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Bose, D.M.

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16. Abstract

An attempt to explain paramagnetic phenomena without assuming the orientation of a molecule or ion in a magnetic field. Only the spin angular momentum is assumed to be responsible. A derivative of the Curie-Langevin law and the magnetic moments of ions are given as a function of the number of electrons in an inner, incomplete shell. An explanation of Gerlach's experiments with iron and nickel vapors is attempted. An explanation of magnetomechanical experiments with ferromagnetic elements is given.

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THE ROLE OF SPINNING ELECTRONS IN PARAMAGNETIC PHENOMENA

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/864*

To explain Curie's observations on the change in the mass susceptibility of oxygen with temperature, Langevin made the fundamental assumption that a paramagnetic molecule as a whole can re-orient itself in a magnetic field. In the quantum theory of this phenomenon, derived by Pauli, Sommerfeld and others, this assumption is accepted with the restriction that the magnetic axes of the molecule can only assume a discrete number of orientations with respect to the field. Langevin's assumption has been seriously attacked primarily for two reasons: 1. Because the Langevin-Weiss formula also reproduces the susceptibility of paramagnetic crystalline solid bodies, in which a rotation of molecules or ions is impossible; and 2. Because all experiments to test the optical and electrical consequences of the orientation of paramagnetic gas molecules in a magnetic field produced negative results. The present article attempts to explain paramagnetic phenomena from assumptions not requiring the orientation of a molecule or ion in a magnetic field. It is assumed that of the two angular momentums of an electron moved in a closed orbit, namely the spin angular momentum characterized by the quantum number s and its orbital angular momentum characterized by $l = k - 1$, only the former is responsible for paramagnetic effects. Furthermore, the axes of rotation of these electrons may be oriented either parallel or antiparallel to the magnetic field, and the resulting magnetic moment of an atom or ion with an incomplete inner shell is equal to the algebraic sum of the spin angular momentums of all electrons that can orient themselves in the magnetic field. Using these assumptions, 1. a

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derivative of the Curie-Langevin law and 2. the magnetic moments of ions are given as a function of the number of electrons in an inner, incomplete shell; 3. an explanation of Gerlach's experiments with iron and nickel vapors is attempted and 4. an explanation of magnetomechanical experiments with ferromagnetic elements is given.

Introduction

It is well known that at present there is no logically satisfactory theory of paramagnetic phenomena that simultaneously reproduces all known phenomena quantitatively. Before we proceed to present a new theory, we want to list the theories proposed to explain the known phenomena of paramagnetism, and see how theoretically satisfactory they are and how well they can represent experimental fact.

Langevin's theory of paramagnetism was introduced to explain the relationship that Curie discovered between the mass susceptibility χ of oxygen and temperature T, namely: /865

$$\chi T = \text{const.}$$

Langevin assumed that each oxygen molecule possesses a magnetic moment μ and that such molecules, when brought into a magnetic field, strive to orient themselves parallel to the direction of the field, unless hindered by collision with other molecules. It is furthermore assumed that the molecules do not reciprocally affect each other. With these assumptions, it can be shown using Boltzmann's theorem that

$$\frac{\bar{m}}{\mu} = \text{ctg hyp } x - \frac{1}{x} = L(x) \text{with } x = \frac{\mu H}{kT};$$

$\bar{m}$ = mean moment of a molecule, and

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \cdots$$

for small values of x.

For small values of x, we can set

$$\overline{m} = \frac{\mu^2 H}{3kT}$$

which can also be put in the form

$$\chi_M = \frac{M}{H} = \frac{M_0^2}{3RT}$$

where χ_M is the molar susceptibility, M is the magnetic moment per gram molecule, and M_0 is the magnetic moment when all molecular axes are parallel to each other. Thus

$$\chi_M T = \frac{M_0^2}{3R} = C.$$

This is Langevin's formulation of Curie's law.

It can be shown in general that for small values of $\frac{\mu H}{kT}$:

$$\chi_M T = \frac{M_0^2}{R} \overline{\cos^2\theta},$$

where θ is the angle between the magnetic axis of a molecule and the direction of the field. By classical theory, all directions are equally probable and thus $\overline{\cos^2\theta} = 1/3$.

Now it was found that Langevin's formula applies not only for paramagnetic gases, but also for diluted solutions of paramagnetic salts and even for crystal powders. For the latter, Weiss proposed a modification of Curie's formula: /866

$$\chi_M = \frac{C}{T - \Delta}.$$

Weiss ascribed the correction term Δ to the presence of an intermolecular magnetic field. Weiss' hypothesis of the magnetic origin of this field has not been confirmed, and therefore at present there is no satisfactory explanation for the term Δ. In

1911 Weiss reported that the molecular magnetic moment M_o of salts of paramagnetic elements as well as iron and nickel, in a state of full saturation, at 0° abs. or at temperatures above the Curie point, could be written as a whole multiple of a unit known as the Weiss magneton M_W = 1123.5 Gauss·cm, i.e., $M_o = n_W M_W$. The value of M_o was derived from the formula $M_o = \sqrt{3RC}$.

Critique of Langevin's Orientation Hypothesis

The fundamental assumption of Langevin's theory is that a molecule with a magnetic moment rotates as a whole in a magnetic field. This would be possible if molecules were rigid bodies like magnetic needles. But we know that an atom or a molecule is composed of certain positive nuclei around which a number of electrons move in closed orbits, and the moment of the molecule is the sum of the moments of these orbits. If they are brought into a magnetic field, these orbits perform precessional movements around the direction of the field, and the molecule will not want to rotate as a whole in the magnetic field. Even if such an orientation were possible for the molecules of a gas or solution, difficulties develop in the attempt to apply the idea to the case of a paramagnetic crystalline solid body obeying Curie's law $\chi_M(T - \Delta) = C$. From x-ray analysis of crystals we know that free rotation of the molecules is impossible, and if to avoid difficulties we assume that the atom can rotate, we run into new difficulties. For according to the theoretical derivation of Curie's law we would then have to require the energy of the thermal rotation of these atoms to have the amount given by the law of equipartition. But our knowledge of the specific heats of single-atom gases tells us that such an assumption is inaccurate. /867

It is interesting that Langevin's assumption was used by Debye to express the dielectric mass susceptibility of a substance

$$\chi_e = \frac{\varepsilon - 1}{4\pi} \cdot \frac{1}{\rho}$$

in the form $\chi_e = A + \frac{B}{T}$

where the second term arises from molecules with permanent electric dipoles that can orient themselves in an electrical field. It develops that the second term is missing for solid dielectrics, and consequently the rotation of an electric dipole is impossible in a solid dielectric. Many experiments have been undertaken to test the optical and electrical consequences of the hypothesis of the orientation of molecules in a magnetic field, all with negative outcomes [1].

This yielded the need for a derivative of the Curie-Langevin formula that did not use the assumption of rotation of molecules in a magnetic field. The first attempt was made by Lenz [2], who assumed that the magnetic molecules of a solid body can flip over either parallel or antiparallel to the direction of the field.

According to him,

$$\frac{\bar{m}}{\mu} = \text{tg hyp}\, x \qquad \text{with} \quad x = \frac{\mu H}{kT}$$

and for small values of x, $\frac{\bar{m}}{\mu} = \frac{\mu H}{kT}$;

-- a formulation of Curie's law, but not in Langevin's form. This formula, as well as one proposed by Ehrenfest, was used by Debye [3] to represent $\frac{\bar{m}}{\mu}$ values for $Gd_2(SO_4)_3$ for large values of x. Neither formula can yield the experimental findings.

Another error in the Lenz theory is the lack of any picture of how the molecular moments of the various paramagnetic ions

change as a function of the distribution of electrons in them -- this point is very important and will be considered below.

The quantum theory of paramagnetic phenomena also assumes that paramagnetic molecules can orient themselves in a magnetic field, but that the magnetic axes have a discrete number of /868 positions with regard to the direction of the field; accordingly, criticism of Langevin's orientation hypothesis is equally directed against the present form of the quantum theory of paramagnetic phenomena.

Quantum Theory of Paramagnetic Phenomena

The development of the quantum theory of serial spectra by Bohr, Sommerfeld and others introduced a new unit of magnetic moment, namely the Bohr magneton μ_1, into theoretical physics:

$$\mu_1 = \frac{eh}{4\pi mc}$$

is the magnetic moment of an electron moving in the first quantum orbit. The magnetic moment per gram atom of an element containing a Bohr magneton is given by $M_B = N\mu_1 = 5584$ Gauss·cm = 4.97 M_W.

The first successful attempt to represent the magnetic moments of paramagnetic molecules as whole multiples of the Bohr magneton, and thus to take into account the spatial quantization of such molecules, was undertaken by Pauli [4] in 1920. If we proceed from the general formula

$$M_0^2 = \frac{CR}{\cos^2\Theta}$$

we can set M_O equal to either $n_W M_W$ or $n_B M_B$, where n_B is the number of Bohr magnetons contained in M_O. Then we have

$$M_0 = n_W M_W = 3RC$$

according to Langevin's theory and

$$M_0 = n_B M_B = \frac{RC}{\cos^2\Theta}$$

according to quantum theory, or

$$n_W = \frac{M_B}{M_W} n_B \sqrt{\cos^2\Theta} = 4{,}97\, n_B \sqrt{\cos^2\Theta};$$

Thus by the above formula we can calculate the number of Weiss magnetons corresponding to a given number of Bohr magnetons. To calculate $\cos^2\theta$, Pauli makes the simple assumption that the molecule contains a whole number of Bohr magnetons, and that the component of the magnetic moment of the molecule in the direction of the magnetic field likewise is a whole multiple of the Bohr magneton. Furthermore, he excludes the state in which the /869 magnetic axis is perpendicular to the direction of the field. Then one gets

$$\sqrt{3\cos^2\Theta} = \sqrt{\frac{(n_B+1)(2n_B+1)}{2n_B^2}}$$

and

$$n_W = 4{,}97 \sqrt{(n_B+1)(n_B+{}^1/_2)}.$$

On the other hand, Sommerfeld [5] assumes that the number of possible orientations of an atom with the inner quantum number j in an outer field is $2j + 1$ and that the magnetic moment is $\mu = jg$, where g is the Landé factor of the anomalous Zeeman effect. This formula is based on other possibilities for calculating μ, which we will describe further below. Sommerfeld calculates the value of $\overline{\cos^2\theta}$ for various values of j and finds that

$$\text{daß } \overline{\cos^2\Theta} = \sqrt{\frac{j+1}{j}}$$

and therefore

$$n_W = 4{,}97\, g \sqrt{j(j+1)}.$$

He furthermore makes the special assumption that the paramagnetic ion is in the s state, corresponding to the value $g = 2$; if we then set $\mu = n_B \mu_1$, we get the relationship $n_B = 2j$. If we then insert the value for j in the above formula, we find:

$$n_W = 4{,}97 \sqrt{n_B(n_B+2)}.$$

But optical examination reveals, as we will see below, that Sommerfeld's assumption that the ion is in the s state is untenable.

Gerlach, Epstein and Sommerfeld [5] have attempted to express the magnetic moments of the ions of the iron group in Bohr magnetons. It develops that when one expresses the moments of these ions in Weiss magnetons [6], one gets an accumulation around figures corresponding to whole multiples of the Bohr magneton. This indicates that there is good justification to assume that the magnetic moment of these ions is a multiple of the Bohr magneton.

The Stern-Gerlach experiment, which shows that after passing through a non-homogeneous magnetic field, a beam of evaporated silver atoms precipitates in two separate strips, is considered the most direct proof of spatial quantization. It was /870 furthermore found that the magnetic moment of a silver atom is equal to one Bohr magneton, within an error of 5%. It is interesting that the largest observed number of separate strips precipitating from the atoms of any element is three, and occurs with nickel. This contradicts the number one would expect from

spectroscopic μ determinations.

The Spectroscopic Method of μ Determination

Sommerfeld was the first to show that using the formula $\mu = jg$ it is possible to calculate the magnetic moment of the atoms of various elements from spectroscopic data alone. From an analysis of spectral terms, using the anomalous Zeeman effect, one can determine the values for j and g for the term corresponding to the unexcited state of the atom, and from this $\mu = jg$ can be calculated for the unexcited atom. We calculate the values for μ and j of the three elements Fe, Co and Ni from spectroscopic data [7], and compare the figures they lead us to expect with the figures yielded by Gerlach's experiment:

Element	Fundamentalterm	j berechnet[a]	b Zahl der Streifen		μ	
			[c] erwartet	[d] gefunden	[c] erwartet	[d] gefunden
Fe	^5D	4	9	1	6	0
Co	^4F	9/2	10	—	6	—
Ni	^3F	4	9	3	5	2

Key: a. calculated
b. number of strips
c. expected
d. found

The observed and calculated values for μ and for the number of strips precipitating in the Stern-Gerlach experiment are thus completely different.

The Hund Method [7] to Calculate the Magnetic Moment of Ions

Hund has reported a very interesting method for the theoretical calculation of various spectroscopic terms corresponding to the electron distribution in one or more incomplete shells. Below we summarize this theory in Sommerfeld's notation [8]. The state of each electron in a given orbit is characterized by two quantum numbers s and l. s can assume the values $\pm$ 1/2, and

until recently the meaning of this number was one of the secrets of the atom's structure. Goudsmit and Uhlenbeck extensively /871 clarified our understanding by identifying this number with the presence of a spin angular momentum in the electron having the value

$$\frac{1}{2}\frac{h}{2\pi}$$

together with a magnetic moment equal to one Bohr magneton. The relationship of the magnetic to the mechanical moment of such an electron equals e/mc, i.e., half the value one gets for the orbital movement of the electron. If several valence electrons are present, we set:

$$\bar{s} = |\Sigma s_i| = |\Sigma \pm \tfrac{1}{2}|.$$

From s one determines the multiplicity $r = 2s + 1$ of the term. The other number characterizing the electron is $l = k - 1$, where k is the azimuthal quantum number of the electron orbit. If several valency electrons are present, then each of them is additionally determined by the magnetic quantum number m_l, where $l \geq m_l \geq -l$, and these combine into the group quantum number $\bar{l} = \Sigma m_l$. The inner quantum number j is composed of $\bar{s}$ and $\bar{l}$ in such a way that $l + \bar{s} \geq j \geq |\bar{l} - \bar{s}|$. Hund furthermore assumes that of all terms constructed in this way, the fundamental term is characterized in that 1. it has the highest multiplicity, and 2. for regular terms it has the smallest value for $j = |\bar{l} - \bar{s}|$, and for inverted terms it has the maximum value for $j = \bar{l} + \bar{s}$. For example,, for z electrons in a level, the highest value for s is $z/2$; the corresponding multiplicity is $r = z + 1$; if $z < 2l + 1$, then

$$\bar{l} = s\left(l - \frac{s-1}{2}\right)$$

and

$$\bar{j} = |\bar{l} - \bar{s}| = s\left|l - \frac{s}{2}\right|.$$

For $z > 2l + 1$, $j = \bar{l} + s$, and after Pauli we must replace z in the formulas for $\bar{l}$ and $\bar{s}$ with $z' = 2(2l + 1) - z$, so that

$$\bar{j} = (\bar{l} + \bar{s}) = s'\left(l - \frac{s'}{2} + 1\right).$$

On the basis of Hund's theory, a great many spectral terms have been calculated theoretically and tested experimentally. Hund himself used his results to calculate the number of magnetons corresponding to various electron numbers in the incomplete shells of ions from Sc to Ni, using the formula

$$g = 1 + \frac{1}{2}\frac{\bar{j}(\bar{j}+1) + \bar{s}(\bar{s}+1) - \bar{l}(\bar{l}+1)}{\bar{j}(\bar{j}+1)}$$

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The corresponding number of Weiss magnetons of these ions is then calculated using the equation

$$n_W = 4{,}97\, n_B \sqrt{\frac{j+1}{j}}$$

In this way, Hund [9] calculated the number of Weiss magnetons contained by the trivalent ions of the rare-earth group, and found a remarkable coincidence between calculated and experimentally determined values. But if one applies the method to the bi- and trivalent ions of the iron group, the two values absolutely do not coincide.

Sommerfeld and Laporte [10] have shown that in this group of elements, the sublevels belonging to a fundamental term have energies that differ by amounts on the order of 0.01 volts. Hence in calculating μ according to these, we must consider not only the contribution of the sublevel with the lowest energy, but

also the contribution of other sublevels belonging to the same term. For their expression for n_W calculated in this way, they consider the two limiting cases 1. $T = 0$, which corresponds to the Hund formula; and 2. $T = \infty$. It develops that although the experiments agree better with the second formula, the agreement is still not satisfactory.

I have attempted [11] using an empirical equation to map the magneton number of these ions as a function of an assumed electron distribution, on the Stoner sublevels M_{32} and M_{33}; but the formula is not based on any theoretical consideration.

Magnetomechanical Anomaly

If a rod of ferromagnetic material such as Fe, Ni, Co, etc., is suspended vertically in a solenoid through which a magnetization current flows, and if the direction of the flow is changed, one finds that the rod suddenly undergoes a rotation around its vertical axis. According to theory, the relationship of the magnetic to the mechanical moment of the rod is:

$$\frac{M}{I} = \frac{O}{H} = \frac{e}{2mc} g,$$

where O is the speed of rotation of the rod around the vertical axis and H is the strength of the magnetic field. /873

According to this formula, the value for M/I in various substances should behave like the value for g. The experiments of Arvidson, Beck, Chattock and Bates on ferromagnetic substances have yielded for all cases the value $g = 2$ within the limits of experimental error.

Thus we see that any comprehensive theory of paramagnetic phenomena must satisfy the following conditions:

1. It must derive the Langevin-Curie law in the form modified by quantum theory, without assuming the rotation of paramagnetic molecules in a magnetic field.

2. It must provide a formula that satisfactorily reproduces the magneton number of paramagnetic ions as a function of the number of electrons in an incomplete shell (i.e., the M_3 shell in the iron group).

3. It must be able to explain the Stern-Gerlach results with ferromagnetic elements.

4. It must provide an explanation of the magneto-mechanical anomaly observed in experiments with ferromagnetic substances.

A Newly Proposed Theory of Paramagnetic Phenomena

It has been shown that the theory of atomic structure, which has been developed for the theoretical derivation of the spectral terms belonging to any electron distribution in a shell, assumes that an electron can have two kinds of angular momentums, 1. one corresponding to the rotation of the electron around its own axis, characterized by the quantum number s, and 2. the one corresponding to its orbital movement, characterized by $l = k - 1$. The present paper will show that the paramagnetic phenomena of the iron group can be explained by the assumption $\tilde{l} = 0$, i.e., <u>only the spin angular momentum of the electrons comes into consideration for magnetic effects</u>.

I. Derivation of the Curie-Langevin Law

We assume that z electrons are present in the incomplete M shell of the iron group; of these, each has a magnetic moment

$$\mu_1 = \frac{eh}{4\pi mc}$$

deriving from its rotation around its own axis.

Furthermore, we will assume that in an external magnetic field these electrons can orient their axes of rotation parallel or antiparallel to the direction of the field. We will consider two cases separately: 1. when $z \leq 2l + 1$ and 2. when $z \geq 2l + 1$ with $l = k - 1$. /874

1. $z \leq 2l + 1$. If μ is the magnetic moment of an ion, then the numbers of the ions oriented in the two directions will be related as

$$Ce^{\frac{\mu H}{kT}} \text{ and } Ce^{-\frac{\mu H}{kT}}$$

and their relative contributions to the entire magnetic moment will relate as

$$\mu Ce^{+\frac{\mu H}{kT}} \text{ and } -\mu Ce^{-\frac{\mu H}{kT}}$$

If all axes of rotation have the same orientation, the ion has achieved its maximum magnetic moment $\mu = z\mu_1$. The following table combines the possible arrangements of the axes of rotation of z electrons of an ion in a magnetic field with the resulting moments:

a Anzahl der parallel zum Felde gerichteten	z	$z-1$	$z-2$	.....	2	1	0
b Anzahl der antiparallel zum Felde gerichteten	0	1	2	.....	$z-2$	$z-1$	z
c Gesamtmoment des Ions	$z\mu_1$	$(z-2)\mu_1$	$(z-4)\mu_1$	.....	$-(z-4)\mu_1$	$-(z-2)\mu_1$	$-z\mu_1$

Key: a. number oriented parallel to the field
b. number oriented antiparallel to the field
c. total moment of the ion

Then, if $\bar{m}$ is the mean moment of an ion,

$$\bar{m} = \frac{z\mu_1 e^{\frac{z\mu_1 H}{kT}} + (z-2)\mu_1 e^{\frac{(z-2)\mu_1 H}{kT}} + \cdots - (z-2)\mu_1 e^{-\frac{(z-2)\mu_1 H}{kT}} - z\mu_1 e^{-\frac{z\mu_1 H}{kT}}}{e^{\frac{z\mu_1 H}{kT}} + e^{\frac{(z-2)\mu_1 H}{kT}} + \cdots + e^{-\frac{(z-2)\mu_1 H}{kT}} + e^{-\frac{z\mu_1 H}{kT}}}$$

and divided by $\mu = z\mu_1$:

$$\frac{\bar{m}}{\mu} = \frac{\frac{z}{z}e^{\frac{z}{z}\frac{\mu H}{kT}} + \frac{z-2}{z}e^{\frac{z-2}{z}\frac{\mu H}{kT}} + \cdots - \frac{z-2}{z}e^{-\frac{z-2}{z}\frac{\mu H}{kT}} - \frac{z}{z}e^{-\frac{z}{z}\frac{\mu H}{kT}}}{e^{\frac{z}{z}\frac{\mu H}{kT}} + e^{\frac{z-2}{z}\frac{\mu H}{kT}} + \cdots + e^{-\frac{z-2}{z}\frac{\mu H}{kT}} + e^{-\frac{z}{z}\frac{\mu H}{kT}}}.$$

For small values of $\frac{\mu H}{kT}$ this yields

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{kT}\frac{2}{z^2}\frac{1}{z+1}\sum_{k=0}^{z/2}(z-2k)^2 \quad \text{for } z = 2n$$

and

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{kT}\frac{2}{z^2}\frac{1}{z+1}\sum_{k=0}^{\frac{z-1}{2}}(z-2k)^2 \quad \text{for } z = 2n+1.$$

It can be shown for both cases that /875

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{kT}\frac{1}{3}\frac{z+2}{z}$$

or

$$\frac{M}{H} = \frac{M_0^2}{3RT}\frac{z+2}{z}$$

2. $z \geq 2l + 1$. We know that for $z = 2(2l + 1)$, the resulting magnetic moment of the shell is zero, and thus according to Pauli's rule, the highest magnetic moment that an ion can have for $z > 2l + 1$ is $\mu = z'\mu_1$, where $z' \geq 2(2l + 1) - z$. According to the view presented here, this means that of the

$2(2l + 1)$ electrons which a shell can accept, no more than $(2l + 1)$ can orient their axes of rotation the same way.

Here we have

$$\frac{\overline{m}}{\mu} = \frac{\mu H}{3kT}\frac{z'+2}{z'}$$

or

$$\frac{M}{H} = \frac{M_0^2}{3RT}\frac{z'+2}{z}.$$

The highest magnetic moment that an ion can ever have is $\mu = z\mu_1$ or $\mu = z'\mu_1$, depending on whether $z \leq 2l + 1$ or $z \geq 2l + 1$. If we identify this with $n_B\mu_1$, the number of Bohr magnetons found experimentally in the ion, we get

$$\chi_M T = \frac{M_0^2}{3RT}\frac{n_B+2}{n_B};$$

and if n_W is the corresponding number of Weiss magnetons, then

$$n_W = 4{,}97\sqrt{n_B(n_B+2)}.$$

This is the Sommerfeld formula (6) for calculating the number of Weiss magnetons in an ion with n_B Bohr magnetons if the ion is in the S state. The essential difference between Sommerfeld's quantum theory and the position presented here is as follows: According to Sommerfeld, the magnetic moment of an atom or ion is an unchangeable value $\mu = n_B\mu_1$, and in a magnetic field, the atom as a whole can orient itself in certain discrete directions relative to the field, given by the condition that the component of the moment parallel to the field must be a whole multiple of the Bohr unit. By the interpretation explained here,

the magnetic moment of the atom or ion is not an unchangeable/876 number and there is no adjustment in the magnetic field. The moment is composed of the algebraic sum of the rotational moments of the electrons in an incomplete shell, some of them parallel and the rest antiparallel to the direction of the field. The state in which all axes of rotation are parallel to the direction of the field is the most probable for any given temperature, and corresponds to the lowest magnetic energy. For $H = \infty$ or $T = 0$, all atoms or ions are in this state.

II. Calculation of the Number of Bohr Magnetons Contained in an Ion as a Function of the Number of Electrons in the M Shell

Hund [12] calculated the values for $\bar{j}$ and g under the assumption that both the spin angular momentum and the orbital angular momentum have effects.

In our opinion, only the spin angular momentum comes under consideration; we can derive our equations for j and g from those of Hund by setting $\bar{l} = 0$ in equations (7) and (8), whence it follows that

$$\bar{j} = \bar{s} = \frac{s}{2} \quad \text{for } s \leqq 2l+1,$$

$$\bar{j} = \bar{s} = \frac{s'}{2} \quad \text{for } s \geqq 2l+1 \text{ with } s' = 2(2l+1) - s.$$

If we insert these values for j in (9), we see that

$$g = 2,$$

and therefore

$$\mu = \bar{j} \cdot g = s \text{ or } s',$$

depending on whether $z \leq 2l + 1$ or $z \geq 2l + 1$.

The corresponding number of Weiss magnetons contained in

these ions is determined by the formula

$$n_W = 4{,}97\, gj \sqrt{\frac{j+1}{j}}$$

For the present case $j = z/2$, $g = 2$, therefore,

or

$$\left.\begin{aligned} n_W &= 4{,}97 \sqrt{z(z+2)} \\ n_W &= 4{,}97 \sqrt{z'(z'+2)} \end{aligned}\right\}$$

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Comparison with Experimental Findings

In Fig. 1, using formula (13), we have graphed the number of Weiss magnetons corresponding to various occupations of the M shell. The same curve contains the experimentally found numbers of Weiss magnetons present 1. in various simple salts of paramagnetic elements and 2. in quadruple complex compounds of the

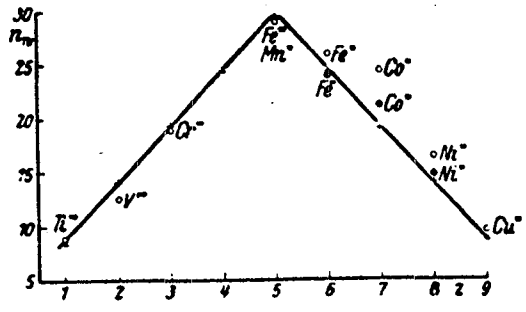


Fig. 1. Number of Weiss magnetons

Key: a. calculated theoretically
b. found experimentally for simple salts
c. found experimentally for quadruple complex compounds

elements Fe, Co and Ni. These latter values are from measurements recently performed at this institution by H.G. Bhar with compounds produced by P. Ray. They will be published later in detail. One can see that in the first part of the curve, i.e. for elements with regular spectra, the theoretical and experi-

mental values are in good agreement, but a considerable difference exists between the calculated values for Fe^{++}, Co^{++} and Ni^{++} and the values found experimentally for simple salts of these elements. By contrast, the values from the measurements in quadruple complex compounds of these elements produce far better agreement. These elements are characterized in that their spectra are of the inverted type, in which Pauli's reciprocity equation is used to calculate the number of electrons effectively contributing to the magnetic moment of the ion. In these, only $z' = 2(2l + 1) - z$ of the available z electrons are oriented in the direction of the magnetic field, while the remainder $z - z' = 2[z - (2l + 1)]$ are unable to do so. It may be that the discrepancy for the bivalent ions of Fe, Co and Ni, discussed here, comes from the fact that these $z - z'$ electrons do not fully neutralize each other in pairs, and therefore contribute somewhat to the magnetic moment. This point will be /878 addressed later in connection with the number of magnetons in complex compounds.

Complex Compounds

An earlier article [13] showed that the number of Bohr magnetons contained in any complex compound can be derived simply from a knowledge of the effective atomic number n' of the central atom. This number defined by Sidgwick gives the number of electrons in the central atom plus the number of electrons whose orbits the central atom shares with the atoms or molecules in the coordinative bond. In the cited article, to determine n' I gave the formula

$$n' = A - P + 2C$$

where A is the atomic number of the element, P is its main valency in the coordination compound, and C is the number of coordinative bonds.

Moreover, the article shows that the number of Bohr magnetons contained in the complex compound is

$$n_B = n - n'$$

where n is the atomic number of the noble gas terminating the group of paramagnetic elements, equal to 36 for the iron group.

If we then turn to the quadruple compounds, we can assume that the central atom has as many electrons in the M_3 shell as the corresponding simple ion plus eight shared electrons on the N_1 and N_2 level, i.e., in the case of the bivalent Fe^{++} ion, we have the following electron distribution:

	M_3	N_1	N_2
a Einfaches Salz	6	—	—
b Vierfache Verbindung . . .	6	2	6

Key: a. simple salt b. quadruple compound

The eight electrons have a resulting moment of zero, and we can therefore expect the quadruple compound to have the same number of magnetons as the simple salt with the same valency. The following table gives the number of magnetons of the quadruple compounds of bivalent Fe, Co and Ni, produced and studied by P. Ray and H.G. Bhar; the numbers are published here with their permission: /879

a Verbindung	n_W beobachtet b		e n_W berechnet
	Einfache c Verbindung	Vierfache d Komplexverbindung	
$[Fe(N_2H_4)_2]Cl_2$	26—27	24,1	24,4
$[Co(N_2H_4)_2]SO_3 + H_2O$ . . .	25	21,3	19,2
$[Ni(N_2H_4)_2]Cl_2$	16—17	14,86	14,1
$[Ni(N_2H_4)_2]SO_3$		14,96	
$[Ni(N_2H_4)_2](NO_3)_2$		14,76	

Key: a. compound b. observed
c. simple compound d. quadruple complex compound
e. calculated

One can see that in each case the number of magnetons of the quadruple coordination compound agrees much better with the theoretical value than does that of the corresponding simple salts. It seems as though with ions having inverted spectra, the eight electrons in the N_1 and N_2 level have a stabilizing influence on the orientation of the electrons in the incomplete M_3 shell.

Sextuple Compounds

In these compounds, the central atom has not only the electrons in the simple ion but twelve shared electrons, eight of them with the N_1 and N_3 level, and the remaining four of which must be set in the incomplete M_3 shell.

Examples of such distributions follow:

Ion	a Zahl der Elektronen				b Zahl der Magnetonen			c
	M_3	N_1	N_2	O_{11} O_{21}	n_B	n_W	n_W beob.	
Cr^{+++} einfach d . .	3	—	—	—	3	—	—	
„ komplex e . .	7	2	6	—	3	19,2	18,9	
Fe^{+++} einfach d . .	5	—	—	—	5	—	—	
„ komplex e . .	9	2	6	—	1	8,6	10	
Fe^{++} einfach d . .	6	—	—	—	4	—	—	
„ komplex e . .	10	2	6	—	0	0	0	
Ni^{++} einfach d . .	8	—	—	—	2	—	—	
„ komplex e . .	8	2	6	4	2	14,1	13,9	

Key: a. number of electrons
b. number of magnetons
c. observed
d. simple
e. complex

In each case, the number of magnetons contained in a complex compound can be calculated from the Pauli rule for equivalent orbits: $\mu = z' = 2(2l + 1) - z = 10 - z$, where z is the number of electrons in the M_3 shell. The case of sextuple nickel

compounds presents certain peculiarities. There is no room in the M_3 shell for four extra electrons, and we therefore assume that they are in the O_{11} and O_{22} orbits. /880

The Experiments of Stern and Gerlach [14]

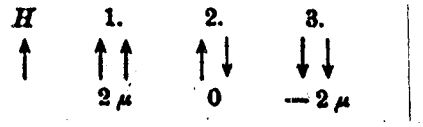
Here we are dealing with the magnetic moments of paramagnetic atoms obtained from the corresponding bivalent ions when one adds two electrons to the N_1 level. We will explain the magneton number of these elements by assuming that from iron upward, six electrons in the M_3 shell together with two in the N_1 shell form an octet with a magnetic moment of zero. We have seen that the six electrons alone in the M_3 level do not form a momentless configuration, but rather that two electrons in the N_1 level must be added to produce Fe atoms with a magnetic moment of zero. This may be the reason for Stoner's subdivision of the M_3 shell into the two sublevels M_{32} and M_{33}, with six resp. three electrons. It is known that the presence of these sublevels cannot be derived from optical data. We give a scheme for the electron distribution in the three ferromagnetic atoms:

Atom	a Zahl der Elektronen			b Zahl der Bohrschen Magnetonen	
	M_3		N_1	c berechnet	d beobachtet
Fe		6	2	0	0
Co	1	6	2	1	—
Ni	2	6	2	2	2

Key: a. number of electrons
b. number of Bohr magnetons
c. calculated
d. observed

For nickel, this scheme is interesting in connection with Gerlach's experimental results. He got three strips, one undeflected and two deflected by the same amount to either side. From the size of the deflection he concluded that the nickel atom contains two Bohr magnetons. According to our scheme, the

magnetic moment must be ascribed to the two spinning electrons that may orient themselves in the field, with the following possible configurations



The undeflected strip stems from atoms in which the two spin axes are oppositely oriented, and not from the magnetic axis /881 of nickel being perpendicular to the direction of the field.

Magneto-Mechanical Anomaly

The general formula for the relationship of the magnetic to the magnetic angular momentum for a rod with which the experiment is performed, is

$$\frac{M}{I} = \frac{e}{2mc} g.$$

To date, all experiments have been performed with ferromagnetic substances, for which according to (12) $g = 2$ and therefore M/I becomes $= e/mc$, in accord with the experimental results.

According to Hund [15], in calculating magnetic moment, $\mu = jg$ must be taken into account for the various ions of the rare-earth group, as well as the spin angular momentum and the orbital angular momentum for the electrons. It would be interesting to see whether gyromagnetic experiments with paramagnetic rare earth compounds provide a g value that differs from the one found for the ferromagnetic elements.

Conclusion

It has been shown that the magnetic properties of the iron

group can largely be explained on the basis of the simple assumption that only the spin angular momentum of the electron contributes to the magnetic moment, and that the atom or ion as a whole is not oriented in the magnetic field. On the other hand, Hund has very successfully explained the experimentally found numbers of Weiss magnetons in the ions of the rare earth group by saying that both the spin angular momentum and the orbital angular momentum are influential, and that these ions can adjust themselves in quantally determined orientations in a magnetic field.

This raises the question of the behavior of ions in the other transitional groups of the elements. In our laboratory, P. Ray and H.G. Bhar have performed preliminary measurements on the trivalent salts, both simple and complex, of Mo (42). This element belongs to the second transitional group and corresponds to chromium (24) in the first long period.

They found that $K_3MoCl_6 + 2\ H_2O$, a double salt, has 18.1 Weiss magnetons, while the sextuple complex compound $[Mo(SCN_6)][(NH_4)_3 + 4\ H_2O$ has 18.4. The nearest whole number of Bohr magnetons is 3, corresponding to 19.2 Weiss magnetons. /882 The electron distribution for Mo^{+++} is consequently:

	Mo^{+++}	N_3	O_1	O_2
a	Einfach. .	3	—	—
b	Komplex .	7	2	6

Key: a. simple b. complex

Here the magneton number can be calculated by the formula we used for the ions of the first transitional group, and consequently here too the spin angular momentum of the electron is responsible for the magnetic moment.

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