parallel} - K_{\perp} = \frac{\chi_b - \chi_a}{\cos^2\alpha - \cos^2\beta},$$

and also

$$K_{\parallel} - K_{\perp} = \frac{\chi_a - \chi_c}{\cos^2\alpha - \cos^2\gamma}.$$

The values of α , β and γ from X-ray data are 73.5° , 32.8° and 62.0° degrees respectively. These together with the data from Tables I and II give

$$\left. \begin{array}{l} K_{\perp} - K_{\parallel} = 258 \\ \bar{K} = 4,050 \end{array} \right\} \times 10^{-6} \text{ at } 30^\circ\text{C.}$$

Hence the anisotropy of the paramagnetic unit in $NiSO_4 \cdot 7H_2O$ is .064.

The above value of ΔK shows that K_{\perp} is greater than K_{\parallel} . Though it agrees well with that of $NiSO_4 \cdot 6H_2O$ but disagrees with the suggestions from X-ray data of interatomic distances in $NiSO_4 \cdot 7H_2O$. Since slight variations, of the coordinates of Ni^{++} ion and oxygens cause a great alteration in the nickel-oxygen distances, and since such variations are not improbable this disagreement of magnetic data with the proposed structure of the crystal by X-ray method is not a serious one.

The squares of the effective moments of the unit are

$$n_{\parallel}^2 = 9.67, \quad n_{\perp}^2 = 10.57, \quad \bar{n}^2 = 10.24.$$

Nickel Tutton Salts.—Krishnan and the present author (1937) made measurements on a large number of nickel tutton salts at room temperature. If the distribution of the oxygen atoms about the Ni^{++} ion is the same as in $NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$ which will be presumably so, then the anisotropy of the paramagnetic units of the crystal, and their relative orientations (2ψ) of the groups can be calculated by using equations (1) since the crystals are all monoclinic and contains two molecules in the unit cell (Hofmann, 1931). The following table gives the calculated values of $(K_{\perp} - K_{\parallel})$ and 2ψ .

It is seen from Table (III) that $Ni(CH_3COO)_2 \cdot 4H_2O$ has the highest percentage anisotropy ($\Delta K/K \times 100$), i.e., 9.2% while the percentage anisotropy for single sulphates and the tutton salts vary from 7.3% to 5.1%.

TABLE III
Temperature 30°C

Crystal.	$K_{\perp} - K_{\parallel}$	\bar{K}	2ψ	$\frac{\Delta K}{K}$ = Anisotropy.
NiRb ₂ (SO ₄) ₂ .6H ₂ O	281	4,080	88.5	.060
NiCs ₂ (SO ₄) ₂ .6H ₂ O	261	4,080	88.5	.064
NiTl ₂ (SO ₄) ₂ .6H ₂ O	222	4,040	88.4	.055
Ni(NH ₄) ₂ (SeO ₄) ₂ .6H ₂ O	212	4,120	84.8	.051
NiK ₂ (SeO ₄) ₂ .6H ₂ O	292	4,160	90	.07
NiRb ₂ (SeO ₄) ₂ .6H ₂ O	307	4,160	88.1	.073
NiCs ₂ (SeO ₄) ₂ .6H ₂ O	290	4,150	84.4	.072
NiTl ₂ (SeO ₄) ₂ .6H ₂ O	236	4,110	87.6	.057
Ni(NH ₄) ₂ (PF ₆) ₂ .6H ₂ O	213	4,060	87.6	.053
NiSO ₄ .6H ₂ O	311	4,040	—	.077
NiSO ₄ .7H ₂ O	258	4,050	—	.064
Ni(CH ₃ COO) ₂ .4H ₂ O	401	4,350	80.4	.092

CONSTANT OF THE CRYSTAL FIELD

The ground state of the Ni⁺⁺ ion is ³F₄, the overall multiplet separation according to Laporte (1928) is 2347 cm⁻¹. Under the influence of a cubic field ³F₄ level splits up into a single and two triplet levels. In case of Ni⁺⁺ ion with positive D in equation (2) the single level lies lowest as is shown in figure (1). If now the spin and its coupling to the orbits is taken into account further splitting takes place. Penney and Schlapp (1932) have worked out the theoretical expressions for the principal magnetic moments of Ni⁺⁺ ions in crystals assuming for simplicity that all the paramagnetic groups in the unit cell of the crystal are oriented parallel to one another. Consequently their expressions refer to magnetic moments in the three directions of the paramagnetic unit.

The Ni⁺⁺ ion is considered to be subjected to an electric field which is predominantly cubic on which is superimposed a weak rhombic field. The axes of the cubic and rhombic fields are taken coincident. The potential of the field in the neighbourhood of the paramagnetic ion is given by

$$\phi = D(x^4 + y^4 + z^4) + Ax^2 + By^2 - (A + B)z^2 \quad \dots (2)$$

Since all the paramagnetic groups are taken as oriented parallel to one another, the squares of the effective magnetic moments, n_1^2 , n_2^2 and n_3^2 of the paramagnetic unit along the z, y, and x-axes of the crystal field have the expressions—

$$\left. \begin{aligned} n_1^2 &= 8 \left[\left\{ 1 + 8\lambda\alpha_1 + \frac{\theta_1}{kT} + \dots \right\} \left\{ -3kT\alpha_1 \right\} \right] \\ n_2^2 &= 8 \left[\left\{ 1 + 8\lambda\alpha_2 + \frac{\theta_2}{kT} + \dots \right\} \left\{ -3kT\alpha_2 \right\} \right] \\ n_3^2 &= 8 \left[\left\{ 1 + 8\lambda\alpha_3 + \frac{\theta_3}{kT} + \dots \right\} \left\{ -3kT\alpha_3 \right\} \right] \end{aligned} \right\} \dots (3)$$

where λ is the coefficient of spin-orbit coupling and is equal to 335 cm^{-1} for Ni^{++} ion.

$$\begin{aligned}\theta_1 &= 2/3\lambda^2(\alpha_2 + \alpha_3 - 2\alpha_1) \\ \theta_2 &= 2/3\lambda^2(\alpha_1 + \alpha_3 - 2\alpha_2) \\ \theta_3 &= 2/3\lambda^2(\alpha_1 + \alpha_2 - 2\alpha_3)\end{aligned}$$

and α_1 , α_2 and α_3 are constants of the crystal field. They are connected with D , coefficient of the rhombic field in the following manner—

$$\left. \begin{aligned}(18Dq_0 - 12\sigma)\left(10Dq_0 + \frac{1}{\alpha_1}\right) &= 60\delta^2 \\ (18Dq_0 - 6\sigma - 6\delta)\left(10Dq_0 + \frac{1}{\alpha_2}\right) &= 15(3\sigma + \delta)^2 \\ (18Dq_0 - 6\sigma - 6\delta)\left(10Dq_0 + \frac{1}{\alpha_3}\right) &= 15(3\sigma - \delta)^2\end{aligned}\right\} \dots (4)$$

where $\sigma = a(A+B)/2$ and $\delta = a(A-B)/2$, q_0 and a are the ratio's of the matrix elements of actual system with eight electrons to those for one electron system for cubic and rhombic field respectively.

Hence it is possible to calculate Dq_0 , aA and aB from a knowledge of α 's, which are calculated from the magnetic measurements by the help of the following equations. These equations are obtained directly from (3)

$$\frac{\alpha_1 - \alpha_2}{n_1^2 - n_2^2} = \frac{\alpha_1 - \alpha_3}{n_1^2 - n_3^2} = \frac{1}{8} \left[\frac{1}{8\lambda - \frac{2\lambda^2}{kT} - 3k'T} \right]$$

and

$$\alpha_1 + \alpha_2 + \alpha_3 = \frac{3}{8} \left[\frac{n^2 - 8}{8\lambda - 3k'T} \right]$$

Table IV gives the values of Dq_0 , aA and aB for the three crystals $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ for which fine structure data are available. n_1^2 , n_2^2 and n_3^2 are taken to correspond n_3 , n_1 and n_1 for the paramagnetic unit, which possesses an approximate axis of symmetry.

TABLE IV

Crystal	n_3^2	n_1^2	\bar{n}^2	$\alpha_1 \times 10^{-5}$ cm^{-1}	$\alpha_2 = \alpha_3$ $\times 10^{-5} \text{ cm}^{-1}$	Dq_0	aA	aB	$\frac{\Delta K}{K} \times 100$
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	9.68	10.51	10.23	-6.0	-9.2	1449	922	922	7.7
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	9.67	10.52	10.24	-6.83	-9.25	1464	926	926	6.4
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	10.28	11.27	10.94	-9.24	-12.03	1087	670	670	9.2

n_3 and n_1 represents the effective magnetic moments of the paramagnetic unit when the magnetic field is applied along and perpendicular to the symmetry axis of the unit and \bar{n} is the corresponding mean moment.

It is very satisfactory that Dq_0 , aA and aB are very nearly equal in the two salts $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. Dq_0 which determines the size of the octahedron of water molecules about the Ni^{++} ion is almost of the same size in the above two salts but considerably greater in $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

RELATIVE CONTRIBUTIONS OF THE DIFFERENT
TERMS TO THE EFFECTIVE MAGNETIC MOMENTS
IN DIFFERENT DIRECTIONS OF THE
PARAMAGNETIC UNIT

Equations (3) shows that in any direction the square of the effective magnetic moment consists of terms which are independent of temperature and terms which vary with temperature. For the three salts namely $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ the contributions by the various terms are shown in Table V.

TABLE V

Crystal	Contribution to n_{\parallel}^2 by			Contribution to n_{\perp}^2 by		
	Temperature in- dependent term.	Temperature dependent term.		Temperature in- dependent term.	Temperature dependent term.	
	$8+64\lambda a_1$	$24kT a$	$8\theta_1/kT$	$8+64\lambda a_3$	$24kT a_2$	$8\theta_2/kT$
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	8+1.479	.3488	-.1296	8+1.972	.4688	+.0647
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	8+1.464	.3458	-.1373	8+1.983	.4688	+.0686
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	8+1.972	.4688	-.1592	2+8.577	.6112	+.0796

It will be seen from the above table that the temperature-dependent term consists of two parts; one part varying directly with temperature while the other inversely as the temperature. At room temperature (*i.e.*, 30°C) the term varying inversely as temperature is almost negligible. It does not contribute anything to the mean effective moment. The magnetic moment along the axis of symmetry of the paramagnetic unit is opposed by it, while it helps moments for directions normal to the axis of symmetry. The temperature-independent term greatly predominates over the contributions by other terms. The contribution of the term varying directly as the temperature is only 3 to 4% of the contribution of the term independent of temperature. The contribution of the spin-orbit interaction between the lowest and the upper components of the ground-term is only 16 to 20% of the spin-only value 8.

STARK SPLITTING AND MAGNETIC ANISOTROPY

If the crystalline field acting on the Ni^{++} ion is purely cubic, then Dq_0 which is proportional to the Stark-splitting by the cubic field is given by

$$Dq_0 = \frac{4}{3} \left[\frac{3kT - 8\lambda}{n^2 - 8} \right]$$

For the three salts $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ these values are 1189, 1184 and 1044 cm^{-1} respectively. The presence of rhombic terms raises these values as shown in Table IV.

The cubic part of the field determines to a first approximation the mean square of the effective magnetic moment n^2 , *i.e.* its deviations from the free ion value and that the rhombic part have very little effect on n^2 though the whole of the anisotropy is due to it. For Ni^{++} ions the cubic splitting also influences the percentage anisotropy to a certain degree. For according to Van Vleck (1932), the magnetic anisotropy of Stark level for Ni^{++} ion with positive D as shown in figure (1) exists only by virtue of the difference between the frequencies $\nu(ab)$, $\nu(ac)$ and $\nu(ad)$ or between $\nu(ac)$, $\nu(af)$ and $\nu(ag)$.

Since the rhombic separation is small in comparison with cubic separation the percentage anisotropy should be small. The following table gives the splitting by the two fields.

TABLE VI

Crystal	Overall Cubic splitting in cm^{-1}	Overall Rhombic splitting of Level 3 (approx) in cm^{-1}	$\frac{\Delta K}{K} \times 100$
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	26,100	7,250	7.4
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	26,350	7,320	6.4
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	23,160	6,400	9.2

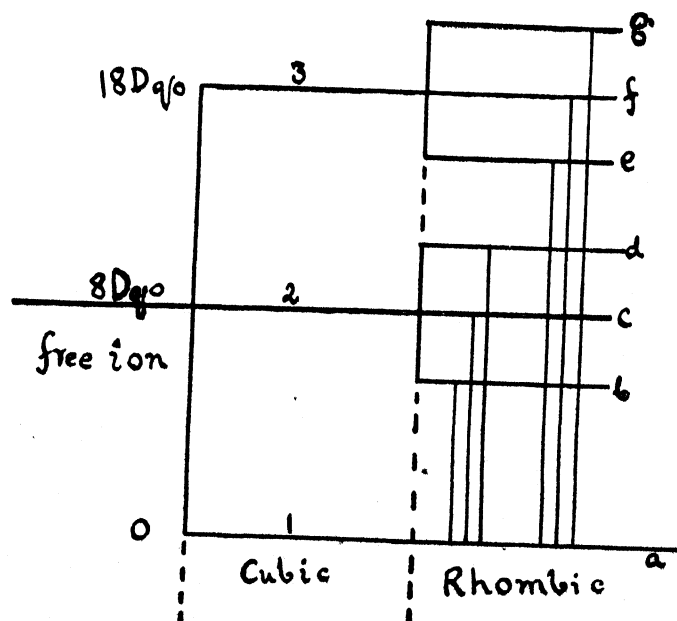
Stark patterns of Ni^{++} ion with positive D,

FIG. 1

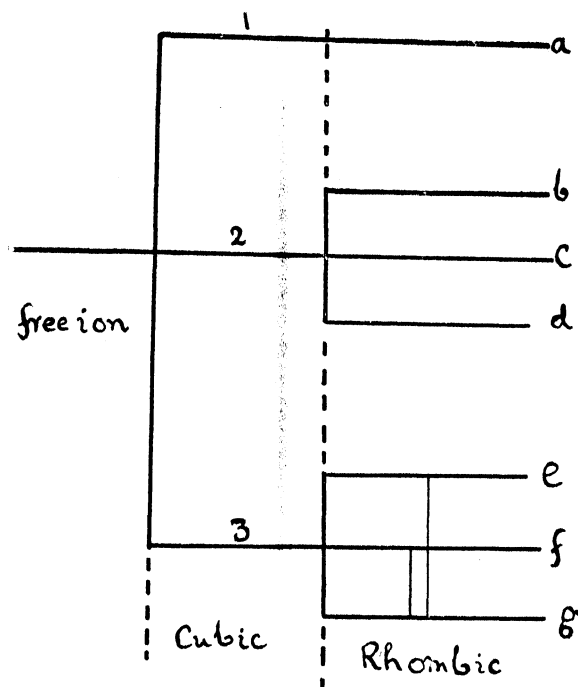
Stark pattern of Co^{++} ion with positive D.

FIG. 2

As will be seen from Table VI the paramagnetic unit in the salt $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ has the least cubic and rhombic splitting but its anisotropy is the highest of the three, indeed it is the highest of all the nickel salts studied so far (Krishnan and Mookherji, 1937). If the rhombic splitting in the three crystals be the same, the less cubic splitting in $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ makes the percentage difference between the frequencies $\nu(ab)$, $\nu(ac)$ and $\nu(ad)$ or between $\nu(ac)$, $\nu(af)$ and $\nu(ag)$ more and hence % anisotropy is also more. As a result of this the general impression is that the more the rhombic splitting the more will be the anisotropy of the paramagnetic unit will not be true for Ni^{++} ions, but will be true for Co^{++} ions. The Stark patterns of Co^{++} ion with positive D as shown in figure 2 is nothing but upside down of the Stark patterns for Ni^{++} ion with positive D. The anisotropy of 'g' in Fig. 2 exists by virtue of the difference between the frequencies $\nu(gf)$ and $\nu(ge)$, 'g' being the ground state. The overall rhombic splitting in case of $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as calculated by Penny and Schlapp (1932) with a field $20(x^2 - z^2)$ is 480 cm^{-1} , hence the percentage anisotropy in Co^{++} ion will be very high, which will be solely influenced by the rhombic splitting alone. In case of Co^{++} ions in crystals rhombic splitting will produce not only all the anisotropy but also will bring down \bar{n}^2 .

For comparison with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ we have studied a cobalt salt namely $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. In the paramagnetic unit of this salt whether

K_{\parallel} is greater or smaller than K_{\perp} , the percentage anisotropy will not vary much from 76% which is the highest of all the cobalt salts studied so far (Krishnan and Mookherji *loc. cit.*). Rhombic splitting seem to be very high in this salt. Taking the same distributions of oxygen atoms about Co^{++} ion as in $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and taking K_{\perp} greater than K_{\parallel} , one can calculate $(K_{\perp} - K_{\parallel})$ since the crystal is monoclinic and contains two molecules in the unit cell (Hull, 1934). The magnetic constants of the paramagnetic unit are

$$\left. \begin{array}{l} K_{\perp} - K_{\parallel} = 7890 \\ \bar{K} = 10,630 \end{array} \right\} \times 10^{-6} \text{ at } 30^{\circ}\text{C.}$$

and the corresponding squares of the magnetic moments are

$$n_{\parallel}^2 = 13.4, \quad n_{\perp}^2 = 32.8, \quad n^2 = 26.3,$$

which approximately fit with a rhombic field $200(x^2 - z^2)$ giving a splitting of $2,400 \text{ cm}^{-1}$. Hence it would be very interesting to study this crystal at low temperatures and see whether the experimental results agree with those calculated by Penny and Schlapp with $Dq_0 = 12.00 \text{ cm}^{-1}$ and a rhombic field $200(x^2 - z^2)$.

In conclusion the author wishes to express his thanks to the Committee of Management of the Indian Association for the Cultivation of Science for the facilities of the Laboratory, where the experimental works were carried out and also to Professor K. Banerjee, D.Sc., F.N.I. for his interest in the work. Thanks are also due to Mr. R. K. Sen, M.Sc., for his valuable discussions.

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