lines obtained by many authors with x-rays using the rotating crystal method of analysis (Sir William Bragg; "An Introduction to Crystal Analysis" 1928, p. 38), however the angular divergence of the original bundle was hardly large enough to give the variation in the angular deflections actually observed. A more promising interpretation is that the lines are due to diffraction of the rays at the two dimensional gratings formed by the rows of atoms in the crystal surface.

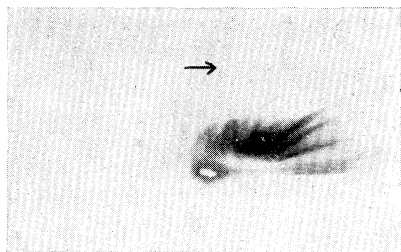By applying a magnetic field it was found hat the whole pattern was shifted as shown



Fig. 2.

n Fig. 2. The arrow shows the direction of the force on a positive particle, and its length indicates the distance in the figures that subtends an angle of 0.01 radian. As the blackening of a photographic plate by positive hydrogen canal rays is chiefly due to charged hydrogen atoms, we may conclude that the pattern is caused by the impact of protons. It is very significant that no undeflected pattern was observed, although neutral hydrogen atoms are present in large numbers in a canal ray beam. The

theories of wave mechanics would not at present distinguish between the wave-lengths associated with a proton and a neutral atom of the same velocity. Since the magnetic field does not destroy the lines, we may consider the different points as corresponding to particles of different velocities. A line is thus a velocity spectrum of the protons; or, in terms of wave mechanics, a diffraction spectrum of their equivalent wave-lengths.

A determination of the wave-lengths involved in the formation of the reflection pattern is a point of great interest. The maximum potential on the discharge tube was approximately 40,000 volts and a magnetic analysis showed that the positive ions were distributed over a considerable range of energies from approximately 40,000 to 15,000 volts. The de Broglie formula $\lambda = h/mv$ gives equivalent wave-lengths of 0.0014A to 0.0023A, and with the Bragg equation $n\lambda = 2d \sin \theta$, the angles are much smaller than those observed. The wave-lengths required if we use the Bragg equation are approximately those given by the de Broglie formula for 40,000 and 15,000 volt electrons. The angles given by diffraction at grazing incidence from the two dimensional grating formed by the atoms in the crystal surface, agree approximately with the observations using the short wave-lengths of 0.0014A to 0.0023A and it is possible that a satisfactory interpretation of the patterns will be reached on this basis.

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## The Effect of Second Order Zeeman Terms on Magnetic Susceptibilities in the Rare Earth and Iron Groups

As one of us has emphasized elsewhere,[1] proper calculation of the susceptibility requires knowledge of the energy to terms of the second order in the field strength. The energy expression $W_0 + g\beta MH$ which is ordinarily used is only a first order one, and includes only the contribution of the part of the magnetic moment $p$ which is parallel to the resultant angular momentum $j$. Actually because of the spin anomaly the vectors $p$ and $j$ are not parallel, and the component of $p$ which is perpendicular to $j$ gives rise to second order

[1] J. H. Van Vleck, Phys. Rev. **31**, 587 (1928).

Zeeman terms which have been calculated in the old quantum theory by Landé and in the new mechanics by Hill and Van Vleck.[2] The complete expression for the susceptibility is[3]

$$\chi = N\frac{\Sigma_j[(\beta^2 g_j^2 j(j+1)/3kT) + \alpha(j)](2j+1)e^{-W_j/kT}}{\Sigma_j(2j+1)e^{-W_j/kT}} \quad (1)$$

[2] A. Landé, Zeits. f. Physik **30**, 329 (1924); E. Hill and J. H. Van Vleck, Phys. Rev. **31**, 715 (1928).

[3] See Eq. (25), p. 604 of ref. 1. The formula there given is for infinitely wide multiplets, but the extension to finite widths is immediate. The diamagnetic term in $\alpha(j)$ is omitted in our calculations, as it is negligible.

where $\beta$ is the Bohr magneton $he/4\pi mc$, and $W_j$ is the energy of the multiplet component of inner quantum number $j$. The expression $\alpha(j)$ arises from the second order Zeeman terms, and is given in Eq. (26) of a previous paper.[1]

The portion of (1) which involves $\alpha(j)$ is that ordinarily omitted, and will be referred to as the "second part" of (1). The purpose of the present note is to give the effect of its inclusion on the numerical values of the susceptibilities calculated for the rare earth group by Hund,[4] and for the iron group by

theory by specializing it to the multiplets of maximum multiplicity consistent with the given number of electrons, such as are supposed characteristic of the ground state by Hund and others. Following Laporte, we take the screening constant $\sigma$ to be 34. *Inclusion of the second part of* (1) *is seen to completely remove the previous glaring discrepancy between theory and experiment for* $Eu^{+++}$*, which marred the otherwise quite satisfactory Hund theory for the rare earths.* The agreement for $Sm^{+++}$ is improved if one accepts Cabrera's experimental value in preference to St. Meyer's. The

TABLE I. *Ions in the first half of the rare earth group.*

| Ion | | La$^{+++}$ | Ce$^{+++}$ | Pr$^{+++}$ | Nd$^{+++}$ | Ill$^{+++}$ | Sm$^{+++}$ | Eu$^{+++}$ | Gd$^{+++}$ |
|---|---|---|---|---|---|---|---|---|---|
| Multiplet type | | $^1S$ | $^2F$ | $^3H$ | $^4J$ | $^5J$ | $^6H$ | $^7F$ | $^8S$ |
| $\mu_B$ | (Hund) | 0 | 2.54 | 3.58 | 3.62 | 2.68 | 0.84 | 0 | 7.9 |
| $\mu_B$ | (now) | 0 | 2.56 | 3.62 | 3.69 | 2.87 | 1.83 | 3.56 | 7.9 |
| $\mu_B$ | (Cabrera) | 0 | 2.39 | 3.60 | 3.62 | — | 1.54? | 3.61 | 8.2 |
| $\mu_B$ | (St. Meyer) | 0 | 2.77(Pr$^{4+}$) | 3.47 | 3.51 | — | 1.32 | 3.12 | 8.1 |

Laporte and Sommerfeld, and later more completely by Laporte.[5] The resulting values of the apparent Bohr magneton number $\mu_B = [3kT\chi/N\beta^2]^{1/2}$, also Hund's original values and the experimental determinations by Cabrera and St. Meyer, are given in Table I.

The multiplets are assumed to conform to the ordinary cosine law, and the over-all multiplet width is taken to be $R(2\pi e^2/hc)^2(Z-\sigma)^4(2L+1)/n^3l(2l+1)(l+1)$, where $R$ is the Rydberg constant, and where we have $n=4$, $l=3$ in the rare earth group and $L$ is the resultant of all the $l$'s. This formula for the over-all width is obtained from Goudsmit's[6]

correction to Hund is seen to be important only for $Eu^{+++}$ and $Sm^{+++}$. The reason for this is that in $^7F$ and $^6H$ multiplets the lowest $j$ values are 0 and $2\frac{1}{2}$ respectively, and the component of $\boldsymbol{p}$ which is perpendicular to $j$ and which gives rise to $\alpha(j)$ in (1), is particularly large in states of small $j$ but large $S$, $L$. Also in such states it is very important to allow for the finite multiplet width. Hund took the multiplet width to be infinite, so that only the lowest multiplet component needed to be considered, but consideration of the finite multiplet width without the second part of (1) is insufficient, as Laporte,[5] omitting this part, obtained a Bohr magneton number of

TABLE II. *Ions in the first half of the iron group.*

| Ion | | Sc$^{++}$ | Ti$^{+++}$ | Ti$^{++}$ | V$^{++}$ | Cr$^{+++}$ | Mn$^{++++}$ | Cr$^{++}$ | Mn$^{+++}$ |
|---|---|---|---|---|---|---|---|---|---|
| Multiplet type | | $^2D$ | $^2D$ | $^3F$ | $^4F$ | $^4F$ | $^4F$ | $^5D$ | $^5D$ |
| $\mu_W$ | (Laporte) | 12.4 | 10.4 | 15.8 | 16.1 | 13.0 | 10.0 | 18.6 | 15.7 |
| $\mu_W$ | (now) | 12.9 | 10.9 | 16.8 | 18.0 | 15.2 | 12.5 | 21.3 | 19.0 |
| $\mu_W$ | (expt.) | — | — | — | — | 18.2–19.1 | 19.8 | 23.8 | 25 |

[4] F. Hund, Zeits. f. Physik **33**, 345 (1925): "Linienspektren," p. 179.

[5] O. Laporte and A. Sommerfeld, Zeits. f. Physik **40**, 333 (1926) (infinitely wide multiplets); O. Laporte, *ibid.* **47**, 761 (1928) (actual, finite widths).

[6] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

only 1.71 for $Eu^{+++}$. The corrections to Hund's values are negligible for the ions $Tb^{+++}$ to $Cp^{+++}$ in the second half of the rare earth group, as they have inverted multiplets and hence their components of small $j$ have a negligible Boltzmann factor. Because the alterations are negligible, we omit these ions

from Table I, also for similar reasons the ions iso-electronic with $Mn^{++}$, $Fe^{++}$, $Co^{++}$, $Ni^{++}$, $Cu^{++}$ from Table II.

Analogous calculations can be made for the rare earth group, and are exhibited in Table II, in which Weiss rather than Bohr magneton numbers are employed to conform with Laporte's usage. The experimental values are taken from Stoner's[7] survey of various measurements on solid and dissolved salts, and in some cases ($Mn^{++}$, $Mn^{+++}$) on oxides. We use the same numerical multiplet widths as Laporte[5] and follow throughout his usage in taking $T=300$. The effect of the second order Zeeman terms is seen to be less pronounced than for certain rare earth ions, although the agreement with experiment is somewhat improved for $Cr^{+++}$, $Mn^{++++}$, $Cr^{++}$, $Mn^{+++}$.

[7] E. C. Stoner, Phil. Mag. Aug. 1929; "Magnetism and Atomic Structure," p. 127 ff, Tables X, XI, XII.

The very bad disagreement (see Laporte[5]) between theory and experiment for the ions $Fe^{++}$, $Co^{++}$, $Ni^{++}$, $Cu^{++}$ in the second half of the iron group, not shown in Table II, still remains, as our corrections are negligible in this half. It seems uncertain whether the discrepancies are due to incorrect assignment of spectral terms to the ground state or, as suggested by Stoner[7] and others, to a different magnetic behavior in the solid and dissolved states than in the theoretical ideal gas condition. The latter explanation would appear more probable for the first than second half of the iron group, as in the second there is almost no correlation between existing theory and experiment.

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## Positive Ion Emission from Tungsten and Molybdenum

The positive ion emission from tungsten and molybdenum has been studied in detail and the nature of the ions emitted at various temperatures has been determined by rather accurate mass spectrograph measurements. These measurements showed that molybdenum and tungsten both emitted positive ions of sodium and potassium at temperatures of about $1700°K$. At a somewhat higher temperature (about $2000°$), ions with an atomic weight of 27.2 were obtained which were attributed to ionized atoms of aluminum. The resolution of the mass spectrograph was high enough easily to distinguish the two isotopes of potassium and indeed these were found. All of these impurities disappeared on aging the filaments for a time at high temperature and at temperatures of about $2500°$ for tungsten and $2300°$ for molybdenum, new ions appeared which had the atomic weight of the metal emitting them. These results corroborate those reported by Wahlin [Phys. Rev. **34**, 164 (1929)].

The temperature variation of the positive ion current has been measured. The positive ion work functions for molybdenum and tungsten have been determined by plotting these results according to an equation developed from thermodynamic arguments which takes into account the heat capacity of the ion in the condensed state, etc. This equation may be stated in the form:

$$\log I = -\frac{\Phi_{+0}e}{300\,kT} + \log T + \frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{p\rho}dT$$
$$-\frac{1}{k}\int_0^T \frac{dT}{T^2}\int_0^T C_{pm}dT + \log\frac{2\pi M k^2 e}{h^3} + \frac{s_\rho}{k}$$
$$+\log(1-r)$$

where $I$ is the positive ion current per $cm^2$ $\Phi_{+0}$ is the positive ion work function in volts at $T=0$, the metal being isolated; $C_{pm}$ is the heat capacity of an ion in the condensed state; $C_p$ denotes the heat capacity associated with the heat of surface charging, $s_\rho$ is the entropy associated with the heat of surface charging at $T=0$, and $r$ is the reflection coefficient of the ions at the metal surface. When the integrals have been evaluated it is possible to determine $\Phi_{+0}$ from the slope of a curve and the constant term can be found from the intercept of the curve. The value of $\Phi_{+0}$ for tungsten was found to be 6.55 volts and for molybdenum, 6.09 volts.

It is possible to compute the value of $\Phi_+$ by a simple cyclic process. Consider an inclosure in which molybdenum is in equilibrium with its radiation at a given temperature $T$ and carry out the following cycle. Remove an electron and positive ion from the metal thus requiring an amount of work $\Phi_{-T}+\Phi_{+T}$, where $\Phi_{-T}$ and $\Phi_{+T}$ are the respective work functions at the temperature $T$; then allow the electron to combine with the