

The Magnetic Properties of the Iron Group Anhydrous Chlorides at Low Temperatures

II. Theoretical*

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A theoretical study is made of the experimental results reported in Part I. The predictions of paramagnetic theory are compared with the room-temperature results, and an attempt is made to explain some of the departures from theory in terms of the crystalline field. The low temperature experimental anomalies require the development of a theory of metamagnetism. The assumption is made that at temperatures below the Curie point neighboring atoms behave as groups, which are spontaneously formed at the Curie point. The atomic magnetic moments within each group are assumed to be either parallel or antiparallel to each other, and the antiparallel arrangement is assumed to have the lowest energy. The theory developed on these assumptions satisfactorily explains the general behavior of the metamagnetic chlorides (CrCl_3 , FeCl_2 , CoCl_2 , and NiCl_2), and also gives a qualitative explanation of the behavior of the other anhydrous chlorides which exhibit a minimum in the reciprocal susceptibility *vs.* temperature curve but do not show any field dependence of the susceptibility.

INTRODUCTION

THE results of the experimental investigation of the magnetic properties of all the anhydrous chlorides of the first transition series, the iron group, have been reported in the preceding paper, Part I.¹ It is the purpose of this paper to present a qualitative theoretical analysis of these results, especially the anomalous magnetization characteristics which are associated with the lowest temperatures used in the investigation. In order to facilitate the discussion of the results a brief review of present paramagnetic theory will be given. For a detailed treatment of this subject reference should be made to Van Vleck² and Stoner.³

The paramagnetic susceptibility of atoms in a given j state results from the statistical distribution of the atoms among the various energy levels which are associated with the removal of the degeneracy of the j state by the applied magnetic field. The determination of the various energy levels and the removal of their degeneracy by applied fields or interaction effects is the basic

problem in determining the susceptibility of paramagnetic compounds. The normal or "ground" state of an atom is determined by the Hund stability rules. These rules specify that in the lowest term the spin momenta combine to give the maximum resultant value of s consistent with the Pauli exclusion principle, and then the orbital momenta combine to give the maximum resultant value of l ; for an incomplete shell of electrons the lowest term $j=l-s$ when the shell is less than half full, and $j=l+s$ when the shell is more than half full. As a result of the various possible combinations of a given resultant s and l , j can assume the values $l+s, l+s-1, \dots, |l-s|$. This results in a natural multiplet of energy levels, in which the difference in energy between different j values is determined by the strength of the interaction between l and s . In the case of wide multiplets, the energy of transition between successive j states is very large compared to kT , the ls coupling is strong, and nearly all the atoms are in their ground state. In the case of narrow multiplets the energy of transition between successive j states is very small compared to kT , the ls coupling is very weak so that the orbital and spin momenta are quantized separately. It has been shown that the presence of an asymmetrical electrostatic field surrounding an atom may render the l moment partially or completely

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¹ See preceding paper "Part I, Experimental."

² J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

³ E. C. Stoner, *Magnetism and Matter* (Methuen and Company, London, 1934).

ineffective by producing a preferred orientation electrostatically, and thus hinder the response to an applied magnetic field. This is similar to the Stark effect. The s moment is unaffected directly by the electrostatic field. In the case of paramagnetic solids the electrostatic "crystalline" field, due to the atoms surrounding the one under consideration, may thus be responsible for the "quenching" of the orbital moment, so that only the spin moment contributes to the magnetic susceptibility.

The theoretical limiting cases for the susceptibility of paramagnetic atoms may be given by the following formulae. The susceptibility per gram mole $\chi_m = (N\mu_B^2 p^2 / 3kT)$, where N is Avogadro's number, μ_B is the magnetic moment of one Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, and p is the effective number of magnetons per atom.

Wide multiplets: $h\nu(jj') \gg kT$

$$p = g[j(j+1)]^{1/2},$$

where g is the Landé splitting factor.

Narrow multiplets: $h\nu(jj') \ll kT$

$$p = [l(l+1) + 4s(s+1)]^{1/2}.$$

Spin only: $p = [4s(s+1)]^{1/2}$.

In the case of wide multiplets, a temperature-independent susceptibility term should be added to the above susceptibility. If the multiplet width is very wide this term is negligible. When the multiplet width is comparable with kT , the statistical distribution of the atoms over all the j states must be considered and more detailed formulae must be used. These are presented in the detailed references.

Table I contains the tabulation of the above limiting p values for the iron group ions. These may be compared with the experimental values found in Part I. The experimental p values are determined from the characteristics of the reciprocal susceptibility *vs.* temperature curve at room temperature. Excluding the uncertain p values for the titanium ions, several generalizations may be drawn from Table I. The Mn^{2+} and Fe^{3+} ions have a 6S ground state and, theoretically, they should exhibit the spin-only value. The experimental p value is actually less than the spin-only value. This result cannot be attributed to experimental error. The excellent agreement

of the experimental p values of the Mn^{2+} and Fe^{3+} ions is a strong indication of the validity of the results. There is also no question concerning the chemical purity of the compounds (see Part I). Table I also shows that in the trichlorides, Cr^3 and V^3 have experimental p values that agree very well with the spin-only values, while in their corresponding dichlorides the experimental p values are considerably larger than the spin-only values. It would thus appear that the orbital magnetic moment is almost completely quenched in the trichlorides and only partially quenched in the dichlorides. When considering the effect of the number of electrons in the $3d$ orbit, it is of interest that although the theoretical spin-only values are symmetrical about the half-filled shell (5 electrons), the experimental p values are larger for the ions in the second half of the shell (5–9 electrons) than in the corresponding ions (same s values) of the first half (1–5 electrons).

CRYSTALLINE FIELD EFFECTS

The theoretical treatment of the effects of the electrostatic crystalline field upon the orbital magnetic moment has been developed by Van Vleck.² The action of the crystalline field may be described as a removal of the degeneracy of the resultant orbital moment of the ion. As in the case of narrow multiplets separate quantization of the orbital and spin moments is assumed, since the crystalline field acts directly only on the orbital moment. If the decomposition of the

TABLE I. Calculated and observed magneton numbers effective in the ions of the first transition series. N is the number of electrons in the $3d$ orbit.

N	GROUND STATE	l	s	j	EFFECTIVE NUMBER OF BOHR MAGNETONS				ION
					WIDE MULTI-PLETS	NARROW MULTI-PLETS	SPIN ONLY	EXP.	
1	$^2D_{3/2}$	2	$1/2$	$3/2$	1.55	3.00	1.73	(1.42)	Ti^3
2	3F_2	3	1	2	1.63	4.47	2.83	(2.05)	Ti^2
								2.85	V^3
3	$^4F_{3/2}$	3	$3/2$	$3/2$	0.77	5.20	3.87	4.15	V^2
								3.90	Cr^3
4	5D_0	2	2	0	0.00	5.48	4.90	5.13	Cr^2
5	$^6S_{5/2}$	0	$5/2$	$5/2$	5.92	5.92	5.92	5.73	Mn^{2+}
								5.73	Fe^3
6	5D_4	2	2	4	6.70	5.48	4.90	5.38	Fe^2
7	$^4F_{9/2}$	3	$3/2$	$3/2$	6.64	5.20	3.87	5.29	Co^2
8	3F_4	3	1	4	5.59	4.47	2.83	3.32	Ni^2
9	$^2D_{5/2}$	2	$1/2$	$5/2$	3.55	3.00	1.73	2.08	Cu^2

orbital energy levels is very large, the ions will mainly reside in the lowest orbital level, and an applied magnetic field will not appreciably change the distribution among the levels. Since the susceptibility is determined by the change in the average energy per ion due to the applied magnetic field, the contribution of the orbital moment is thus effectively quenched. The spin moments remain effective although the freedom of the spins is hindered by the spin-orbit coupling. The magnitude of the deviation of the susceptibility from the spin-only value depends, to a first approximation, upon the ratio of the spin-orbit interaction energy (as determined from the free ion multiplet width) to the crystalline field splitting.

The detailed calculations have been made by Schlapp and Penney⁴ for the ions Cr^3 , Co^2 , and Ni^2 , which are all in F states ($l=3$). The crystalline field was assumed to consist of a strong field of cubic symmetry and a superimposed weak field of rhombic symmetry. As will be shown later, this type of field would be expected in the anhydrous chlorides. The effect of the cubic field upon the F state (7-fold orbital degeneracy) is to split it into one singlet level and two triply degenerate levels, the two latter being resolved completely by the rhombic field. In the case of Ni^2 and Cr^3 the singlet level is lowest, and since the splitting due to the strong cubic field is large, the susceptibility approaches the spin-only value. In the case of Co^2 the triplet level is lowest, and since the splitting due to the weak rhombic field is small, the effects are more complicated and large deviations from the spin-only value would be expected. The Hamiltonian function in a magnetic field H was assumed to be of the form

$$D(x^4+y^4+z^4)+AX^2+By^2-(A+B)z^2 \\ +\lambda(l \cdot s)+\mu_B H(l+25),$$

where A , B , D are constants specifying the crystalline field, the cubic term D predominating, and λ is the constant of spin-orbit interaction. The theoretical analysis resulted in susceptibilities for Ni^2 and Cr^3 equal to the spin-only susceptibility multiplied by a factor depending on λ/D . If p is the actual effective magneton

number, p_s the spin-only value, and q is a positive constant, then this multiplying factor is

$$(p/p_s) = (1 - 4\lambda/5Dq) \text{ for } \text{Ni}^2, \text{ and} \\ (p/p_s) = (1 - 2\lambda/5Dq)^2 \text{ for } \text{Cr}^3.$$

The value of λ , as determined from the free ion multiplet width, is equal to -335 cm^{-1} for Ni^2 , and $+87 \text{ cm}^{-1}$ for Cr^3 . From the experimental p values in Table I, Dq is equal to 710 cm^{-1} for Ni^2 , and -4700 cm^{-1} for Cr^3 . These values of Dq are widely different from those found by Schlapp and Penney⁴ and Janes⁵ on more magnetically dilute salts. The value for Cr^3 also has the wrong sign, since Gorter⁶ has shown that if a metal ion is surrounded by an octahedron of negative charges (as is the case here), D should be positive.

Theoretical studies of the crystalline field effect in other ions of the iron group have been carried out by Jordahl⁷ and Siegert.⁸ The inversion of the splitting of the orbital levels due to a cubic field for pairs of ions with the same l value, as in Ni^2 and Co^2 , has been shown by Van Vleck⁹ to be characteristic of any pair of ions for which the number of $3d$ electrons adds up to 5, 10, or 15, such as $(\text{Co}^2, \text{Ni}^2)$, $(\text{Fe}^2, \text{Cu}^2)$, $(\text{Co}^2, \text{Cr}^3)$, $(\text{V}^3, \text{Ni}^2)$; and the splitting is such that the quenching of the orbital moment should be largest for the second member of each pair provided the spin-orbit interaction is the same. However, for a given l and s , the multiplet width is proportional to the j value, and is, therefore, largest for the ions in the second half of the iron group. The larger spin-orbit interaction may account for the fact that the experimental p values for the ions in the second half of the group deviate very much more from the spin-only values than those of the first half.

In the above treatment of the crystalline field effects, the possible influence upon the susceptibility of the dipole-dipole and exchange effects has been neglected. Since the crystalline field cannot account for the low temperature anomalies observed in the anhydrous chlorides (see Part I), and as the concentration of magnetic ions in these

⁵ R. B. Janes, Phys. Rev. **48**, 78 (1935).

⁶ C. J. Gorter, Phys. Rev. **42**, 437 (1932).

⁷ O. M. Jordahl, Phys. Rev. **45**, 87 (1934).

⁸ A. Siegert, Physica **3**, 85 (1936); **4**, 138 (1937).

⁹ J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).

⁴ R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932).

compounds is very large, it is probable that the neglected interactions must be considered even at room temperatures.

Van Vleck and Penney¹⁰ have discussed the fact that Mn^{2+} and Fe^{3+} show less than spin-only values. Although they attribute this discrepancy to experimental error they suggest a number of possible causes of such an effect. As has been mentioned above, this is not a case of experimental error. Dipole-dipole and exchange interactions are considered too small to be a satisfactory explanation. The most probable suggested explanation assumes the presence of incipient jj coupling (arising from the coupling between the spin moment of each electron and its own orbital moment). Under such circumstances it is not sufficient to consider only the Russell-Saunders coupling (between the resultant s and l of the ion), and the Hund rule is not valid. Van Vleck¹¹ has pointed out that the energy of the ion in the crystalline field is a minimum when the resultant spin has its lowest possible value. The internal energy of the ion is a minimum when the resultant spin has its maximum value, i.e., when the Hund rule is valid. Therefore, the combined action of the crystalline field and the incipient jj coupling would result in decreased effective spin for the ion, and the experimental p value would be less than the spin-only value. The observed low temperature curvature of the reciprocal susceptibility *vs.* temperature curve of FeCl_3 (Fig. 1, Part I) may be a consequence of this crystalline field effect. As has been suggested above the crystalline field in the trichlorides is apparently very much more effective than in the dichlorides. This may account for the fact that MnCl_2 does not show the same curvature as FeCl_3 . The difference between the dichlorides and trichlorides may also be due in part to the difference in exchange effects between the magnetic ions. In the trichlorides each metal ion has three metal-ion near neighbors, and in the dichlorides there are six near neighbors.

CRYSTAL STRUCTURES

The crystal structure of about half of the iron group anhydrous chlorides have been determined

¹⁰ J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934).

¹¹ J. H. Van Vleck, *J. Chem. Phys.* **3**, 807 (1935).

from x-ray studies.¹² These crystal structures are all of the layer lattice type; each layer of metal atoms is separated by two layers of chlorine atoms from the next metal atom layer. The dichlorides have the typical CdCl_2 structure, each metal atom layer forming a two-dimensional hexagonal network in which every metal atom has six near neighbors. The trichlorides are similar, except that a metal atom is missing from the center of each hexagon so that every metal atom has three near neighbors. The dimensions of these structures are given in Table II. CrCl_3 and FeCl_3 differ slightly, in that the layers of Cl atoms are so stacked as to produce cubic close packing of the Cl atoms in CrCl_3 , and hexagonal close packing in FeCl_3 .

Each metal atom in these structures is surrounded by six Cl atoms at the corners of an octahedron. Three of these Cl atoms are in the layer above the metal atom layer, and three are below, so that the axes of the octahedron do not coincide with the hexagonal axes of the crystal as a whole. The octahedra are distorted slightly by the crystal forces, and the distortion is probably greater in the trichlorides than in the dichlorides. It can thus be seen that the crystalline potential surrounding each metal atom is adequately described by a large cubic (octahedral) term and a small rhombic term.

THEORY OF METAMAGNETISM

The iron group anhydrous chlorides which have a positive Curie temperature (Θ) at room temperature exhibit a typically anomalous low temperature magnetic behavior (see summary, Part I). This behavior is characterized by (1) a large dependence of the susceptibility upon the field strength, (2) no apparent spontaneous magnetization, and (3) no large hysteresis effects. The first characteristic is not typical of paramagnetism, and the second and third are not typical of ferromagnetism. For this reason it has been suggested¹³ that the magnetic behavior of these compounds should be classified as "metamagnetism." No adequate explanation of

¹² R. W. G. Wyckoff, *The Structure of Crystals* (1931) and *Strukturbericht*, [II] (Akademische Verlagsgesellschaft, Leipzig, 1937).

¹³ J. Becquerel and J. van den Handel, *J. de phys. et rad.* **10**, 10 (1939).

metamagnetism has been presented. Landau¹⁴ suggested that some of the properties of metamagnetics are due to the presence of spontaneously magnetized metal atom layers, oppositely oriented. This is similar to the theories of antiferromagnetism suggested by Néel¹⁵ and others.¹⁶ These suggestions, in a modified form, are developed in this paper into a theory which is applicable to the metamagnetic chlorides (CrCl_3 , FeCl_2 , CoCl_2 , and NiCl_2).¹⁷

The specific heat characteristics of the metamagnetic chlorides (Part I, reference 7) indicate a Curie point anomaly of the cooperative type. Such an anomaly would result from a spontaneous arrangement of magnetic moments either parallel, as in ferromagnetism, or antiparallel. This ordering process may occur either throughout the crystal as a whole (long range order) or in small groups, or clusters, of neighboring atoms (short range order). The fact that no spontaneous magnetization occurs below the Curie point temperature may be explained by assuming a group behavior, with either (1) a haphazard orientation of atom groups, each group having a permanent moment due to parallel alignment of the atomic magnetic moments within it, or (2) a zero resultant moment for each atom group due to some antiparallel alignment of the atomic magnetic moments. Because of the complexity of the problem it is not practically feasible to calculate the energies of all the possible magnetic moment configurations in a crystal, and thus to determine theoretically which of the above explanations is most likely. The answer to this question is suggested by the fact that the initial susceptibility of FeCl_2 decreases as the temperature decreases. This indicates that, as the temperature is decreased, there is an increase in the number of atomic groups whose energy is unaffected by the application of a magnetic field. Since a decrease of temperature increases the population of the lowest energy levels, the assumption (2), that the atomic groups with zero

TABLE II. *Layer lattice dimensions of the iron group anhydrous chlorides.*

COMPOUND	METAL ATOM DISTANCES (ANGSTROMS)		METAL ION RADIUS	RATIO OF NEAREST NEIGHBOR DISTANCE TO ION RADIUS
	BETWEEN LAYERS	BETWEEN NEAREST NEIGHBORS		
CrCl_3	5.76	3.46	0.70	4.95
FeCl_3	5.75	3.42	0.67	5.10
MnCl_2	5.86	3.682	0.83	4.43
FeCl_2	5.84	3.580	0.80	4.48
CoCl_2	5.79	3.546	0.78	4.55
NiCl_2	5.78	3.544	0.74	4.79

resultant moment have the minimum energy, is substantiated. CrCl_3 does not behave the same as FeCl_2 , but an explanation of this effect, not in contradiction with the above, will be presented later.

The theoretical development will be based upon the simple model suggested by the above analysis of the general character of the experimental results. Below the Curie point the atoms are assumed to behave as groups. Within each group the atomic magnetic moments may be parallel or antiparallel. The antiparallel configuration produces a zero resultant moment for the group and has the minimum energy. The resultant moment produced by the parallel configuration is assumed to be in the same or opposite direction as an applied magnetic field. Thus, in the presence of an applied field there are three group energy levels, the lowest one of zero resultant moment, a higher one with the effective resultant moment parallel to the field direction, and the highest one with the effective resultant moment antiparallel to the field direction. Above the Curie point the spontaneously formed groups no longer exist, although the interaction between near neighbors is such that the antiparallel and parallel energy levels are applicable to the atoms individually. The further assumption is made that the average field acting on any one group due to the neighboring groups is proportional to the average magnetization of the crystal. Finally, only one zero moment configuration is assumed to exist. This model is obviously oversimplified by the restrictions upon the direction of the resultant moments and upon the number of zero moment configurations. However, from the point of view of the analysis and general consideration of the experimental

¹⁴ L. Landau, Phys. Zeits. Sowjetunion **4**, 675 (1933).

¹⁵ L. Néel, Ann. de physique **18**, 5 (1932).

¹⁶ F. Bitter, Phys. Rev. **54**, 79 (1938).

¹⁷ After this paper was written, Professor Van Vleck brought to the author's attention an unpublished paper by J. Becquerel, presented in May, 1939, at the Strasbourg conference on magnetism of the Institut International de Coopération Intellectuelle, in which similar considerations are applied to the problem of paramagnetic rotatory power.

results, such an idealized model has many advantages as compared with a more rigorous and elegant theoretical treatment.

Consider the above model at a temperature below that of the Curie point. Designate N the number of atoms per group, μ the atomic magnetic moment, σ the average magnetization per atom (averaged over the whole crystal), ϵ the energy difference between groups with a resultant moment (parallel atomic moments) and groups with zero resultant moment (antiparallel atomic moments), and H the magnetic field applied to the groups. The average magnetization per group,

$$N\sigma = kT \partial(\log Z) / \partial H,$$

where the partition function

$$Z = 1 + e^{-(\epsilon - N\mu H)/kT} + e^{-(\epsilon + N\mu H)/kT}.$$

Let $\alpha = \epsilon/kT$ and $\beta = N\mu H/kT$. Then

$$\frac{\sigma}{\mu} = \frac{2 \sinh \beta}{e^\alpha + 2 \cosh \beta}. \quad (1)$$

This is plotted in Fig. 1 for various values of α . When $\alpha = -\infty$ this equation reduces to the usual hyperbolic tangent relationship. The magnetic field acting on each group is assumed to be $H = H_a + D\sigma$ where H_a is the applied field and D is the internal field coefficient. The differential atomic susceptibility is

$$\chi = \frac{d\sigma}{dH_a} = \frac{N\mu\sigma(\text{ctnh } \beta - \sigma/\mu)}{kT - DN\mu\sigma(\text{ctnh } \beta - \sigma/\mu)}. \quad (2)$$

At a temperature above that of the Curie point Eq. (1) is still valid, but the atoms now act individually, $N=1$, and ϵ is the difference in energy between the parallel and antiparallel alignment of an atom with its near neighbor.

When β is large (>2), Eq. (1) reduces to

$$\sigma/\mu = 1/(e^{\alpha-\beta} + 1). \quad (3)$$

This equation is plotted in Fig. 2, and represents the general S type form of the magnetization curve at low temperatures. Since $\alpha - \beta = (\epsilon - N\mu H)/kT$, the effect of decreasing temperature is to increase the step-like character of the curve of σ vs. H , so that at absolute zero the

magnetization changes abruptly from zero to saturation when $N\mu H = \epsilon$. For this value of the field the magnetization is independent of temperature, and the curves of σ vs. H for different temperatures should all cross at the point where σ is one-half saturation. This is approximately what was found for FeCl_2 (Fig. 2, Part I).

When the applied field approaches zero, $\beta \rightarrow 0$, and the initial susceptibility is

$$\chi_i = \Theta / [D(T - \Theta)], \quad (4)$$

where $\Theta = 2N\mu^2 D / k(2 + e^\alpha)$. The usual form of expressing the atomic susceptibility is $\chi(T - \Theta) = (p\mu_B)^2 / 3k$ where p is the effective number of Bohr magnetons and μ_B is the magnetic moment of the Bohr magneton. In comparison with the usual form, Θ is as given and

$$p\mu_B = \mu [6N / (2 + e^\alpha)]^{1/2}.$$

Because of the presence of e^α , Θ and p are functions of temperature, decreasing as the temperature decreases. Eq. (4) may also be put into the form

$$\frac{1}{\chi_i} = \frac{N\mu^2}{\epsilon} = \frac{2 + e^\alpha}{2\alpha} - \frac{N\mu^2 D}{\epsilon}. \quad (4a)$$

Equation (4a), without the constant term $N\mu^2 D / \epsilon$, is plotted in Fig. 3 where $kT/\epsilon = 1/\alpha$.

For high temperatures or small α , Eq. (4) reduces to

$$\chi_i(T + \epsilon/3k - 2N\mu^2 D/3k) = 2N\mu^2/3k. \quad (5)$$

If $N\mu^2 D/\epsilon$ is greater than $\frac{1}{2}$, then the Θ as measured at high temperatures will be positive, as is found in the metamagnetic chlorides. The dotted line of Fig. 3 illustrates Eq. (5) when $D=0$.

If the difference in energy per atom between a parallel and an antiparallel arrangement is δ , then $\epsilon = N\delta$. Figure 3 is then the plot of $\mu^2/\chi\delta$ vs. $kT/N\delta$. Assume that δ is independent of the size of the group. Above the Curie point the atoms act individually, $N=1$, and kT/δ is large. The applicable part of the reciprocal susceptibility curve has a positive slope (right-hand part of Fig. 3). At the Curie point, group formation spontaneously occurs, N is large, and kT/ϵ is now a fraction of its former value. This places the reciprocal susceptibility in the region of

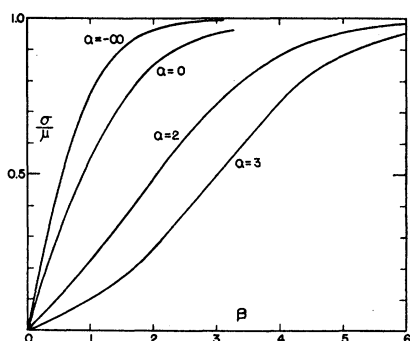


FIG. 1. The relative magnetization as a function of β , for various values of α .

negative slope (left-hand part of Fig. 3). Such a process would explain the reciprocal susceptibility characteristic of a metamagnetic chloride such as FeCl_2 (Fig. 1, Part I). The whole of Fig. 3 may be applicable to those anhydrous chlorides whose experimental characteristics are similar to those of chromium, nickel, copper and vanadium chlorides shown in Part I, Fig. 1. These will be discussed later.

COMPARISON WITH EXPERIMENT

The constants used in the theoretical development may be approximately determined from the experimental results by means of the appropriate theoretical equations. Below the Curie point μ , N , and ϵ are assumed independent of temperature and field strength. The experimental values for FeCl_2 (Table II, Part I) result in $\epsilon/k = 59^\circ$. With this value of ϵ/k the magnetization curves determined from Eq. (1) are plotted in Fig. 4 for the two temperatures, 20.4° and 13.9° . As was noted above, the two curves cross for

$$N\mu H = \epsilon = 59k \quad \text{and} \quad \sigma/\mu = \frac{1}{2}.$$

Figure 4 should be compared with the experimental curves for FeCl_2 of Fig. 2, Part I.

The outstanding differences between the theoretical and experimental curves are the accentuated step-like character of the 13.9° experimental magnetization curve, as compared with the theoretical, and the fact that the 20.4° experimental curve has an apparent saturation value appreciably less than that of the 13.9° curve.

If only the spin magnetic moment is effective in these compounds $\mu = 4\mu_B$ for the Fe^{2+} ion. The saturation moment per gram mole is then

22,200 and the theoretical intersection point of the two curves is 11,100. The experimental intersection point is 11,700, in good agreement with the theory. The experimental initial susceptibilities give $N = 9$ atoms per group, approximately. The value of H at the intersection point is then 24,500 gauss. The applied field at the intersection point $H_a = 13,500$ gauss. The difference may be due to the internal field or to the fact that N and ϵ are not independent of temperature and field strength as has been assumed. It is also possible that the magnetization of the groups with an effective resultant moment increases with decreasing temperature, as in the theory of ferromagnetism. The possible ferromagnetic behavior of the small groups postulated above is not known. It may be of interest in this connection that Peierls¹⁸ has shown that in the Ising model, which is similar to the above, all lattices except the linear chain may be ferromagnetic.

Information as to the nature of the interaction effects which give rise to the internal field coefficient D above the Curie point may be found from its value. The high temperature $\Theta = 2\mu^2 D/3k$ approximately, as can be seen from Eq. (5). For FeCl_2 , $\Theta = 48^\circ$ at room temperature (Part I, Table I). The experimental result is $D = 7 \times 10^{24}$. Actual calculation of D assuming magnetic dipole-dipole interaction in a two-dimensional hexagonal network gives a value of 10^{23} approximately. The Lorentz field (spherical cavity) value is even less. It is apparent, therefore, that the actual interaction is more than 10 times as strong as magnetic dipole-dipole interaction. In view of the small distances between near neigh-

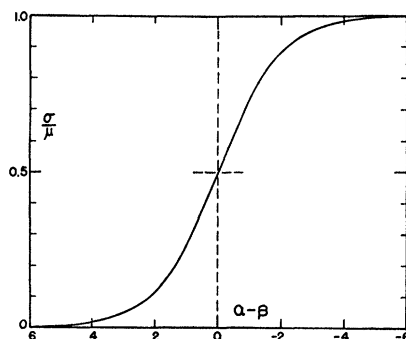


FIG. 2. The relative magnetization as a function of $\alpha - \beta$ when $\beta > 2$.

¹⁸ R. Peierls, Proc. Camb. Phil. Soc. **32**, 477 (1936).

bors in these lattices (Table II), it is probable that the exchange interaction is the principal cause of these effects, as in ferromagnetics. Since the ratio of nearest neighbor distance to the ion radius in these compounds is only slightly greater than in the ferromagnetic metals (ratio is about four in Ni), it appears reasonable that the exchange interaction should be appreciable.

The magnitude of the specific heat jump at the Curie point (Part I, reference 7) is of interest. The experimental values in cal./mole were 4.54 for FeCl_2 , 1.50 for CoCl_2 , 0.66 for CrCl_3 , and 0.13 and 0.18 for NiCl_2 . If only the spin moments are effective, the theoretically predicted values for a simple ferromagnetic model³ are 4.57 for FeCl_2 , 4.38 for CoCl_2 , and CrCl_3 , and 3.97 for NiCl_2 . The agreement in the case of FeCl_2 is very good but for the others the experimental value is too low. This latter discrepancy may be due to the incipient formation of groups above the Curie point, so that the total change is spread out. The specific heat anomaly is approximately the same for an antiparallel group formation as it is for a parallel group, since the entropy change is of the same magnitude.

The behavior of CoCl_2 and NiCl_2 is similar to that of FeCl_2 , although the effects are appreciably smaller. Calculations, as above, for CoCl_2 result in an ϵ/k of 28° . The predicted intersection point magnetization per mole is 8300 and the experimental is 5900. The initial susceptibilities give $N=5$. The resulting intersection value of $H=28,000$ gauss, while the applied field at this point is $H_a=14,800$ gauss. Similar calculations for NiCl_2 result in an ϵ/k equal to 24° . No intersection point can be chosen from the results. The initial susceptibility gives $N=3$.

FIG. 3. The reciprocal initial susceptibility per atom, multiplied by $N\mu^2/\epsilon$, as a function of kT/ϵ .

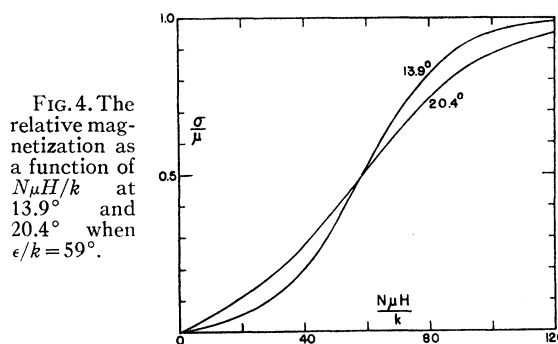
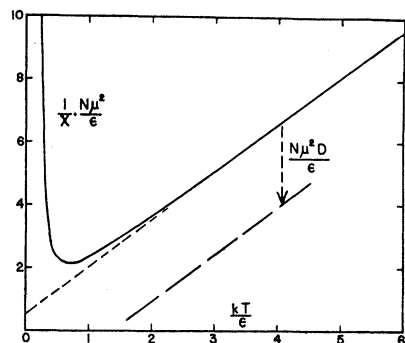


FIG. 4. The relative magnetization as a function of $N\mu H/k$ at 13.9° and 20.4° when $\epsilon/k=59^\circ$.

The behavior of CrCl_3 (Figs. 1 and 2, Part I) differs from that of the other metamagnetic chlorides. The magnetization characteristics of CrCl_3 require that α be either very small or negative, as can be seen from Fig. 1. The fact that the slope of the experimental reciprocal susceptibility *vs.* temperature curve is constant down to low temperatures indicates that Θ is independent of temperature above the low temperature region. This requires that ϵ^a be constant or negligible if Eq. (4) is to be applicable. The behavior of CrCl_3 may, therefore, be made consistent with the theory by assuming that $\epsilon/k=0$ or $-\infty$. Experimentally a field of 30,000 gauss at 13.9° results in a magnetization approximately 0.8 of saturation. This gives $N=4$ for $\epsilon/k=0$, and $N=2$ for $\epsilon/k=-\infty$. Since the Curie point from the specific heat anomaly is 16.8° and a field dependence occurs at 20.4° , it is probable that incipient group formation occurs above the actual Curie point temperature.

The anhydrous chlorides CrCl_2 , CuCl_2 , VCl_2 and VCl_3 (Fig. 1, Part I) are apparently not metamagnetic. However, they all do exhibit the behavior indicated by Fig. 3. Group formation apparently does not occur in these compounds and, therefore, they have no Curie points. The applied magnetic fields are only sufficiently large to indicate the beginning of paramagnetic saturation. These compounds all show the negative Θ predicted by Eq. (5). The theory and experiment do not agree quantitatively, but that may be due to the simplicity of the theory and the fact that other effects, such as the crystalline field, while comparatively negligible in the metamagnetic chlorides, are not negligible in these compounds.

The theory does not explain the absence of

large interaction effects in MnCl_2 and FeCl_3 . The crystal structures of these compounds are the same as that of the corresponding metamagnetic chlorides. The only apparent point of difference is that the ground state of these ions

is a 6S state. This would indicate that the exchange interaction is negligible for a 6S state, even though the electron shell is incomplete.

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Mobilities in Hydrogen at High Current Densities

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The conditions in an investigation of the silent electric discharge from sharp points and fine wires in hydrogen at atmospheric pressure are such that the discharge itself purifies the gas from electron-attaching impurities, so that the conditions of the discharge are productive of free electron conduction. Measurements are made of the generalized coefficient of mobility for the drift of free electrons in hydrogen, and of the mobility of hydrogen positive ions in hydrogen. Past observers have usually had doubts concerning the purity of the gas prepared by chemical means, but the results here reported involve a demonstrably sustained purification during the measurement itself.

WHEN the point is negative in a point-to-plane arrangement of electrodes, it is supposed that the silent discharge is caused by electrons arising at the tip of the point and producing ionizations by collision in avalanches, until the avalanche fronts have moved away from the tip of the point to a place where the electric field is no longer sufficient to support ionizations by collisions. The number of electrons freed by ionizations in an avalanche may be considered to be equal to 2^N where N is the number of ionizations an original electron makes. By considering directions of propagation of an avalanche increasingly removed from the axis of symmetry such as, for example, along the direction of the line, B , in Fig. 1, the electric field is less intense at any given distance from the metal than along a direction such as A , and so the number of ionizations that the original electron can produce is less. For example, if the number of ionizations along a direction A , is 30, while the number along a direction like B , is 20, an avalanche along the direction B will produce less than 1/1000 as much charge as an avalanche along the direction A (i.e., in the ratio 2^{10}). Thus, ionizations which are responsible for most of the current occur within a

region approximating a hemispherical shell, such as CC . The region between the point and the shell and including the shell may be called the "ionizing sheath." In hydrogen, this sheath appears to be about 0.2 cm thick. Such a hemispherical cap is generally observed in this form of discharge.

STABILITY OF SHEATH

A rather detailed discussion of the negative point-to-plane discharge in air has been published by Trichel, and by Loeb and Kip.¹

These observers report on a pulsating character of the negative corona discharge, which they attribute to the attachment of electrons to oxygen molecules to form negative molecular ions, and, due to the much smaller mobility of ions than electrons, the suppression of further ionizations in the sheath until ions have had time to move away. Their supposition is that each step in the sequence: avalanching, electron attaching, movement away of ions, *et seq.* must advance well toward completion before the next step in the sequence can begin.

¹ G. W. Trichel, Phys. Rev. **54**, 1078 (1938); L. B. Loeb and A. F. Kip, J. App. Phys. **10**, 142 (1939).