

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

I. Experimental*

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The magnetic susceptibility of the anhydrous chlorides of the iron group have been studied as a function of field strength up to 32,000 gauss and as a function of temperature down to 13.9°K. Those compounds whose room temperature susceptibility characteristic indicates a positive Curie temperature, also show a field strength dependence of the susceptibility at 13.9°K and 20.4°K. Chromic chloride has a very steep magnetization curve at these low temperatures, with a large initial susceptibility increasing with decreasing temperature. Ferrous, cobaltous, and nickelous chlorides have an S-type magnetization curve characterized by a small initial susceptibility which decreases with decreasing temperature, followed by a very large susceptibility and eventual approach to saturation, both increasing with decreasing temperature. The susceptibility of many of the compounds reaches a maximum at temperatures which do not appear to be correlated with the presence of field dependence, but these temperatures do correspond to the temperatures of known specific heat anomalies.

INTRODUCTION

THE behavior of the magnetic susceptibility of most paramagnetic substances at ordinary temperatures is adequately described by the Curie-Weiss law, $\chi(T - \Theta) = C$, where χ is the susceptibility, T is the absolute temperature, Θ is the Curie temperature, and C is a constant. Theoretical considerations indicate that the value of Θ is determined by the nature and magnitude of the interaction within the magnetic atoms (spin-orbit coupling) and between the magnetic atoms and their surrounding atoms. This latter interaction may be either between the magnetic atoms themselves, both dipole-dipole and exchange effects, or between the magnetic atoms and the crystalline (electric) field produced by the neighboring ions in the substance. When all interactions become negligible, as in a gas of free carriers of magnetic moment, Θ reduces to zero, and the susceptibility follows Curie's law, $\chi T = C$. A magnetic carrier may be considered as free when the energy required to rotate it against interaction forces is small compared to kT . Thus the deviations from Curie's law are sufficiently enhanced at low temperatures to be a valuable source of information concerning the interaction effects.

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The anhydrous chlorides of the elements of the first transition series, the iron group, are of particular interest because the magnetic atoms are sufficiently concentrated to produce large interaction effects. In addition, the crystal structures of this group of compounds appears to be isomorphic, although crystal structure studies have not been made for all the compounds. This facilitates comparison between the atoms of varying magnetic moment. Finally, there seems to be no indication of any metallic or semiconducting behavior in these compounds, so the complication that electrical conductivity introduces into magnetic properties does not have to be considered.

The cryomagnetic anomalies associated with some of these compounds have been studied at the Kamerlingh Onnes Laboratory of the University of Leiden, with many interesting results. The present investigation is an elaboration of this work.

METHOD OF MEASUREMENT

The measurements were made with a Bitter type high field solenoid (magnet No. 1 of the M. I. T. magnet laboratory)¹ which permitted investigation up to 32,000 gauss. A nonhomo-

¹ F. Bitter, *Rev. Sci. Inst.* **10**, 373 (1939).

geneous field method (Curie) described by Bitter and Kaufmann² was used for the determination of the susceptibilities. The specimens consisted of the powdered compound sealed off in a thin-walled Pyrex ampoule. The lower part of the ampoule was shaped as a cylinder, 8 mm O.D. and 1 cm high, and this joined to a long tubular neck, 3 mm O.D. and 5 cm long. The cylindrical part of the ampoule was filled with the powder under investigation and a short glass-wool plug was placed in the neck to keep the powder in place. The ampoule was then filled with helium gas and sealed off at the top.

The experiments were carried on in a long Dewar flask (2 cm I.D.) which fitted in the magnet. A cylindrical copper working chamber, connected to and supported by a long, 9 mm supernickel tube, was placed within the Dewar at a suitable region of the magnetic field. The specimen tube hung within the copper chamber and was supported by a gold chain connected to one arm of an analytical balance. This arrangement permitted independent control of the atmosphere surrounding the specimen tube and of the refrigerant contained in the Dewar flask. The following fixed temperatures were used in the measurements: solid CO₂ (193°K), boiling N₂ (77.3°K), freezing N₂ (63.1°K), boiling H₂ (20.4°K), and freezing H₂ (13.9°K). For the liquid N₂ temperatures and above, H₂ gas was slowly passed out of the neck of the supernickel tube to prevent condensation of water and air on the specimen tube. For the temperatures made available by liquid H₂, helium gas was used in the working chamber.

PREPARATION OF SPECIMENS³

As a result of the extremely hygroscopic nature of the anhydrous chlorides of the iron group, all preparations and transfers were made in glass vessels, in vacuum or dry inert gases, and the final specimen tubes were sealed off with dry helium. The helium was used to insure rapid temperature equilibrium throughout the specimen at all the temperatures used.

² F. Bitter and A. R. Kaufmann, Phys. Rev. **56**, 1044 (1939).

³ The compounds were prepared by Professor R. C. Young of the M.I.T. Chemistry Department in collaboration with the first author.

NiCl₂, CoCl₂, FeCl₂, MnCl₂.—These compounds were all made from the C.P. hydrates. The hydrates were dehydrated in vacuum at 100 to 200°C. The resultant product, containing an appreciable quantity of oxychloride, was then heated in vacuum to about 650°C. The pure chlorides sublime and condense in characteristic crystals on the cold portions of the tube, the oxide impurities remaining behind. The sublimed crystals have a very high purity, and in the case of ferrous chloride, less than 0.1 percent of ferric ion was present.

FeCl₃, CrCl₃.—These were made from commercially available C.P. anhydrous sublimed material. They were resublimed in vacuum, the FeCl₃ at 250°C, the CrCl₃ at 650°C.

VCl₃.—Made by decomposition of VCl₄ at 160°C in dry CO₂. The VCl₄ was produced by reacting Cl₂ with V metal at 500°C.

VCl₂.—Made by reduction of VCl₃ at 500°C with H₂.

TiCl₃.—Made by reduction of TiCl₄, commercially available, at 650°C with H₂ and condensing the TiCl₃ on a cold surface.

TiCl₂.—Made by vacuum decomposition of TiCl₃ at 475°C.

CuCl₂.—Made by reacting Cl₂ with Cu at 400°C.

RESULTS

The results of the measurements are shown in Figs. 1 and 2 and in Tables I and II, where χ is the susceptibility per gram mole and σ is the magnetization per gram mole in c.g.s. units. H is the field strength in gauss, and T is the absolute temperature in °K, unless otherwise specified. Figure 1 shows the reciprocal susceptibility as a function of temperature. Figure 2 shows the magnetization as a function of field strength for those compounds which exhibited a dependence of the susceptibility upon the field strength. For these latter compounds, the initial differential susceptibility, $\chi = d\sigma/dH$, is used in the reciprocal susceptibility plots.

The susceptibility constants given in Table I have all been corrected for the diamagnetism of the cation and anion. The susceptibility values used in the graphs are the total measured values, except in the case of the titanium compounds where the corrected values are used. The values

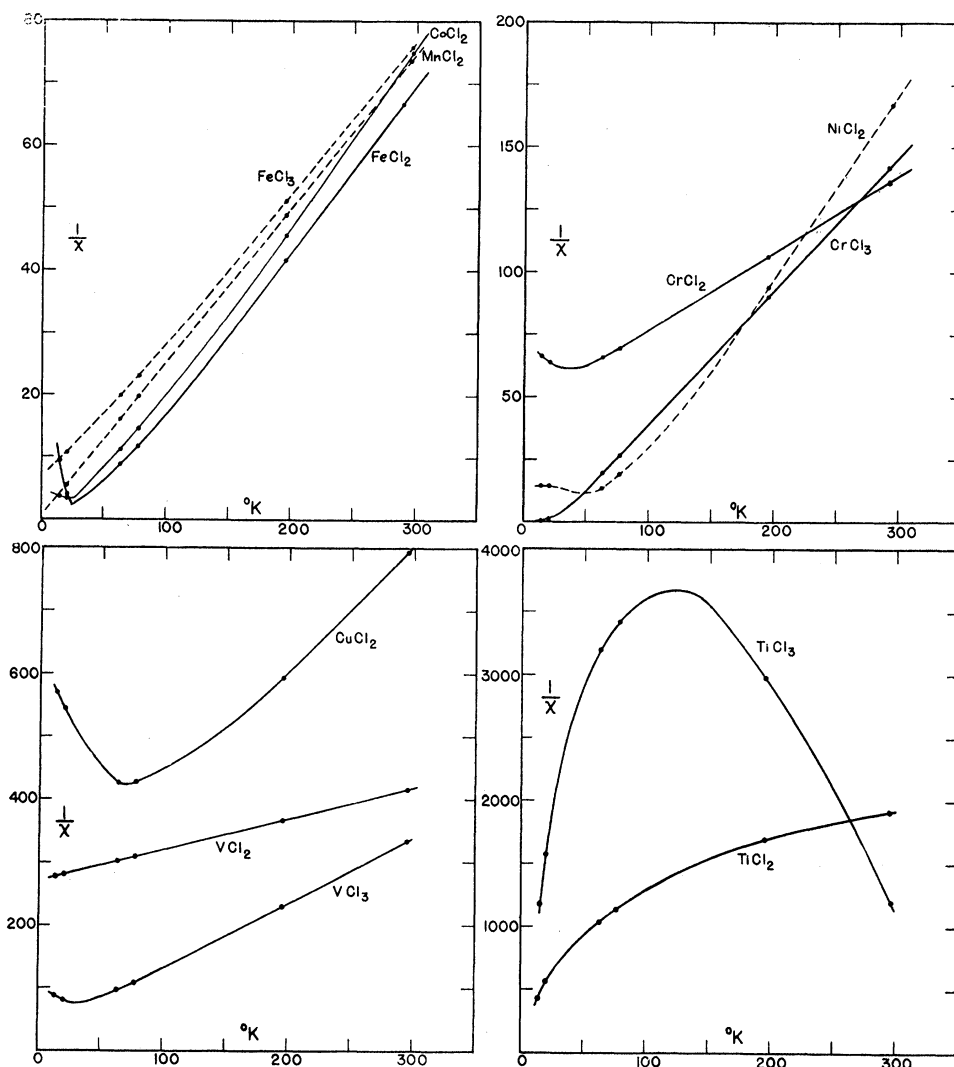


FIG. 1. The reciprocal susceptibility per gram mole as a function of the absolute temperature for FeCl_3 , FeCl_2 , MnCl_2 , CoCl_2 , CrCl_3 , CrCl_2 , NiCl_2 , VCl_3 , VCl_2 , CuCl_2 , TiCl_3 and TiCl_2 . The correction for the diamagnetism of the cation and anions in TiCl_3 and TiCl_2 has been applied.

given in Table I for the diamagnetic susceptibility per gram mole, χ_d , have been calculated for the complete compound (cation plus anion) by the method of Angus⁴ for modifying Slater's⁵ formula for ionic diamagnetic susceptibilities. This modification is used since the empirical agreement is improved, although the theoretical basis of Slater's method is better.

The value of the Curie temperature* was

⁴ W. R. Angus, Proc. Roy. Soc. **A136**, 569 (1932).

⁵ J. C. Slater, Phys. Rev. **36**, 57 (1930).

* In this paper the term "Curie temperature" refers to the value of Θ found from the extrapolation of measurements made at comparatively high temperatures. The term "Curie point" refers to the actual temperature at which the magnetic behavior sharply changes in character,

determined from the slope of the reciprocal susceptibility *vs.* temperature curve at room temperature, corrected for the diamagnetic susceptibility. The effective number of Bohr magnetons, p , was calculated by means of the formula $p = 2.84[\chi(T - \Theta)]^{1/2}$. The temperature of the maximum susceptibility given in Table I corresponds to the temperature of the reciprocal susceptibility minima (where such exist) in Fig. 1.

Specific heat studies of the nickel, cobalt, ferrous, manganous and chromic chlorides have

as determined by actual measurements in this temperature range. This distinction is similar to the usual distinction between the paramagnetic and ferromagnetic Curie point.

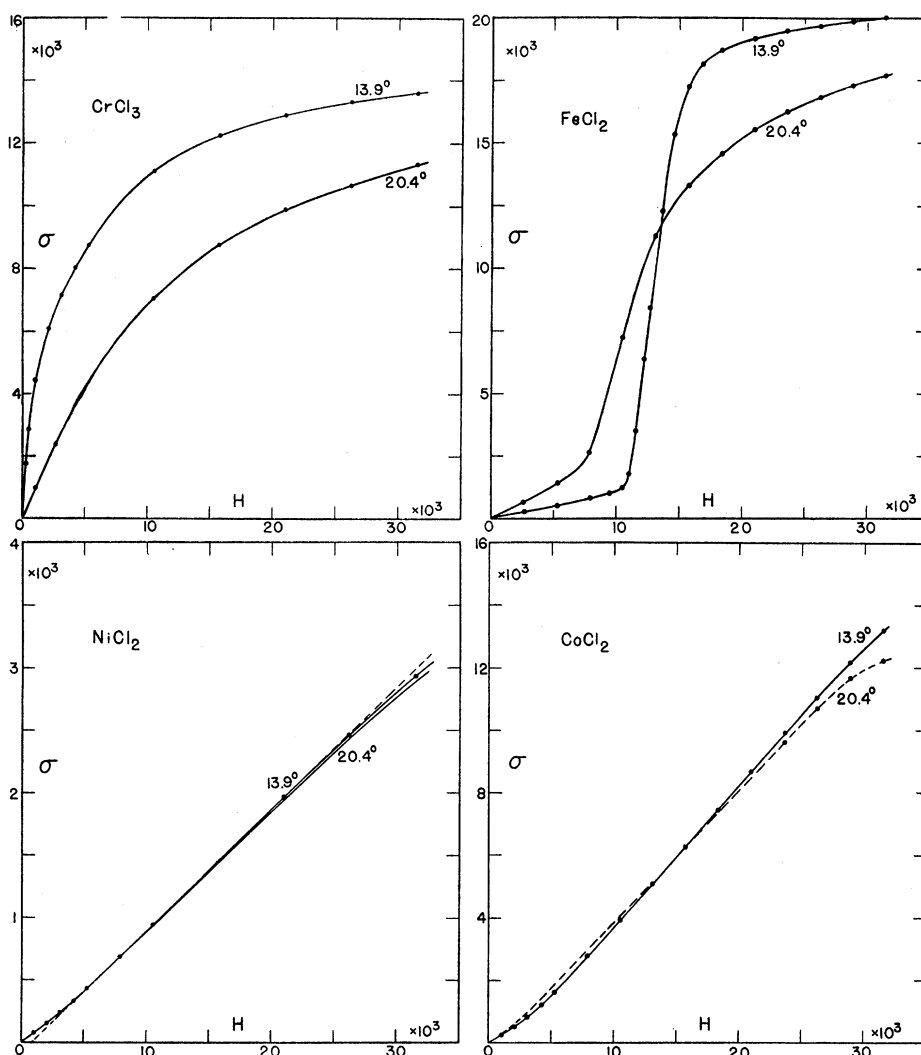


FIG. 2. The magnetization per gram mole as a function of the field strength at 20.4°K and 13.9°K of CrCl₃, FeCl₂, NiCl₂, and CoCl₂. In the case of NiCl₂ the dotted line represents the straight line continuation of the maximum slope of the curve. In order to maintain the clarity of the figure most of the experimental points on the 20.4° magnetization curve for CoCl₂ are not shown.

been made by Trapeznikowa and Schubnikow,⁶ and their results, tabulated in Table I, show that the anomalies in the specific heats occur at temperatures which correspond closely to the temperatures of maximum susceptibility.

In Table II, the magnetization data are listed for the compounds, which showed a field dependence of the susceptibility at H₂ temperatures. The differential susceptibility (slope of the magnetization curve) is given for the temperature of boiling H₂, 20.4°, and freezing H₂, 13.9°, and

⁶ O. Trapeznikowa and L. Schubnikow, Phys. Zeits. Sowjetunion 7, 66 and 255 (1935); O. Trapeznikowa, L. Schubnikow and G. Miljutin, Phys. Zeits. Sowjetunion 9, 237 (1936); O. Trapeznikowa and G. Miljutin, Phys. Zeits. Sowjetunion 11, 55 (1937).

both the initial and maximum values are presented. As can be seen in Fig. 2, the magnetization curves for 20.4° and 13.9° cross each other in the case of FeCl₂ and CoCl₂. The magnetization and field strength of this point of intersection is shown in Table II.

The precision of the results was not the same for all the specimens, and depended chiefly upon the magnitude of the forces involved. The analytical balance could detect changes of 0.1 milligram force, but this sensitivity could only be used with great difficulty because of the disturbance created by the gas escaping from the specimen chamber. This reduced the working sensitivity of the balance to about 1 milligram.

The forces were usually between 1 gram and 100 grams for the highest field strengths. Generally, the accidental error in any measurement was about 0.1 percent. The sources of systematic errors were as follows: (1) calibration of the field and field gradient, (2) change of position of the specimen in the field caused by the stretching of the gold chain or thermal contractions, (3) errors in the weight of the compound in the specimen tube, and (4) error in the diamagnetic susceptibility correction for the Pyrex specimen tube and gold chain. These errors were probably of the order of magnitude of 1 percent. For specimens of very small susceptibility, such as the titanium compounds, the forces are very small and the correction (4) is relatively large, so that the systematic error may be 10 percent or more.

Another source of error was found in compounds with very large susceptibilities at liquid H_2 temperatures, such as $FeCl_2$. In these cases the forces on the individual crystals are sufficiently large to pack the crystals together. This causes the density of the specimen to be increased slightly, when the magnetic field is applied, in a manner not completely reversible. This packing effect results in an apparently increased magnetization of the specimen when the field is being decreased from its maximum value, as compared to the magnetizations at the same fields when the field is being increased to its maximum value. After repeated magnetizations at the highest fields, the measurements follow a reproducible hysteresis loop in which the difference between increasing and decreasing field points is about 1 percent. This difference could be greatly in-

TABLE I. Susceptibility data for the anhydrous chlorides of the elements of the first transition series.

COMPOUND	$-\chi_d \times 10^6$	$\chi(T-\Theta)$	ρ	Θ	TEMP. OF MAX. χ	TEMP. SPEC. HT. ANOMALY
$TiCl_3$	80.4	0.25	1.42			
$TiCl_2$	66.7	0.521	2.05	-702		
VCl_3	82.3	1.005	2.85	-30.1	30	
VCl_2	66.9	2.13	4.15	-565		
$CrCl_3$	82.9	1.89	3.90	27.0	~20	16.8
$CrCl_2$	66.1	3.26	5.13	-149	~40	
$MnCl_2$	65.0	4.07	5.73	-3.3		None
$FeCl_3$	82.5	4.07	5.73	-11.5		
$FeCl_2$	63.9	3.59	5.38	48.0	24	23.5
$CoCl_2$	62.8	3.46	5.29	38.1	25	24.9
$NiCl_2$	61.8	1.36	3.32	68.2	~50	49.6
						57.0
$CuCl_2$	60.8	0.536	2.08	-109	~70	

creased by shaking the specimen tube and loosening the crystals. Repeated magnetizations re-established the small hysteresis loop. For this reason, the curves in Fig. 2 have been plotted from measurements taken in the direction of decreasing field strength after stabilization by repeated magnetizations.

It is of interest that most of these compounds form layer lattice crystals, so that the individual crystal particles take the form of flat flakes. When

TABLE II. Magnetization data for the compounds whose susceptibility is a function of magnetic field strength.

COM- POUND	DIFFERENTIAL SUSCEPTIBILITY				INTERSECTION POINT	
	INITIAL 20.4°	13.9°	MAXIMUM 20.4°	13.9°	σ	H
$CrCl_3$	0.947	6.75				
$FeCl_2$	0.248	0.102	1.88	4.27	11,700	13,500
$CoCl_2$	0.294	0.272	0.422	0.456	5900	14,800
$NiCl_2$	0.0700	0.0700	0.0961	0.0981		

packed into the specimen ampoule, the flakes tend to lie parallel to the base of the ampoule (i.e., at right angles to the direction of the field). Since the individual crystals are undoubtedly anisotropic, this results in a small anisotropy of the specimen. Serres⁷ has found that this specimen anisotropy is about 1 percent at room temperature for $CrCl_3$ crystals. This type of specimen anisotropy was probably present in all the compounds studied.

The correction for the demagnetizing field has not been made, since it is not certain whether the specimen is behaving as a whole or each individual flat crystal is demagnetizing itself. The true magnetic field inside the crystals is $H_t = H_a - DI$, where H_a is the applied field, D is the demagnetizing coefficient, and I is the magnetization per unit volume. This leads to the formula $1/\chi_t = 1/\chi_a - D\rho/M$, where χ_t and χ_a are the gram mole differential susceptibility ($d\sigma/dH$) true and apparent, respectively, ρ is the density, and M is the molecular weight of the compound. The maximum correction would apply when the flat crystals are demagnetizing themselves individually; $D = 4\pi$ and ρ is the crystal density, and $D\rho/M = 0.3$ to 0.2 approximately. The minimum correction would apply when the specimen ampoule is demagnetizing as a whole; $D = 4$ and ρ is the specimen density (approximately $\frac{1}{2}$ the

⁷ A. Serres, Ann. de physique 17, 5 (1932).

crystal density) and $D\rho/M=0.05$ to 0.03 , which is about $\frac{1}{6}$ as much as in the maximum case. The demagnetizing correction is largest for the initial susceptibility of CrCl_3 at 13.9° , $\chi_a=6.75$. The maximum assumption would be more than sufficient to make this initial susceptibility infinite. The minimum assumption would make the true initial susceptibility about 9.0 . At 13.9° , FeCl_2 has a maximum differential susceptibility, $\chi_a=4.27$. The maximum demagnetization assumption would make this differential susceptibility infinite. The minimum assumption would raise it to $\chi_t=5.1$. These demagnetization corrections are so very large as compared with the usual correction for paramagnetics because the above molar susceptibility for CrCl_3 is about 50 times as large as the value for dilute chromic compounds (spin-only value), and for FeCl_2 is about 20 times as large as the value for dilute ferrous compounds.

No remanences were observed in any of the specimens, within the sensitivity of the apparatus. The magnetizations were measured with the field first in one direction and then reversed. Any remanence would appear as a difference between the two sets of measurements. No such difference was observed. The recent Leiden measurements,⁸ however, indicate that some of these compounds exhibit remanence. Inasmuch as the apparatus used for the Leiden work had a very high sensitivity their results may not be at variance with the present work.

DISCUSSION AND COMPARISON OF RESULTS

CuCl_2 .—The specimen used contained sufficient impurity in the form of CuCl to invalidate the absolute values of the measured susceptibility. The relative values agreed very well with the Leiden measurements,⁹ so the absolute values of the results were adjusted to agree with the Leiden susceptibility at room temperatures. The CuCl contributes only a diamagnetic correction. No field dependence of the susceptibility was found. The adjusted results are shown in Fig. 1.

NiCl_2 .—The room temperature value of the susceptibility agrees very closely with that found

by Serres¹⁰ who reports a Curie temperature of 95°K . The field dependence at hydrogen temperatures agrees qualitatively with that found at Leiden.¹¹ The Leiden measurements show no dependence upon the temperature from H_2 temperatures to He temperatures, but their investigations went only to 20,000 gauss.

CoCl_2 .—The room temperature value of the susceptibility agrees reasonably well with that of Fehrenbach¹² who found a Curie temperature at 26.6° . The recent measurements of deHaas and Schultz⁸ do not agree with the older Leiden measurements,¹¹ but are in good qualitative agreement with the present work. They find a Curie temperature of 19° . They also report that the magnetization curves at boiling and freezing H_2 cross at a field of 6500 gauss, as compared with the 14,800 gauss in the present work. Their ratio of initial susceptibilities is about the same, although their values are lower.

FeCl_2 .—The Leiden measurements¹³ on this compound are very unsatisfactory as they used an incomplete Gouy method, and the results do not permit simple interpretation in terms of magnetization. They found indications of a maximum in the susceptibility at H_2 temperatures, the maximum decreasing and shifting to higher field strengths with decreasing temperature. The present results are at variance with this.

FeCl_3 .—The room temperature results of Lallemand¹⁴ agree very well with the present work. No field dependence was found at any temperature. The susceptibility deviates slightly at low temperatures from the Curie-Weiss law.

MnCl_2 .—The present work agrees qualitatively with the Leiden measurements¹⁵ on this compound, and is in good quantitative agreement with the room temperature results of Lallemand¹⁴ and Fehrenbach.¹² At the temperature of freezing H_2 (13.9°) the expected beginning of paramagnetic saturation could be observed. No other field dependence of susceptibility was found.

¹⁰ A. Serres, *Ann. de physique* **20**, 441 (1933).

¹¹ H. R. Woltjer, *Leiden Comm.* 173b (1925); H. R. Woltjer and H. Kamerlingh Onnes, *Leiden Comm.* 173c (1925).

¹² C. Fehrenbach, *J. de phys. et rad.* (7) **8**, 11 (1937).

¹³ H. R. Woltjer and E. C. Wiersma, *Leiden Comm.* 201a (1929).

¹⁴ A. Lallemand, *Ann. de physique* **3**, 97 (1935).

¹⁵ H. Kamerlingh Onnes and E. Oosterhuis, *Leiden Comm.* 129b (1912).

⁸ W. J. de Haas and B. H. Schultz, *Physica* **6**, 481 (1939); W. J. de Haas, B. H. Schultz and J. Koolhaas, *Physica* **7**, 57 (1940).

⁹ W. J. de Haas and C. J. Gorter, *Leiden Comm.* 215a (1931).

CrCl_2 .—The work of Serres⁷ at room temperature agrees very well with the present work. Serres reports a Curie temperature of -115.5° . Lips¹⁶ studied this compound down to 55°K , and his values, which indicate a Curie temperature of -128° , are in excellent agreement with the present ones. No field dependence of the susceptibility was found.

CrCl_3 .—The Leiden results¹¹ are in good agreement with the present work on this compound. It is of interest that this compound was the only one that exhibited simple, steep magnetization curves. In this connection it should be noted that the Curie point indicated by the specific heat measurements is 16.8° , although the field dependence of the susceptibility occurs above this temperature as well as below.

VCl_2 , VCl_3 .—The previous work of Klemm and Hoschek¹⁷ down to 90°K is in good quantitative agreement with the present results. No field dependence of the susceptibility was found at any temperature.

TiCl_2 , TiCl_3 .—These compounds have not been investigated before, probably because of the chemical difficulties involved in their production. The dependence of their susceptibility upon temperature is completely different from that of the other compounds. No field dependence of the susceptibility was found. The values shown in Table I for TiCl_3 were calculated from the room temperature value of the susceptibility, with Θ assumed equal to zero.

SUMMARY

The salient features of the experimental results may be summarized as follows:

¹⁶ E. Lips, *Helv. Phys. Acta* **7**, 537 (1934).

¹⁷ W. Klemm and E. Hoschek, *Zeits. f. anorg. allgem. Chemie* **226**, 359 (1936).

(1) None of the compounds showed any dependence of the susceptibility upon field strength at temperatures above 63°K .

(2) At H_2 temperatures (13.9° and 20.4°) a dependence of the susceptibility upon field strength was found for NiCl_2 , CoCl_2 , FeCl_2 , and CrCl_3 . These compounds are the only ones which exhibit positive Curie temperatures (Θ) at room temperature.

(3) In the case of CrCl_3 the specific heat anomaly indicates a Curie point of 16.8°K . A field dependence of the susceptibility was found above this temperature, as well as below. The initial susceptibility increases with decreasing temperature and may be infinite, or very large, at 13.9° if the demagnetization correction is applied.

(4) FeCl_2 exhibits an S-type magnetization curve at H_2 temperatures. This magnetization curve is characterized by a very small initial susceptibility which decreases with decreasing temperature, followed by a very large differential susceptibility and eventual approach to magnetic saturation, both increasing with decreasing temperature. CoCl_2 and NiCl_2 exhibit this S-type magnetization curve in lesser degree.

(5) MnCl_2 exhibits no deviations from the Curie-Weiss law, although its crystal structure is very similar to that of the other anhydrous dichlorides.

(6) Many of the compounds exhibit a minimum in the reciprocal susceptibility *vs.* temperature curve, but apparently this is not necessarily connected with any field dependence of the susceptibility.

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