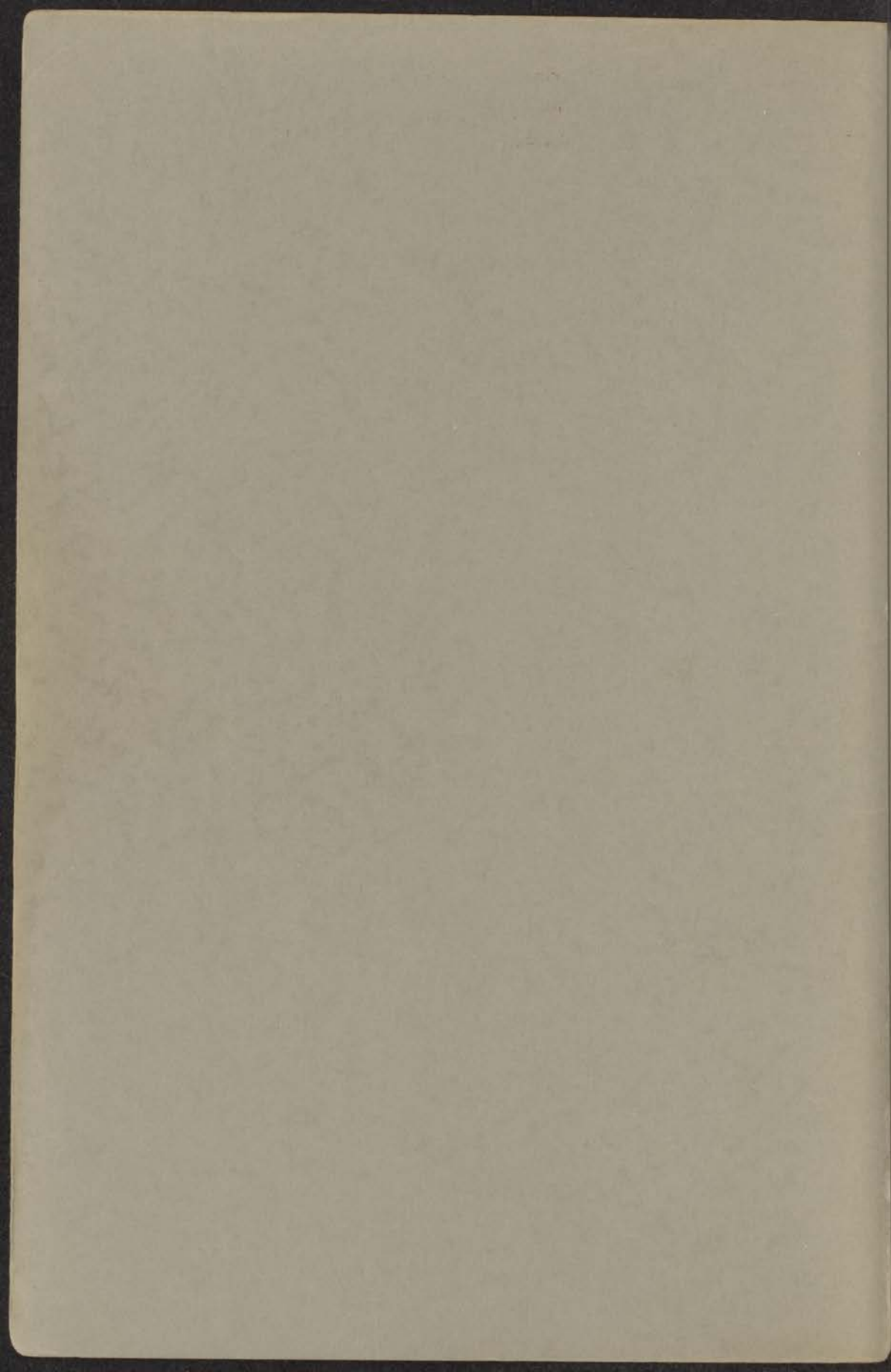


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Anorganisch Chemisch Laboratorium  
Hugo de Grootstraat 27  
Leiden

MAGNETIC PROPERTIES OF COBALT  
IN  $\text{Co}_3\text{O}_4$  AND OTHER OXIDES

P. COSSEE



## STELLINGEN

- 1) Het is zeer gewenst, dat bij de opleiding van kristallografen en chemici meer de aandacht wordt gevestigd op het verschil tussen de Ångström en de „Siegbahn eenheid“.
- 2) Door het verwaarlozen van het temperatuur-onafhankelijk paramagnetisme is de conclusie, die Greenwald, Pickart en Grannis uit de susceptibiliteitsmetingen aan  $\text{CoAl}_2\text{O}_4$  trekken, onjuist.  
S. Greenwald, S. J. Pickart and F. H. Grannis.  
*J. Chem. Phys.* 22, 1597 (1954).
- 3) De extrapolatiemethode die Hall en Fuoss toepassen op viscositeitsmetingen aan polymeeroplossingen leidt niet tot de ware intrinsieke viscositeit bij een schuifspanning nul.  
H. T. Hall, R. M. Fuoss. *J. Am. Chem. Soc.* 73, 265 (1951).
- 4) In het magnetisch gedrag van mengkristallen van  $\text{CoAl}_2\text{O}_4$  en  $\text{MgAl}_2\text{O}_4$  zijn aanwijzingen te vinden dat  $\text{MgAl}_2\text{O}_4$  een gedeeltelijk omgekeerd spinel is.
- 5) In het artikel van Ogston komt niet voldoende tot uitdrukking dat er in principe geen verschil bestaat tussen de specifieke werking van een asymmetrisch enzym, enerzijds op één van de vormen van een optisch antipodenpaar en anderzijds op één van de twee identieke groepen Z van een symmetrische verbinding  $\text{CXYZ}_2$ .  
A. G. Ogston. *Nature* 162, 963 (1948).
- 6)  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , door Selwood aanbevolen als ijkstof voor magnetische susceptibiliteitsmetingen, voldoet niet aan alle voorwaarden die aan een dergelijke stof gesteld mogen worden. Het nikkelanalogon van deze verbinding is een veel betere standaard.  
P. W. Selwood. *Magnetochemistry* (1943) p. 29.
- 7) De berekeningen van Kordes over stralen en polariseerbaarheden van ionen in kristalroosters leveren geen nieuwe gezichtspunten op.  
E. Kordes, *Die Naturwissenschaften* 21, 488 (1952).

- 8) De algemeen gebruikelijke methode \*) voor het rechtzetten van slecht gevormde kristallen in draaikristalcameras met behulp van zwenkopnamen kan in vele gevallen met vrucht gewijzigd worden door de beide justeerwiegen onder een hoek van  $45^\circ$  met de invallende bundel te plaatsen.

\*) C. W. Bunn. Chemical Crystallography (1948)  
p. 173-175.

- 9) Voor de verklaring van de para-Claisen omlegging verdient het reactiemechanisme via het diénon de voorkeur boven dat van een  $\pi$ -complex.

D. Y. Curtin, H. W. Johnson, J. Am. Chem. Soc. 78,  
2611 (1956).

J. P. Ryan, P. R. O'Connor, J. Am. Chem. Soc. 74,  
5866 (1952).

- 10) In coordinatieroosters waarin niet-geïsoleerde complexe groepen voorkomen is voor de beschrijving van de bindingstoestand de M. O. methode van Mulliken te prefereren boven de methode der gerichte valentie van Pauling.

- 11) Om psychologische redenen verdient het aanbeveling het gebruik van z. g. „buddy-seats" op bromfietsen aan beperkende bepalingen te onderwerpen.

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# MAGNETIC PROPERTIES OF COBALT IN $\text{Co}_3\text{O}_4$ AND OTHER OXIDES

## PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR  
IN DE WIS- EN NATUURKUNDE AAN DE RIJKS-  
UNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE  
RECTOR MAGNIFICUS DR. P. A. H. DE BOER,  
HOGLERAAR IN DE FACULTEIT DER GODGE-  
LEERDHEID, TEGEN DE BEDENKINGEN VAN DE  
FACULTEIT DER WIS- EN NATUURKUNDE  
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DONDERDAG 4 OCTOBER 1956  
TE 16 UUR

DOOR

PIETER COSSEE  
GEBOREN TE LEIDEN IN 1926

UITGEVERIJ EXCELSIOR - ORANJEPLEIN 96 - 'S-GRAVENHAGE

THE PROPERTIES OF ALUMINA  
AND OTHER OXIDES

Promotor: Prof. Dr. A. E. van Arkel

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## INTRODUCTION

The object of the present investigation is the solution of some of the problems concerning the cobalt oxide  $\text{Co}_3\text{O}_4$ . This compound has been subjected to chemical, crystallographic and magnetochemical investigations.

From crystallographic work we know that  $\text{Co}_3\text{O}_4$  crystallizes in the so-called spinel lattice. This type of crystal structure is essentially a cubic close-packed lattice of the anions in which the cations occupy  $1/8$  of the tetrahedral interstices and  $1/2$  of the octahedral interstices. In a cubic close-packed lattice there are as many octahedral interstices as there are anions and twice as many tetrahedral interstices. For a more detailed description of the spinel structure we may refer to the work of Gorter <sup>1</sup>).

For a spinel with the general formula  $\text{MN}_2\text{X}_4$  in which M and N are di-, tri- or tetravalent ions there arise four possibilities as to valence and distribution of the cations between the possible positions. (In this thesis we adopted the general rule of enclosing the cations in the octahedral interstices between square brackets.)

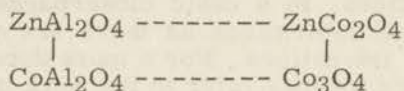
- A)  $\text{M}^{2+} [\text{N}_2^{3+}] \text{X}_4$  (normal 2-3 spinel)
- B)  $\text{N}^{3+} [\text{M}^{2+}\text{N}^{3+}] \text{X}_4$  (inverse 2-3 spinel)
- C)  $\text{M}^{4+} [\text{N}_2^{2+}] \text{X}_4$  (normal 4-2 spinel)
- D)  $\text{N}^{2+} [\text{N}^{2+}\text{M}^{4+}] \text{X}_4$  (inverse 4-2 spinel)

For  $\text{Co}_3\text{O}_4$ , which may be written as  $\text{Co}(\text{Co}_2\text{O}_4)$ , the four possibilities were discussed by Verwey and de Boer <sup>2</sup>) who postulated the structure  $\text{Co}^{4+}[\text{Co}_2^{2+}]\text{O}_4$ , while Robin <sup>3</sup>) supposed  $\text{Co}_3\text{O}_4$  to be the normal 2-3 spinel  $\text{Co}^{2+} [\text{Co}_2^{3+}]\text{O}_4$ .

The magnetic properties of  $\text{Co}_3\text{O}_4$  were determined by Bhatnagar <sup>4</sup>) and co-workers who found a mean magnetic moment for Co of  $2.98 \mu_B$  while the spin-only value per Co ion is  $4.58 \mu_B$  if the substance contains 1  $\text{Co}^{2+}$  and 2  $\text{Co}^{3+}$  ions and  $4.65 \mu_B$  in case the composition is 1  $\text{Co}^{4+}$  and 2  $\text{Co}^{2+}$  ions. A brief discussion of these papers will be given in the chapter dealing with  $\text{Co}_3\text{O}_4$ . For the moment it is sufficient to state the two problems which have largely determined the present investigation. They are first, the uncertainty about the distribution and valence of the Co ions in the octahedral and tetrahedral interstices and secondly, the low value of the mean magnetic moment of Co in this substance. Moreover, the recent investigations in the field of oxidic ferromagnetic materials, mainly ferrites, made it interesting to see if the magnetism of the cobaltites could be explained by Neel's <sup>5</sup>) theory of ferrimagnetism or by the modification of Yafet and Kittel <sup>6</sup>). Very

recently Lotgering's work <sup>7)</sup> was published in which several chromites and cobaltites were discussed. The chromites could be treated by the method of Yafet and Kittel; the cobaltites showed a less simple behaviour and most of them could not be explained by one of the theories.

From the beginning it was clear that crystallographic methods could not lead to a satisfactory answer to the questions, as the scattering factors of  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  for X-rays are too much alike. The only possibility seemed to be to study separately the magnetic properties of  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$  and eventually  $\text{Co}^{4+}$  in the different interstices of a spinel lattice and to try to find a suitable distribution of Co ions in  $\text{Co}_3\text{O}_4$  which would fit the magnetic data. The original scheme contained the investigation of the following square of mixed crystals:



Of these mixed crystals the series between  $\text{CoAl}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  has not been prepared; the results of the other series made the study of this one superfluous. In addition, mixed crystals of  $\text{CoO} - \text{MgO}$  and  $\text{CoO} - \text{ZnO}$  (up to 20%  $\text{CoO}$ ) were made to study the the magnetic behaviour of  $\text{Co}^{2+}$  ions in octahedral and tetrahedral interstices respectively. The mixed crystals  $\text{CoO} - \text{MgO}$  have the rock salt structure of  $\text{MgO}$ ; those of  $\text{CoO} - \text{ZnO}$  crystallize in the wurtzite structure of  $\text{ZnO}$ . Finally, the influence of dilution with Mg on the magnetic properties of  $\text{CoAl}_2\text{O}_4$  was studied in some mixed crystals between  $\text{CoAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ .

The systems  $(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$  and  $(\text{Co}, \text{Mg})\text{Al}_2\text{O}_4$  are not of direct importance for the understanding of the magnetic behaviour of  $\text{Co}_3\text{O}_4$ , but are interesting from the viewpoint of whether  $\text{CoAl}_2\text{O}_4$  is a normal or a partly inverse spinel.

## Chapter I

### PREPARATIVE AND ANALYTICAL PROCEDURES

#### 1.1. Preparation of the materials

In order to avoid difficult and time-consuming separations of metals such as Co and Zn and subsequent gravimetric analyses of these elements, we used only quantitative methods of preparation.

There are two principally different methods of predetermining the amount of the various metals in the final oxides.

a) Standard solutions of accurately known concentrations of the metals can be used. In this way the required quantity of a metal is added to the mixture by means of a burette.

b) A solid standard substance of the metal can be weighed out.

The former method is quick and has the advantage of the ease with which the various metals are mixed. The latter method is somewhat more laborious but has a greater accuracy as to the ratio between the metals and may be used to make larger amounts of material.

The following standards were used during this investigation:

Substance	Metal content	Method of analysis
Co(NO <sub>3</sub> ) <sub>2</sub> solution	0.0388 mAt/cc	Co metal
Zn(NO <sub>3</sub> ) <sub>2</sub> solution	0.1652 mAt/cc	Zn oxinate
Mg(NO <sub>3</sub> ) <sub>2</sub> solution	0.1571 mAt/cc	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Al(NO <sub>3</sub> ) <sub>3</sub> solution	0.598 mAt/cc	Al oxinate
Co(COOH) <sub>2</sub> · 2H <sub>2</sub> O	32.0%	Co <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Zn(COOH) <sub>2</sub> · 2H <sub>2</sub> O	34.6%	Zn oxinate
MgCO <sub>3</sub>	24.9%	MgO

Metal oxalates were for the same purpose also used by Robin<sup>8</sup>). The solutions were prepared by dissolving Merck *pro analysi* compounds in distilled water and a small amount of HNO<sub>3</sub>. The oxalates were precipitated from boiling solutions of the nitrates with oxalic acid. The precipitate was washed and filtered and allowed to stand overnight in 96% ethyl alcohol, again filtered and dried *in vacuo*. MgCO<sub>3</sub> was a *p. a.* sample of Merck.

For a number of compounds *e. g.* preparations of ZnCo<sub>2</sub>O<sub>4</sub>, it was extremely important to use the exact ratio of Zn:Co. Therefore the Co analyses were subjected to a critical examination. We found the pyrophosphate method to be the best one, for using the electrolytic determination as Co metal we obtained 32.2% which is a little higher. This is probably due to a slight oxidation of the metal surface in spite of the addition of a little hydrazine sulphate before electrolysis.

We will now discuss a number of procedures which were followed in the preparation of our materials.

#### Procedure A

Calculated volumes of two or three different standard solutions of metal nitrates were added together into a weighed porcelain crucible, evaporated to dryness over infrared lamps, preheated at 300 to 350°C in air in order to decompose the nitrates and finally allowed to stand for several hours in air until no change in weight could be detected. Then the substance was collected as completely as possible in an agate mortar, ground and weighed into a platinum boat. In this boat the final firing took place under the conditions chosen for the particular substance. After this firing the final weight must agree with the calculated one.

#### Procedure B

Calculated volumes of the different standard solutions were combined in a weighed porcelain crucible. The metals were simultaneously precipitated with a  $(\text{NH}_4)_2\text{CO}_3$  solution. The whole mass was evaporated to dryness over infrared lamps. From this point the same procedure as described under A was followed.

#### Procedure C

Calculated weights of the different standard solids were combined in a weighed porcelain crucible. They were dissolved in concentrated  $\text{HNO}_3$  and evaporated to dryness according to procedure A which was followed further.

#### Procedure D

Calculated weights of the standard substances were thoroughly mixed in a mortar and subjected at once to the final firing.

An important precaution to observe in all four methods is of course strict quantitative handling of all solutions and solids, except for the transport of the preheated mass to the platinum boats where this is really impossible. Here, however, the loss factor is known and must be accounted for in the theoretical calculation of the final weight.

Advantages of procedure A are its quickness and ease especially in the cases where three different metals are involved. It is, however, less accurate. All substances of the series of mixed crystals  $(\text{Co,Zn})\text{Al}_2\text{O}_4$  and  $\text{Zn}(\text{Co,Al})_2\text{O}_4$  are made according to this method.

Procedure B is used when solubility and stability of the nitrates of two metals are very different, which may cause an inhomogeneity in the preheated mass. This danger existed in the case of the mixed crystals of  $(\text{Co,Mg})\text{O}$ , where method B was applied with success. The advantages of procedure C have already been mentioned in this section.

A modification is possible when a Pt crucible instead of a porcelain crucible is used. The transport of the preheated mass is avoided, so that no loss factor has to be introduced in the calculation of the final weight. This is important in cases where the final weight is used to check the oxidation of the metal to another.

valence. We used this method for the preparation of some of the  $\text{ZnCo}_2\text{O}_4$  samples.

In some cases a combined method AC was applied. One of the metals was weighed as a standard solid and the other metal was added in the form of a solution. The method is suitable if the required ratio is such that a large volume of one solution and a very small volume of the other are to be used.

Procedure D, although very easy and quick, did not appear very satisfactory. The few materials made according to this method showed inhomogeneities. The procedure is, however, very valuable when only one metal is involved. All our  $\text{Co}_3\text{O}_4$  samples were made in this way. The firings of our materials were all carried out in platinum boats or crucibles. Platinum appeared very resistant to heating with the oxides of Mg, Co and Zn up to temperatures of  $1250^\circ\text{C}$ . The firings may be varied with respect to atmosphere and temperature. We have only used the oxidizing gases air and oxygen and further a vacuum of about 1 mm Hg. The temperatures used ranged up to  $1250^\circ\text{C}$ . Sometimes the method of cooling after the firing is important. Samples may be quenched or annealed.

The method of mixing (A, B, C, D or AC) and the conditions of firing and cooling will be given in the following chapters, where this is important for a discussion of the results of the magnetic measurements.

## 1.2. Chemical analysis

Besides the gravimetric analyses of the standard substances already mentioned in section 1.1, no other determinations of the metals have been carried out. The quantitative way of preparation made such an analysis superfluous. An excellent check of the whole preparative procedure is found in the final weight of the material. In most cases this final weight agreed with the calculated value within 1%. Samples for which this final weight differed more than 2% from the theoretical value were discarded.

For some of the compounds containing Co of a valence higher than two the oxidizing power was determined in the following way. Into a small glass tube with thin bottom 100 mg of the substance is weighed, 1 to 1.5 gr of KI (Merck *p. a.*) are added, the tube is evacuated on the oil pump and sealed off. The closed tube is placed upside down in a Carius tube together with a glass rod which serves as a hammer and 7.5 cc of HCl (fuming HCl *pro analysi* diluted 1 : 4). The Carius tube is cooled in ice, evacuated on a water suction pump, lifted out of the ice bath and warmed up by hand. The liquid in the tube is allowed to boil under reduced pressure for one to two minutes to drive out the oxygen. Now the tube is sealed off and the bottom of the little tube inside is broken with the "glass hammer".

A heating period of 6 hours at about  $125\text{-}130^\circ\text{C}$  in a Carius furnace is sufficient to bring the substance completely into solution. The contents of the Carius tubes are finally titrated with thio-sulphate in a closed vessel under nitrogen.

We have worked out the analysis in the above way for several reasons. These are:

a)  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$  are only very slowly soluble in diluted or concentrated acids, the more so if they are fired at a higher temperature.

b) In the reaction of compounds containing tri- or tetravalent cobalt with HCl a part of the oxidizing power may disappear by the escape of oxygen gas<sup>9</sup>).

c) The use of  $\text{H}_2\text{SO}_4$  and Mohr's salt is not advisable. The colour of the  $\text{Co}^{2+}$  ion interferes with the determination of the end point of the titration and the reaction in the sealed tube between  $\text{H}_2\text{SO}_4$  and  $\text{Co}_3\text{O}_4$ , for example, is much slower than that between HCl and  $\text{Co}_3\text{O}_4$ . We tried to find the proper conditions for this reaction but could not obtain reliable results. This method was abandoned.

A disadvantage of the method with HCl and KI is the sensitivity of the titration to oxydation by air. Moreover, the reaction in the sealed tube appeared to show a blank value which could not be determined very exactly. We tried to find a relation between the blank value and the volume of the vacuum above the reaction mixture. The possibility may not be excluded, that on cooling, the equilibrium  $2\text{HJ} \rightleftharpoons \text{H}_2 + \text{I}_2$ , which is shifted to the right side at  $125^\circ\text{C}$ , cannot shift completely to the left, since  $\text{H}_2$  gas may partly fill the vacuum and  $\text{I}_2$  may dissolve in the liquid.

The experiments with Carius tubes of different sizes are combined in Fig. 1.1. If there exists such an effect, it does not appear to be very pronounced from the experimental data, probably due to other effects such as different  $\text{O}_2$  contents of the HCl solution.

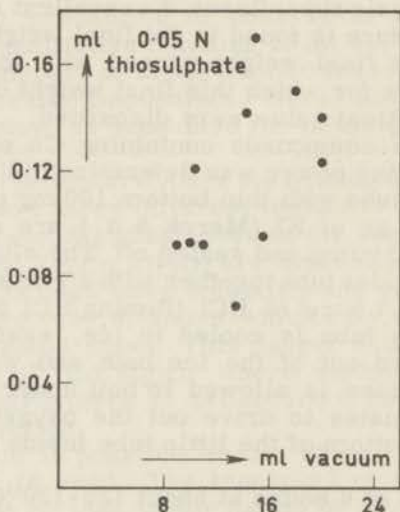


FIGURE 1.1.

We adopted a mean value of 0.006 meq. thiosulphate. The error was estimated at  $\pm 25\%$ . As we used in a titration approximately 1 meq. thiosulphate, this error in the blank value is not a very serious one. We estimated the error in a determination of the oxidizing power to be  $\pm 1\%$ . The results obtained with this method were reliable and the absolute values very satisfactory. Data will be given in the chapters dealing with  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ .

### 1.3. X-ray analysis

A powder diagram was made to check crystal structure and homogeneity of all materials used in magnetic measurements. All photographs were made with  $\text{FeK}\alpha$ -radiation. ( $\lambda\text{FeK}\alpha_1 = 1.93597 \text{ \AA}$ ).

The following cameras were used. A Unicam 9 cm powder camera (van Arkel method of film mounting) was especially suitable for the determination of cell edges. A Philips 11.5 cm powder camera (Straumanis method of film mounting) was also used.

The structures found were all of the spinel, the rock salt or the wurtzite type. No really important deviations were found. In the series of mixed crystals of  $(\text{Co}, \text{Mg})\text{O}$  and  $(\text{Co}, \text{Zn})\text{O}$  some of the materials were discarded because of their incorrect X-ray diagram.

## Chapter II

### APPARATUS AND TECHNIQUE

#### 2.1. The principle of the measurements

The magnetic susceptibilities were determined by the Faraday method, that is, by using small amounts of powdered samples suspended in that inhomogeneous part of the field of an electromagnet where the product of field strength and field gradient is a maximum.

With the apparatus described in the following sections of this chapter the field strength could be varied up to approximately 5500 Oersted; the temperature dependence of the susceptibility could be studied from  $-190^{\circ}\text{C}$  to about  $930^{\circ}\text{C}$  so covering more than  $1100^{\circ}$  of the absolute temperature scale. The measurements made in this way are not absolute. The combination of balance and magnet was calibrated against some standard substance for which the gram susceptibility is accurately known. One of the sections of this chapter will deal with the choice of this standard substance.

#### 2.2. The balance

The magnetic force on the specimen was determined with the aid of a torsion balance placed in a metal box which could be evacuated. This torsion balance, a somewhat modified form of that described by Volger, de Vrijer and Gorter<sup>10</sup>), is given schematically in fig. 2.1.

In this section we will discuss only those aspects of the balance where improvements have been introduced with respect to the original model, which was placed at our disposal by Philips Research Laboratories, Eindhoven.

a) The zero point of the balance arm can be seen through a lens in the balance case. The setting of the two points, however, can be made easier and more accurate with the aid of a light signal which comes from a fixed point, traverses a weak positive lens, is reflected from a small mirror mounted on the balance arm above its fulcrum, and finally gives an image on a divided glass scale after passing through a prism and being reflected from a distant mirror. In this way, the total deviation of the end point of the balance arm of approximately 3 mm could be enlarged to a 20 cm deviation of the light spot on the scale. A schematic drawing of the course of the light beam is given in fig. 2.2.

b) One of the most difficult and at the same time most critical features of the Faraday method is the reproducible suspension of the sample. Originally the small containers, which can very easily be made the same size, were suspended from a thin platinum wire. It is, however, extremely difficult to maintain a platinum wire



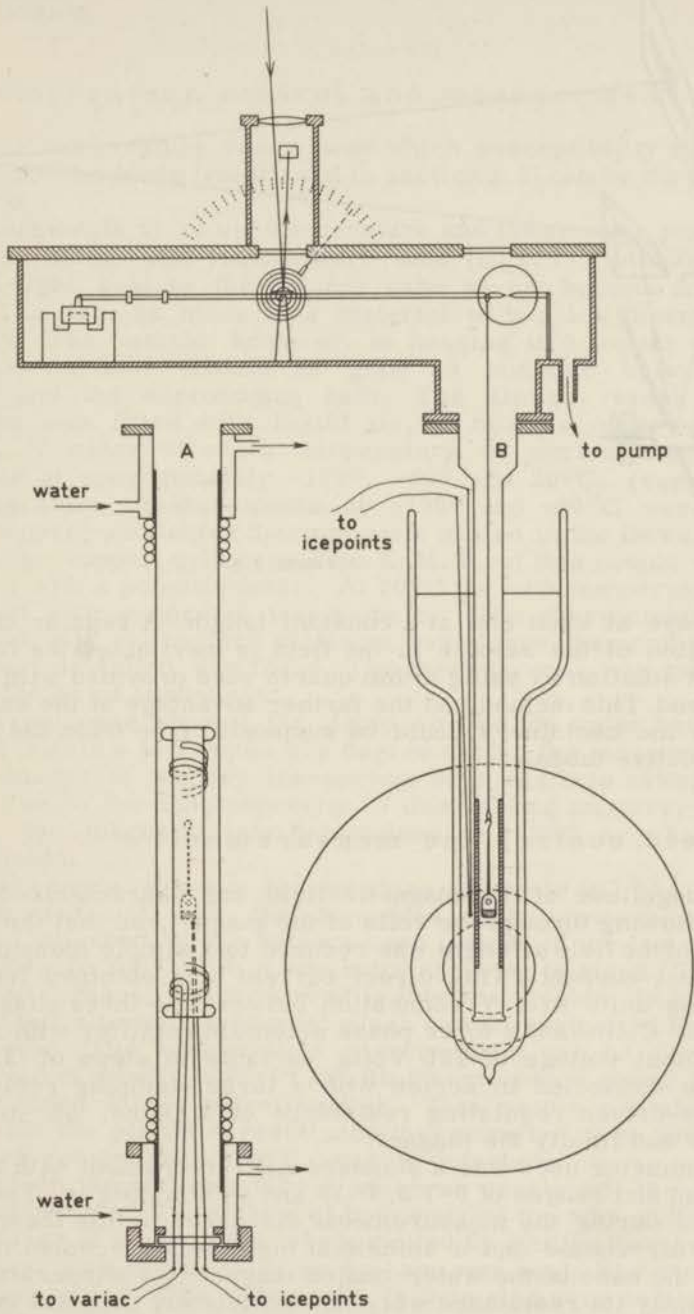


FIGURE 2.1.

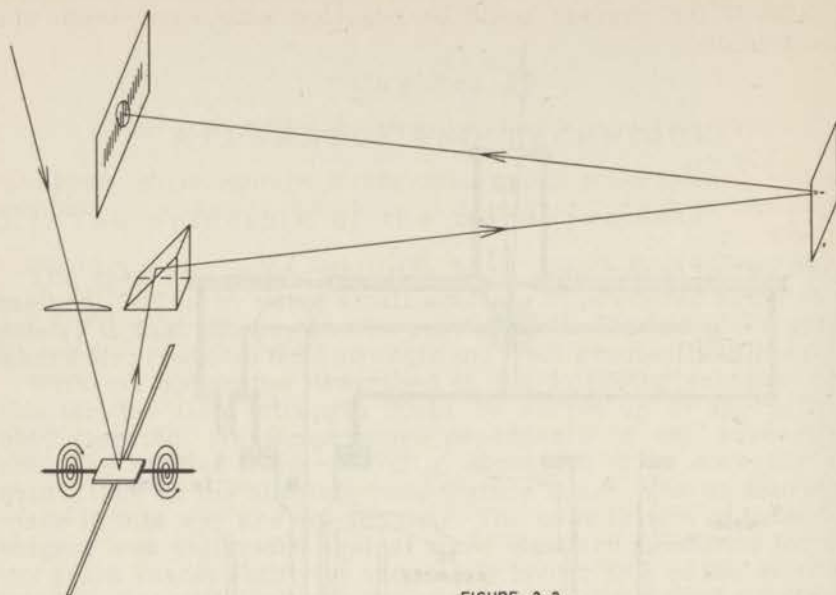


FIGURE 2.2.

with an eye at each end at a constant length. A regular check of the position of the sample in the field is inevitable. We found an excellent solution by using a thin quartz wire provided with a hook at each end. This method had the further advantage of the easy way in which the containers could be suspended free from the wall of the respective tubes.

### 2.3. Field control and measurement

The magnitude of the magnetic field was characterized by the current flowing through the coils of the magnet, so that the measurement of the field strength was reduced to a simple measurement of a direct current. This direct current was obtained from two stabilizing units in a V connection between the three phases of a 220 Volt A. C. line and a three phase selenium rectifier with a maximum output voltage of 126 Volts variable in steps of 2 Volts. This was connected in series with a large damping resistance, a spindle-driven regulating resistance of 5 Ohms, an accurate ammeter and finally the magnet.

The ammeter used was a standard AEG instrument with a scale of 150 mm and ranges of 0-7.5, 0-15 and 0-30 amperes. The magnets used during the measurements discussed in this thesis were a small air-cooled and a somewhat bigger water-cooled magnet. Even in the case of the water-cooled magnet, its temperature and subsequently its resistance were not sufficiently constant but rose during the measurement. Therefore all the experiments had to be done by two operators, one handling the balance, the other switching the magnet current on and off and keeping it constant with the

aid of the spindle-driven resistance. By making use of stabilized A. C. voltage the current could be adjusted within one-tenth of a scale division.

#### 2.4. Temperature control and measurement

A wide temperature range over which susceptibility measurements could be made (mentioned in section 2.1) can be divided into two parts.

Measurements at room temperature and lower were performed in the so-called low temperature tube (L. T. T.) attached by a vacuum-tight seal to the balance case as can be seen from fig. 2.1B. The tube is made of a material with a low thermal conductivity. The sample, however, is hanging in a copper cylinder to ensure a heat contact as good as possible between the sample and the surrounding bath. The Dewar vessel around this tube was filled with liquid air, a mixture of dry ice and acetone or water at room temperature in performing measurements at approximately  $-190^{\circ}$ ,  $-80^{\circ}$  and  $20^{\circ}\text{C}$ , respectively.

Temperature measurements at  $-190^{\circ}$  and  $-80^{\circ}\text{C}$  were made with a copper-constantan thermocouple placed in the Dewar vessel next to the copper cylinder. The E. M. F. of this couple was determined with a potentiometer. At  $20^{\circ}\text{C}$  the bath temperature was measured with a normal thermometer. The thermometer was compared with a standard platinum resistance thermometer; no significant deviation was found. The thermocouple was calibrated against the same instrument.

The experience showed the liquid air and the water bath to be constant within a few tenths of a degree during the measurements. The constancy of the dry ice-acetone bath was less satisfactory, mainly due to the inhomogeneity of this cooling mixture. Consequently, the magnetic data determined at  $-80^{\circ}\text{C}$  are somewhat less reliable.

Measurements at room temperature and up to  $927^{\circ}\text{C}$  ( $1200^{\circ}\text{K}$ .) were carried out with the so-called high temperature tube (H. T. T.) attached to the balance case instead of the low temperature tube. In fig. 2.1 A a schematic drawing is given. The bifilar-wound furnace, which is readily interchangeable, is heated by a stabilized alternating current which can be controlled by means of a Variac. The temperature measurement can be performed with the aid of a built-in Pt-Pt 10% Rh thermocouple whose E. M. F. is determined with a potentiometer. This couple was also compared with the platinum resistance thermometer up to  $500^{\circ}\text{C}$ . No deviations greater than  $2-3^{\circ}\text{C}$  could be detected.

In the high temperature tube A which we developed, the difficult soldering of metal to porcelain at both ends of the tube which was a disadvantage of the original tube supplied by Philips Research Laboratories, was replaced by an Apiezon wax seal. The metal lids are water-cooled. The outer tube is thus also very easily interchangeable. This is an advantage, for sometimes sealed containers may explode during the measurements; then not only the furnace but also the outer tube is destroyed. A second advantage is

a consequence of the cooling of the lower lid. The original tube, when used at very high temperatures, needed air cooling of the lower lid to prevent leakage through the Plexiglas ground plate. The position of the thermocouple directly under the hanging container is very important. The distance between the container and couple was adjusted to less than 5 mm.

The measurements done *in vacuo*, needed a heating period of forty-five to sixty minutes to ensure complete temperature equilibrium between furnace, thermocouple and sample. In this way the temperature remained constant within 2 degrees C during the measurement.

## 2.5. Calibration of balance in combination with low temperature tube and estimation of errors

When a paramagnetic substance is attracted by a magnetic field the magnitude of the force is given by

$$K = p \cdot \chi_g \cdot G \cdot H \cdot \frac{\delta H}{\delta X} \quad 2.5.1.$$

where  $p$  is a constant,  $\chi_g$  is the gram susceptibility of the substance,  $G$  is the mass of the sample and  $H$  and  $\frac{\delta H}{\delta X}$  are the field strength and field gradient respectively. This force  $K$  is measured with the aid of a torsion balance, so that

$$U - U_v = q \cdot K, \quad 2.5.2.$$

where  $U$  is the angle over which the torsion head must be turned to compensate the magnetic force on the container and sample measured on an arbitrary scale.  $U_v$  has the same meaning as  $U$  but now for the empty container. (It is to be noted that this relation only holds when the distortion of the torsion spring is small compared to its total length. In our case this distortion did not exceed 5%).

$$U - U_v = p \cdot q \cdot H \cdot \frac{\delta H}{\delta X} \cdot \chi_g \cdot G \quad 2.5.3.$$

We combine  $p, q, H$  and  $\frac{\delta H}{\delta X}$  into one constant  $\frac{1}{C_i}$  where the index  $i$  denotes that this constant is still dependent on the magnet current. The basic formula now becomes

$$(U - U_v)_i C_i = \chi_g \cdot G \quad 2.5.4.$$

The constant  $C_i$  can be determined when the measurement is done with a substance of which the  $\chi_g$  and its temperature dependence are well-known.

We have chosen as a standard substance nickel ammonium sulphate hexahydrate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ .

This substance has been subjected to absolute measurements by Kamerlingh Onnes and Jackson<sup>11</sup>). From their publication we used the following data:

T	$\chi_g 10^6$	$\chi_{\text{corr.}} 10^6$
286.5	10.68	10.98
77.15	39.55	39.85

where the third column is the paramagnetic  $\chi_g$  value corrected for the diamagnetism of the substance itself using the tables given by Klemm 12). We found the Curie constant  $C = 3174 \cdot 10^{-6}$  and the Curie temperature  $\theta = 2.5^\circ\text{K}$ . The formula which gives the  $\chi_g$  of this Ni salt at every point between liquid air and room temperature is

$$\chi_g = \left( \frac{3174}{T+2.5} - 0.30 \right) \cdot 10^{-6} \text{ e. m. u.} \quad 2.5.5.$$

To prepare very pure  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , we recrystallized a product of Merck, crushed the crystals in a mortar and separated the bigger crystals and the powder by a sieve. The result was a quantity of small crystals of uniform size (about 0.3 millimeter in diameter). These crystals were stored in a desiccator above a mixture of powder and big crystals of the same substance and a small amount of distilled water, to make sure that the correct vapour pressure was maintained. For the reasons which have led us to this choice and method of preparation see section 2.8 of this chapter, where the experiments with other calibrating substances are discussed. Six calibrations with this  $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  are collected in table 2.1.

Table 2.1.  
Calibrations in low temperature tube.

Cal n <sup>o</sup>	85	86	87	88
i	$C_i^L \cdot 10^{10}$	$C_i^L \cdot 10^{10}$	$C_i^L \cdot 10^{10}$	$C_i^L \cdot 10^{10}$
17A	214	214	217	215
15A	244	243	246	244
13A	288	287	289	287
11A	359	360	363	360
9A	510	506	511	506
7A	821	821	827	839
Temp.	R.	R.	R.	L.
Cal n <sup>o</sup>	89	90		
i	$C_i^L \cdot 10^{10}$	$C_i^L \cdot 10^{10}$	$\overline{C_i^L} \cdot 10^{10}$	$\pm m$
17A	218	217	216	0.8%
15A	247	247	245	0.7%
13A	292	290	289	0.7%
11A	364	364	362	0.6%
9A	513	514	510	0.7%
7A	836	843	831	1.1%
Temp.	L.	L.		

In this table the magnet current  $i$  is given in amperes, the temperature is indicated by R. when the measurement is made at room temperature, by L. when at the temperature of liquid air. The constant  $C_i^L$  is that from eq. 2.5.4. (the superscript L denotes that measurement is made in the low temperature tube),  $m$  is defined by  $m = \sqrt{\frac{\sum d_i^2}{n-1}}$  the standard deviation 13) where  $d_i$  is the deviation from the arithmetic mean of one of the  $n$  observations  $i$ . Three important features appear from the table.

a) There is no difference within the experimental error between calibrations at room temperature and those at liquid air temperature, as ought to be expected.

b) The standard deviation  $m$  is in agreement with the error estimated in the following way: In eq. 2.5.4 we can take  $\chi_g = Q/T$  where  $Q$  is a constant from the literature. A rough calculation shows that  $C_i \approx C \cdot i^{-1.5}$ . Hence,

$$C = \frac{Q \cdot G \cdot i^{1.5}}{T(U-U_V)} \quad 2.5.5.$$

and

$$\Delta C = \frac{\delta C}{\delta G} \Delta G + \frac{\delta C}{\delta i} \Delta i - \frac{\delta C}{\delta(U-U_V)} \Delta(U-U_V) - \frac{\delta C}{\delta T} \Delta T \quad 2.5.6.$$

Carrying out the differentiations we get

$$\frac{\Delta C}{C} = \frac{\Delta G}{G} + 1.5 \frac{\Delta i}{i} + \frac{\Delta(U-U_V)}{U-U_V} + \frac{\Delta T}{T} \quad 2.5.7.$$

The following list gives the estimated errors in the case of a calibration at room temperature. (Approximately the same values can be used in the case of most of the measurements at room temperature.)

$\Delta G$	= 0.00005 g.	$G$	= 0.1 g.
$\Delta i$	= 0.1 scale division	$i$	= 100 scales divisions
$\Delta(U-U_V)$	= 0.2 scale division	$(U-U_V)$	= 50 scales divisions
$\Delta T$	= 0.3°	$T$	= 300°K.

Inserting these values in 2.5.7. gives

$\frac{\Delta C}{C} = 0.0005 + 0.0015 + 0.004 + 0.001 = 0.007$  in close agreement with  $m = 0.8\%$ . The standard deviation as well as the estimated value of the error indicate that a measurement at room temperature can be made with a precision of 1%, or somewhat better if the susceptibility at a given temperature is determined by taking the mean of the measurements at three different field strengths.

The absolute error with respect to  $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  is estimated to be 2%. It should be noted that the measurements at liquid air temperature may be somewhat less accurate as a consequence of the greater influence of the temperature on the susceptibility.

c) The accuracy of the constant  $C_i$  at a magnet current of 7 amp. is less than that of the others. Experience showed us that in the lower field strength region ( $i = 6, 5$  and  $4$  amp.) the reliability of the constants was even worse. This is the reason that no lower field strengths are incorporated in table 2.1, the measurements all being made with the higher field strengths. We determined, however, some of the lower field constants but used them only to detect ferromagnetic impurities.

## 2.6. Calibration of balance in combination with high temperature tube

Contrary to expectation, we discovered a difference in the measurements carried out at room temperature in the L.T.T. and the H.T.T. It seemed that the magnetic field or its gradient is influenced by the respective tubes in a different way. The following experiments were made at one temperature with a sealed container with one of our paramagnetic substances:

1. Measurement in the complete H.T.T. (normal situation)
2. Measurement in H.T.T. without the furnace
3. Measurement in H.T.T. without asbestos
4. Measurement in the outer tube of the H.T.T. with a copper cylinder at the same height and of the same dimensions as in the L.T.T.
5. Measurement in L.T.T. with Dewar vessel (normal situation)
6. Measurement in L.T.T. without Dewar vessel
7. Measurement in L.T.T. with the outer tube of the H.T.T. around it.

The measurements 1 to 4 showed torsion readings 1% to 1.5% higher than the measurements 5 to 7. We concluded that neither parts of the H.T.T. nor the copper cylinder of the L.T.T. were the reason of the difference, but that the nickel alloy of the L.T.T. diminished the product of field strength and field gradient in the tube. It was therefore necessary to calibrate the balance in combination with the high temperature tube. Six calibrations with  $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  were carried out at room temperature. The data can be found in table 2.2.

To test the accuracy of the measurements at high temperatures we determined the susceptibility of gadolinium oxide. This substance apparently has excellent properties for use as a secondary standard at high temperature, for the electrons responsible for its paramagnetic behaviour lie in the 4f shell of the  $\text{Gd}^{3+}$  ion protected by the filled 5s and 5p shells. Moreover the  $\text{Gd}^{3+}$  ion is in an S state (half filled 4f shell). One may expect no influence of surrounding oxygen ions on the magnetic shell, no or very small coupling effects between the  $\text{Gd}^{3+}$  ions and no possibility for the 4f electrons to escape to a higher energy level when the temperature is raised and finally no chemical decomposition of the oxide. A disadvantage of  $\text{Gd}_2\text{O}_3$  is the fact that a very pure sample is not readily accessible. Contamination with the diamagnetic  $\text{Y}_2\text{O}_3$  is very likely. For the same reason it is very difficult to find the ab-

solute value in the literature, so we used it only as a secondary calibration to check if it is permissible to use the same constants at both very high and at room temperatures.

Table 2.2.  
Calibrations in high temperature tube.

Cal n <sup>o</sup>	94	95	96	97
i	$C_i^H \cdot 10^{10}$	$C_i^H \cdot 10^{10}$	$C_i^H \cdot 10^{10}$	$C_i^H \cdot 10^{10}$
17A	214	214	213	213
15A	243	243	241	242
13A	287	286	284	286
11A	359	358	356	357
9A	508	506	499	505
7A	818	814	796	812
Temp.	R.	R.	R.	R.
Cal n <sup>o</sup>	98	99		
i	$C_i^H \cdot 10^{10}$	$C_i^H \cdot 10^{10}$	$C_i^H \cdot 10^{10}$	$\pm m$
17A	213	214	213 <sup>5</sup>	0.3
15A	241	244	242	0.6
13A	283	287	286	0.6
11A	359	359	358	0.4
9A	508	493	503	1.2
7A	805	825	812	1.3
	R.	R.		

The sample used was one of „New Metals and Chemicals“ and very kindly placed at our disposal by Philips Research Laboratories. The measurements were made in two independent series, the results of which are collected in table 2.3 and in fig. 2.4.

Table 2.3.

seriesno.	T	$\chi_A \cdot 10^3$	$\chi_A \cdot (T-7)$	mean Curie const.	$\theta$
1	293	24.1 <sup>6</sup>	6.91	6.88	+7 <sup>o</sup>
	439	15.8 <sup>6</sup>	6.85		
	546	12.7 <sup>8</sup>	6.89		
	686	10.1 <sup>4</sup>	6.88		
	876	7.9 <sup>4</sup>	6.90		
	971	7.1 <sup>4</sup>	6.88		
	1070	6.4 <sup>7</sup>	6.88		
2	291	24.5 <sup>2</sup>	6.96	6.97	+7 <sup>o</sup>
	396	19.1 <sup>9</sup>	6.95		
	499	14.2 <sup>3</sup>	7.00		
	648	10.9 <sup>3</sup>	7.01		
	820	8.5 <sup>9</sup>	6.98		
	958	7.3 <sup>1</sup>	6.95		



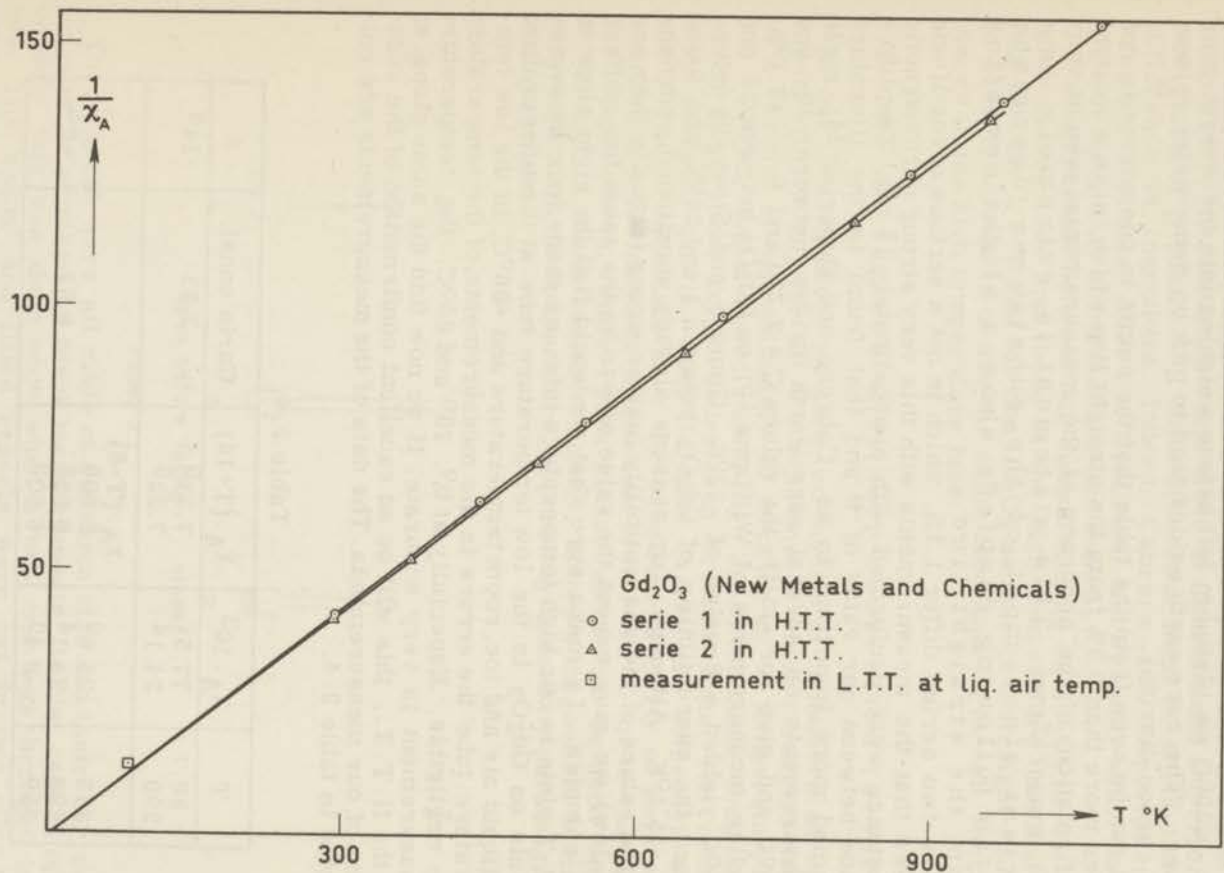


FIGURE 2.4.

The  $\chi_A$  in this and following tables means the susceptibility of a mass of the substance containing one gram atom of the magnetic ion. Thus, in the case of  $Gd_2O_3$   $\chi_A = 1/2\chi_M$ . The values of  $\chi_A$  are corrected for the diamagnetism of the substance itself following the tables given by Klemm<sup>12</sup>). The gadolinium oxide was heated to 700 - 800°C on platinum foil before weighing into the quartz container. (The rare earth oxides tend to pick up some water vapour and carbon dioxide).

It can be seen from the table that the points in one series do not differ more than 0.5% from the straight line which is an excellent confirmation of the accuracy of the measurements even at very high temperatures. This statement is extremely important since most of the substances described in the following chapters show a slight deviation from the straight line.

The two series differ 1.3%, which is not a serious error if one knows that the measurements with this very strong paramagnetic substance were performed with approximately 15 mg. The difference between our value of  $\theta$  and that found in the literature seemed more important to us. Cabrera and Duperier<sup>14</sup>) made measurements on several rare earth oxides between 20 and 400°C and give for  $Gd_2O_3$  the values  $C = 7.730$  and  $\theta = -13.30^\circ K$ . Earlier measurements of Williams<sup>15</sup>) on  $Gd_2O_3$  between 20 and 300°C yielded a  $\theta$ -value of  $-12^\circ K$ . Giaque and Stout<sup>16</sup>) determined the susceptibility of  $Gd_2O_3$  between 1 and 20°K and found  $\theta = -15.5^\circ K$ . Although, for reasons already mentioned, our absolute values of the susceptibility may be wrong (actually they are too low) we may expect the value of  $\theta$  to be the same for different samples. To make sure that we would find the right slope of  $1/\chi$ -T plots in our high temperature tube, we made four measurements on  $Gd_2O_3$  in the low temperature tube at the temperature of liquid air and ice, room temperature and  $+86^\circ C$ . In the low temperature tube the errors in the measurements of the temperature are negligible. Especially at  $0^\circ$ ,  $20^\circ$  and  $86^\circ C$ , the temperature measurement is very accurate. If we now find the same slope as in the H. T. T., this will be an excellent confirmation of the accuracy of our measurements. The data of the measurements are collected in table 2. 4.

Table 2. 4.

T	$\chi_A \cdot 10^3$	$\chi_A \cdot (T+14)$	Curie const.	$\theta$
80.7	77.5	7.33 <sup>9</sup>	7.33	-14 <sup>0</sup>
290	24.14	7.32 <sup>9</sup>		
273	25.6 <sup>9</sup>	$\chi_A \cdot (T-8)$ 6.80 <sup>8</sup>	6.81	+8 <sup>0</sup>
290	24.14	6.82 <sup>8</sup>		
359	9.40	6.80 <sup>9</sup>		

We have now three independent measurements determining the slope of the  $1/\chi$ -T plot at room temperature giving for  $\theta$  7<sup>0</sup>, 7<sup>0</sup> and 8<sup>0</sup>K and for the Curie constants 6.88, 6.97 and 6.81 re-

spectively. Table 2.4 shows that by combining the room temperature measurement with that at liquid air temperature one obtains a value for  $\theta$  of  $-14^{\circ}\text{K}$ , so the liquid air point does not fit in the straight line found at room temperature and more elevated temperatures. There remains also the discrepancy between our high temperature measurements and those of Cabrera and Duperier <sup>14)</sup> and those of Williams <sup>15)</sup>. This difference must be attributed to a difference in impurities. Indeed, Cabrera and Duperier used samples of Urbain, Auer von Welsbach, and Prandtl, while no details of the purity of our sample are known.

The agreement between our measurements on  $\text{Gd}_2\text{O}_3$  in the low temperature tube and those in the high temperature tube and the fact that the  $1/\chi$ -T plot for one  $\text{Gd}_2\text{O}_3$  sample is a straight line up to  $1100^{\circ}\text{K}$  allows us to use the same constants  $C_i$  for all temperatures in the high temperature tube.

## 2.7. The containers and their correction factors

In our investigations we used two models of containers: an open vessel (fig. 2.3A) for all the substances, which remained stable in a vacuum of approximately 10 mm Hg up to temperatures of  $800 - 900^{\circ}\text{C}$ , and a closed model (fig. 2.3B) for those compounds which might loose oxygen under such circumstances. The vessels were made of quartz. Both Hereaus quartz and Vitreosyl were used. These materials have the excellent property of showing a temperature-independent magnetism from  $-200^{\circ}\text{C}$  up to the highest temperatures, while Pyrex glass, which can be used up to  $500^{\circ}\text{C}$  and is much easier to handle, shows a magnetism which is very dependent on temperature, apparently caused by paramagnetic impurities.

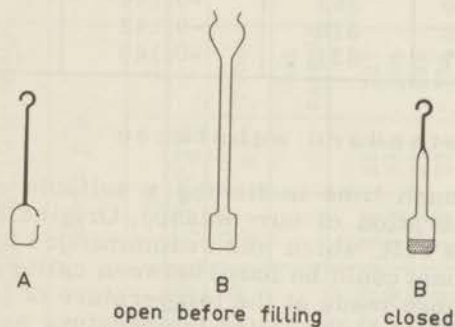


FIGURE 2.3.

The vessels were all made of the same size and their correction was determined by blank measurements. In the case of open vessels this was done once when a new one was brought into use. The sealed and filled vessels were cut in two after the measurement, cleaned, the two parts joined and their correction determined. The lower part could be used many times.

Two important features will be discussed briefly.

a) It is impossible to see if the empty vessel is hanging at the right position in the field by moving the balance step by step in a vertical direction and looking for the maximum repulsion. In the position, where the filled vessel shows its maximum attraction (position where  $H \frac{\delta H}{\delta X}$  is a maximum), the empty one shows no maximum repulsion on account of the fact that now the magnetic material is not condensed in a thin layer of approximately 4 mm in height. Also for this reason the introduction of a quartz wire instead of a platinum wire to suspend the vessel was a great improvement.

b) From eq. 2.5.4., one obtains

$$(U_i)C_i - (U_v)_i \cdot C_i = \chi_g \cdot G \quad 2.7.1.$$

It now appeared that  $(U_v)_i C_i$  was independent of the field strength. This is not very remarkable since  $(U_v)_i C_i$  has the dimension of a susceptibility. We therefore called it  $\chi_v$ . In all our measurements the correction for the empty vessel is introduced in the calculation in the form of  $\chi_v$ , which is a quicker and above all a more accurate way. In table 2.5 we shall give as an example the correction of one of our open quartz vessels.

Table 2.5.  
Correction for quartz vessel no. 442.

i	$(U_v)_i$	$C_i \cdot 10^{10}$	$(U_v)_i C_i \cdot 10^6$	$\chi_v \cdot 10^6$
17A	-6.6	216	-0.143	-0.142
15A	-5.7	245	-0.140	
13A	-5.0	289	-0.144	
11A	-4.0	362	-0.144	
9A	-2.8	510	-0.142	
7A	-1.7	831	-0.140	

## 2.8. Choice of standard substance

We have spent much time in finding a suitable standard substance for the calibration of our balance. Originally we used for this purpose Mohr's salt, which was recommended by Selwood (17). However no agreement could be found between calibrations at room temperature and those made at the temperature of liquid air. The constants  $C_i$  determined at the latter temperature were approximately 11% smaller than those obtained at room temperature. (Table 2.6, column 1 and 2).

To make sure that this difference was not inherent in our apparatus, we did several experiments under different conditions to exclude this possibility.

a) Two calibrations were made with Mohr's salt (Merck *p. a.*) at the temperature of liquid nitrogen. The values of  $C_i$  were the same as those found at the temperature of liquid air. (Table 2.6 column 3).

Table 2.6.

Substance	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O				FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O		FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	CoSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	NiSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	NiSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O			
Quality	Merck <i>p. a.</i>				Merck <i>p. a.</i> recrystallized		Analar A. R.	own preparation	own preparation	own preparation recrystallized			
Calibration no.	11 - 26			27	28	29	30	31 - 35		36 - 41		42	43
10 <sup>10</sup> . C <sub>i</sub> or $\bar{C}_i(n)$	$\bar{C}_i(7)$	$\bar{C}_i(7)$	$\bar{C}_i(2)$	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	$\bar{C}_i(3)$	$\bar{C}_i(2)$	$\bar{C}_i(4)$	$\bar{C}_i(2)$	C <sub>i</sub>	C <sub>i</sub>
Temperature	room	liq. air	liq. N <sub>2</sub>	room	room	liq. air	liq. air	room	liq. air	room	liq. air	room	liq. air
Other conditions				thin sample									
Magnet current =													
= 14	247	217	223	237	251	210	227	217	182	237	239	232	239
13	270	239	240	264	276	230	247	238	199	260	261	257	264
12	300	268	269	295	309	257	278	268	221	291	292	288	295
11	343	307	307	338	353	289	318	303	251	332	337	329	338
10	403	362	362	394	418	338	374	356	295	388	393	390	398
Column no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Difference	11%		7.5%				17%		18%		unimportant		

$\bar{C}_i(n)$  = mean value of C<sub>i</sub> from n calibrations.

The magnet current is given in an own arbitrary scale (small air-cooled magnet was used and a shunted galvanometer as an ammeter) and is not the same as that given in table 2.1 where a bigger water-cooled magnet and an AEG. ammeter were used for the definite calibrations.

The column numbers correspond with those mentioned in the text.

Table 2. 7.

Substance	NiSO <sub>4</sub> · (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> · 6H <sub>2</sub> O										Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> · 24H <sub>2</sub> O.	FeSO <sub>4</sub> · (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> · 6H <sub>2</sub> O.		
Quality	own preparation		Merck								own preparation		Merck <i>p. a.</i>	
Calibration no.	44	45	46	47	48	49	50	51	52	44 - 52	55	53	54	
10 <sup>10</sup> · C <sub>i</sub> or C <sub>i</sub> (n)	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub> (9)	C <sub>i</sub>	C <sub>i</sub>	C <sub>i</sub>
Temperature	room	room	room	room	liq. air	liq. air	liq. air	dry ice acetone	room			liq. air	room	liq. air
Other conditions														
Magnet current =														
= 11	199	206	200	202	202	210	202	209	204	204	204	205	214	186
10	226	228	222	225	225	233	225	231	225	227	227	228	237	209
9	259	257	253	256	256	264	257	264	258	258	258	262	271	238
8	304	303	298	301	300	306	301	312	302	303	303	308	319	280
7	389	370	370	366	369	381	371	385	373	375	375	380	392	342
6	499	486	485	497	488	500	486	506	493	493	493	500	520	460
Difference											5%		12%	

In this table the magnet current is given in amperes.

The calibrations were carried out with the small air-cooled magnet and an AEG. ammeter. This is a situation different from that in the tables 2. 1 or 2. 6.

This experiment showed first, that the influence of the paramagnetic oxygen (from the liquid air in the Dewar vessel) on the field strength in the tube is negligible. Secondly, it showed the reliability of the temperature measurement in this region. It was already known that an error in the determination of this temperature could not be the reason for this difference in the calibration series because of the fact that the deviation at liquid air temperature would indicate a temperature during the measurement below that of liquid nitrogen.

b) Two calibrations were made, one at room temperature, the other at liquid air temperature, but both with the same weight of Mohr's salt. The first one agreed within 3% with the other room temperature measurement. (Table 2.6 column 4). Thus the thickness of the layer of the substance in the quartz container has no influence on the magnitude of the constants  $C_i$ .

c) Calibrations were made at the two different temperatures with a sample of Mohr's salt (Merck *p. a.*) which was recrystallized from a solution in distilled water. The constants  $C_i$  now differed approximately 17% (original difference found with Mohr's salt, Merck *p. a.*, was 11%) (Table 2.6, columns 5 and 6).

d) Finally a calibration at liquid air temperature with Mohr's salt (Analar A. R) differed no more than 7.5% with the mean value at room temperature (Table 2.6 column 7).

Our conclusion from these facts must be that  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  has not the proper qualities to be a good standard substance. We tried the other two compounds of which absolute measurements are given in the article of Jackson 11) *i. e.* the analogous Co and Ni salts. With  $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  we found a difference between the room temperature- and liquid air temperature constants of 18%. (Table 2.6 column 8 and 9). With the Ni-salt, however, we obtained a very satisfactory agreement between the constants determined at different temperatures (Table 2.6. column 10 and 11), while no important change in the magnitude of the  $C_i$ 's occurred after recrystallization (Table 2.6. column 12 and 13).

In another series of measurements (carried out with another magnet), no difference could be detected between calibrations with our own substance and a sample of Merck. Excellent agreement was further found between these figures and those obtained from a calibration with  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  at the temperature of liquid air. The results are given in table 2.7. (In the last two columns of this table two calibrations with  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  are added for comparison).

This  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  thus seemed to be a convenient standard substance, although the standard deviation in a series of calibrations appeared to be approximately 2%. A striking peculiarity was the fact, that the constants  $C_i$  for the different magnet currents in one calibration were all too high or all too low. There exist indeed two factors which are not incorporated in our theoretical estimation of the error in section 2.5. They are the re-

producibility of the position of the sample in the magnetic field and inhomogeneities in the standard substance. Both factors are constant during one calibration. This observation led to the introduction of the quartz wire to suspend the sample (already discussed in section 2.2b) and the use of uniformly sized crystals of the standard substance (section 2.5). These two measures appeared to be important improvements; the results are already given in table 2.1, which shows that the standard deviation is now less than 1%, in close agreement with the estimated error.

In tables 2.6 and 2.7 are collected mean values of  $C_i$  and  $C_j$  values from some typical calibrations. They are chosen from an extensive series of measurements which gave us the detailed information about the problem of the standard substance and the most favourable working conditions of the apparatus.

We have paid no further attention to the reasons of the failure to calibrate the apparatus with  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . We may only mention first, that the low value of the constants at liquid air temperature compared to those at room temperature indicate a higher susceptibility at the former temperature than calculated according to Jackson 11). Secondly, that the values of the constants determined at the temperature of dry ice-acetone agreed very well with the room temperature values. Thirdly, that Fox 18) found similar deviations for  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in the lower temperature region. For a possible explanation of the deviations at lower temperatures we may draw attention to the facts that the lowest energy levels of  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  are greatly influenced by the electric crystal field, which is not the case in the  $\text{Ni}^{2+}$  ion where the singlet level is lying lowest and not split up by cubic crystal fields. A second difference between Ni, Co and Fe is that the former element only occurs as divalent ion. At the end of this section we will give, for the sake of completeness, the  $\chi$ -formulae for the different compounds used in this investigation.

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \quad \chi_g = \left\{ \frac{9500}{T+1} \right\} 10^{-6} \quad 11.) \quad 17.)$$

$$\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \quad \chi_g = \left\{ \frac{7659}{T+20.4} \right\} 10^{-6} \quad 11.)$$

$$(\text{NiSO}_4) \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \quad \chi_g = \left\{ \frac{3065}{T+0.5} \right\} 10^{-6} \quad 11.)$$

$$\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O} \quad \chi_g = \left\{ \frac{8956}{T+3} - 0.23 \right\} 10^{-6} \quad 19.)$$

For the definitive calibrations (section 2.5) with  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  the somewhat better formula

$$\chi_g = \left\{ \frac{3174}{T+2.5} - 0.30 \right\} 10^{-6}$$

was calculated from Jackson's 11) data, where the term  $-0.30 \cdot 10^{-6}$  is the diamagnetic correction according to Klemm 12). The difference between the two formulae, however, is extremely small.



## Chapter III

### THE SYSTEM CoO-MgO

#### 3.1. Introduction

The investigation of these mixed crystals was undertaken in order to determine the magnetic behaviour of divalent cobalt in the octahedral interstices of an oxygen lattice. The system CoO-MgO, in which a continuous range of mixed crystals can be made, crystallizes in the rock salt structure. In this structure the anions form a cubic close-packed lattice. The cations occupy all the available octahedral interstices. Crystallographic work on the system Co-Mg-O has been done by Robin<sup>20</sup>). Magnetic investigations on these mixed crystals were made by Elliot<sup>21</sup>). Of nine substances with a CoO percentage ranging from 100 to 5, the susceptibility was determined between 300 and 500°K. He mentioned a mean Curie constant of 3.23 and consequently a moment for Co<sup>2+</sup> of 5.1 Bohr magnetons. The substances with more than 20% CoO show  $1/\chi$ -T curves convex to the T axis. Although this paper appeared during our investigation, we proceeded with the work on this system, as the measurements of Elliot were carried out in a rather limited temperature range.

We did not prepare pure CoO, since excellent susceptibility measurements up to approximately 800°K were made by Trombe<sup>22</sup>).

From 450°K up to 800°K the Curie-Weisz law is obeyed.  $\theta$  is found to be -280°K and  $\mu = 4.96 \mu_B$ .

#### 3.2. Experimental part

The preparation of the samples caused some difficulties. The original method of mixing solutions of nitrates and evaporating to dryness, which was applied with success in making the aluminates, was abandoned. Five products of different Co content showed too low final weights and some of the Debye-Scherrer diagrams showed at low angles a number of very weak unidentifiable reflections. We believe that the products were not quite homogeneous as a consequence of the different temperature of decomposition of Mg(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub>, the former being a more stable compound. These five products were discarded.

The decomposition of a mixture of the nitrates or a mixture of MgCO<sub>3</sub> and Co oxalate at 870°C *in vacuo* also did not lead to the required result. For this special case method B (described in chapter I) was developed. A mixture of carbonates was precipitated from a solution of nitrates and the whole mass evaporated to dryness. Although the composition of the precipitate is not exactly known and some of the cobalt remains in solution as a complex

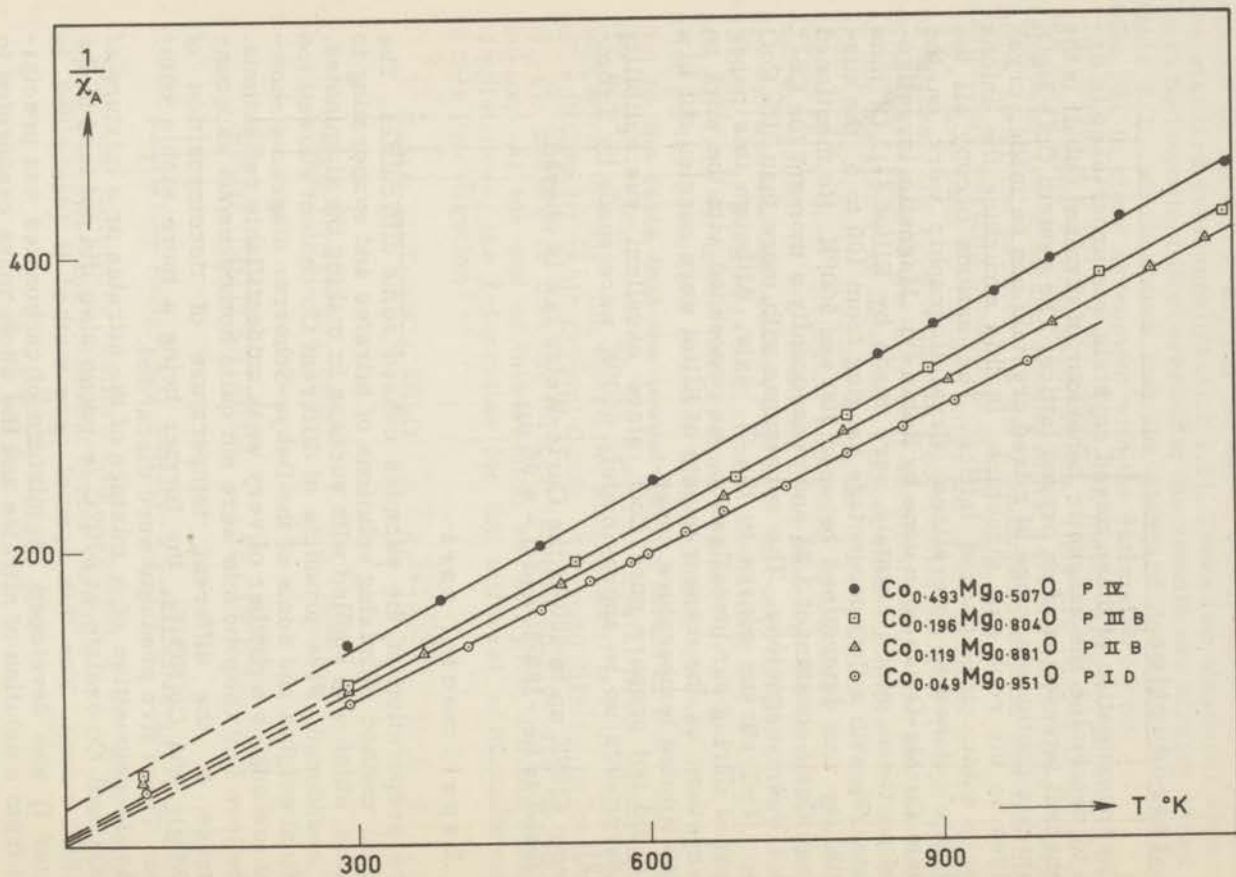


FIGURE 3.1.

Table 3.1

Substance	Prepared from:	Method:	Structure	M <sub>A</sub>	χ <sub>D</sub> ·10 <sup>3</sup>	Firing	Product	χ <sub>A</sub> ·10 <sup>3</sup> (roomtemp.)	
Co <sub>0.049</sub> Mg <sub>0.951</sub> O PI	MgCO <sub>3</sub> Co(NO <sub>3</sub> ) <sub>2</sub>	ACB	Rocksalt	857	-0.62	12h. 840°C. Vac.	PIA	9.71	
						12h. 940°C. O <sub>2</sub>	PIB	10.26	
						40h. 920°C. O <sub>2</sub>	PIC	10.39	
						60h. 920°C. O <sub>2</sub>	PID	10.43	
Co <sub>0.119</sub> Mg <sub>0.881</sub> O PII	MgCO <sub>3</sub> Co(NO <sub>3</sub> ) <sub>2</sub>	ACB	Rocksalt	374	-0.28	45h. 900°C. O <sub>2</sub>	PIIA	9.51	
						55h. 940°C. O <sub>2</sub>	PIIB	9.46	
Co <sub>0.196</sub> Mg <sub>0.804</sub> O PIII	MgCO <sub>3</sub> Co(NO <sub>3</sub> ) <sub>2</sub>	ACB	Rocksalt	240	-0.15	45h. 900°C. O <sub>2</sub>	PIIIA	9.18	
						55h. 940°C. O <sub>2</sub>	PIIIB	9.27	
Co <sub>0.493</sub> Mg <sub>0.507</sub> O PIV	MgCO <sub>3</sub> Co(NO <sub>3</sub> ) <sub>2</sub>	ACB	Rocksalt	115	-0.07	24h. 1200°C O <sub>2</sub>			
Co <sub>0.049</sub> Mg <sub>0.951</sub> O (PID)		Co <sub>0.119</sub> Mg <sub>0.881</sub> O (PIIB)		Co <sub>0.196</sub> Mg <sub>0.804</sub> O (PIIIB)		Co <sub>0.493</sub> Mg <sub>0.507</sub> O (PIV)			
T	χ <sub>A</sub> ·10 <sup>3</sup>	T	χ <sub>A</sub> ·10 <sup>3</sup>	T	χ <sub>A</sub> ·10 <sup>3</sup>	T	χ <sub>A</sub> ·10 <sup>3</sup>	T	χ <sub>A</sub> ·10 <sup>3</sup>
292	10.43	804	3.80	80	23.2	80	20.6	294	7.39
415	7.45	862	3.58	292	9.46	291	9.27	388	6.01
489	6.34	863	3.57	370	7.67	528	5.32	489	4.95
540	5.61	914	3.35	509	5.67	691	4.04	607	4.06
582	5.25	990	3.09	679	4.23	803	3.46	836	3.03
599	5.08			801	3.58	888	3.12	893	2.86
600	5.09			908	3.17	1066	2.60	956	2.68
639	4.73	83	27.5	1017	2.82	1190	2.34	1014	2.54
677	4.47			1116	2.56			1087	2.37
741	4.17			1174	2.43			1193	2.18
θ	0°K			θ	-6°K	θ	-11°K	θ	-72°K
C	3.05			C	2.90	C	2.87	C	2.78
μ	4.94 μ <sub>B</sub>			μ	4.82 μ <sub>B</sub>	μ	4.80 μ <sub>B</sub>	μ	4.71 μ <sub>B</sub>

The letters in the column "method" correspond to the description given in section 1.1.

The structure was determined with the Philips 11.5 cm powder camera.

M<sub>A</sub> is the molecularweight per gramatom of cobalt.

χ<sub>D</sub> is the diamagnetic correction per gramatom of cobalt (in this case estimated from the measurement on Co<sub>0.049</sub>Mg<sub>0.951</sub>O (PID)).

ion with  $\text{NH}_3$ , the solid obtained after evaporation is much more homogeneous than that obtained after direct evaporation of the nitrates.

In this way the series PI to PIV were prepared. All the experimental data concerning these substances are combined in table 3.1 and fig. 3.1.

The products of series PI, PII and PIII were fired at 920 and 940°C until the susceptibility at room temperature remained constant. Only the products PID, PIIB and PIIB were subjected to high temperature measurements.

The substance with equal amounts of CoO and MgO could not be made homogeneous by firing at 900 - 1000°C. Satisfactory results were obtained when the firing was performed at 1100 - 1200°C.

An important remark must be made with respect to the diamagnetic correction in the column  $\chi_D \cdot 10^3$  in table 3.1. The values mentioned there are not those calculated according to the tables of Klemm<sup>12)</sup> but are determined from our own measurements in a way described in detail in the next section.

### 3.3. Discussion

As may be seen from the  $1/\chi$ -T plots in fig. 3.1, these substances follow the Curie-Weisz law with a vanishing value for  $\Theta$  when CoO becomes more and more diluted. This reasoning, however, is not quite correct, since for the substance  $\text{Co}_{0.049}\text{Mg}_{0.951}\text{O}$  (PID), the  $1/\chi$ -T curve is made straight by adaptation of the diamagnetic correction.

Originally, when the diamagnetic corrections of Klemm<sup>12)</sup> were used, the curves for the substances with approximately 5, 10 and 20% CoO were convex to the T axis even up to 1200°K. For the lower part of the curve, such a bending is very comprehensible. Since we know that the pure component CoO is a strongly antiferromagnetic substance, we may expect for the more dilute compounds a similar although less pronounced behaviour in the low temperature region. A nonlinear dependence of  $1/\chi$  on T is found in the theory of ferrimagnetism of Néel<sup>5)</sup> but only curves concave to the T axis can be accounted for. For real antiferromagnetic substances in which a negative coupling occurs between two equivalent sub-lattices which are equally occupied, Néel's theory prescribes a linear dependence of  $1/\chi$  on T for temperatures above the Curie point.

Curves concave to the T axis are also found when temperature-independent paramagnetism plays a role (see chapter IV). Convex curves, however, would require a "negative temperature-independent paramagnetism". Our substance with 5% CoO could be described by the formula  $\chi = A + \frac{C}{T - \Theta}$  in which A was found to be  $-0.37 \cdot 10^{-3}$  e. m. u. (a value of  $-0.24 \cdot 10^{-3}$  for  $\chi_D$  is incorporated in the  $\chi$ ).

For the other mixed crystals with 10 and 20% CoO, respectively, the bending in the high temperature region of the  $1/\chi$ -T curves diminished with increasing Co content.

The substance  $\text{Co}_{0.493}\text{Mg}_{0.507}\text{O}$  (PIV), which was especially prepared to study this dependence, showed practically no deviation from the straight line, and Trombe <sup>22)</sup> observed that pure  $\text{CoO}$  above  $450^\circ\text{K}$  obeys the Curie-Weisz law. This excluded the possibility of a temperature-dependent moment of  $\text{Co}^{2+}$  ions in octahedral interstices. No other physical significance than diamagnetism could be assigned to this negative temperature-independent part, so we had to conclude that the applied diamagnetic correction was wrong. To find the correct value for this diamagnetism we assumed for the substance  $\text{Co}_{0.049}\text{Mg}_{0.951}\text{O}$  (PID) this term to be the sum of the diamagnetic correction according to Klemm <sup>12)</sup> and the observed negative part A. Thus

$$\chi_D^{\text{corr.}} = \chi_D + A$$

$$\chi_D^{\text{corr.}} = -0.25 \cdot 10^{-3} - 0.37 \cdot 10^{-3} = -0.62 \cdot 10^{-3}$$

The other diamagnetic corrections could be calculated according to the following scheme (The formulae are simplified):

	$\chi_D \cdot 10^3$ (Klemm)	$\chi_D \cdot 10^3$ (estimated)
$\text{CoO}(\text{MgO})_{19}$	-0.25	-0.62
$\text{CoO}$	-0.02	-0.04
$(\text{MgO})_{19}$	-0.23	-0.58
$\text{MgO}$	-0.01 <sup>2</sup>	-0.03

Hence:

$\text{CoO MgO}$	-0.03	-0.07
$\text{CoO}(\text{MgO})_4$	-0.07	-0.16
$\text{CoO}(\text{MgO})_8$	-0.11	-0.28

The result of applying the newly-calculated diamagnetic corrections is very satisfactory.

All the substances now obey the Curie-Weisz law, the constants of which may be read from table 3.1.

We will now mention briefly the several reasons which might justify our treatment of the experimental data.

a) There is no physical significance for a negative constant magnetism other than diamagnetism.

b) The bending of the curves diminishes as the  $\text{Co}^{2+}$  ions are accompanied by less diamagnetic material.

c) The magnetic behaviour of all four substances becomes normal in applying only one adopted new value of the diamagnetism.

d) As we will see in chapters IV and V the diamagnetic corrections of  $\text{ZnO}$  and  $\text{ZnAl}_2\text{O}_4$  calculated according to Klemm <sup>12)</sup> also appear to be wrong.

e) We have tried to determine the diamagnetism of MgO by direct measurement. With a MgO sample prepared by decomposing  $MgCO_3$  we found an effect of practically zero. With a much denser sample prepared by powdering MgO which had been crystallized from the melt we obtained a diamagnetism of  $-0.017 \cdot 10^{-3}$  e. m. u. /mol. Kittel and Hüttig<sup>23</sup>) obtained decreasing values for the diamagnetism of MgO samples of increasing density, the smallest value being  $-0.020 \cdot 10^{-3}$  e. m. u. /mol. and the others  $-0.033$ ,  $-0.041$  and  $-0.088 \cdot 10^{-3}$  e. m. u. It is thus impossible to obtain a reliable value from direct measurement or from other investigations. However, if the effect described by Kittel and Hüttig exists and is not an incidental one, our adapted value of  $-0.030 \cdot 10^{-3}$  e. m. u. is not very improbable for the moderate dense samples of (Co, Mg)O.

Finally we must discuss the magnitude of the moment found for  $Co^{2+}$ . As may be seen from table 3.1, this moment shows a gradual decrease from  $4.94 \mu_B$  for  $Co_{0.049}Mg_{0.951}O$  (PID) to  $4.71 \mu_B$  for  $Co_{0.493}Mg_{0.507}O$  (PIV). The former value is in excellent agreement with the value of  $4.96 \mu_B$  found by Trombe<sup>22</sup>) for the undiluted CoO. We are not able to explain the lower values for the other substances.

The agreement with the results of Elliot<sup>21</sup>) is also satisfactory. Although the latter author mentions a mean Bohr magneton number of 5.1, a careful examination of his experimental data showed that this value is only found in the case of the highest dilution, *i. e.* for a substance with 5% CoO.

For the other substances we calculated, with the aid of his table of  $\chi$  values, the following constants.

	$\theta$	C	$\mu$
5.00% CoO	$-16^\circ K$	3.23	5.08
9.01% CoO	$-38^\circ K$	3.19	5.05
16.00% CoO	$-48^\circ K$	3.20	5.06
20.83% CoO	$-34^\circ K$	2.92	4.83
21.09% CoO	$-36^\circ K$	2.96	4.86

For the substances with a higher Co content it is not permissible to carry out a calculation, as it is impossible to determine the value of  $\theta$  from  $4 \chi$  points in a temperature region (300-500°K) where the  $1/\chi$ -T plots show a pronounced convex character due to antiferromagnetic coupling. It is interesting to note that although the values are somewhat higher than ours, the same irregularities are encountered.

As a result of the combined efforts, we may conclude that  $Co^{2+}$  in the octahedral holes of a cubic close-packed structure of oxygen ions exhibits a moment independent of temperature up to 1200°K with values of 4.8 - 5.1 Bohr magnetons.

In hydrated salts where the  $Co^{2+}$  ions are surrounded by six water dipoles, values of the order of 5 Bohr magnetons are also usually found.

When it was necessary to carry out simple calculations involv-

ing  $\text{Co}^{2+}$  in octahedral interstices, we have used throughout this thesis a Bohr magneton number of 5.

### Summary of chapter III

Mixed crystals of  $\text{CoO}$  and  $\text{MgO}$  were prepared and susceptibility measurements were carried out up to  $1200^\circ\text{K}$ . The interpretation of the experimental data required the assumption that the diamagnetic corrections of Klemm <sup>12)</sup> could not be applied. For  $\text{MgO}$  the much higher value of  $-0.03 \cdot 10^{-3}$  e.m.u./mol. was adopted. With this new value all the substances obeyed the Curie-Weisz law. Values of 4.71 to  $4.94 \mu_{\text{B}}$  were found for the moment of  $\text{Co}^{2+}$  ions in octahedral interstices. The results were compared with those of Trombe <sup>22)</sup> on  $\text{CoO}$  ( $4.96 \mu_{\text{B}}$ ) and those of Elliot <sup>21)</sup> on mixed crystals of  $\text{CoO}$  and  $\text{MgO}$  ( $4.86 - 5.08 \mu_{\text{B}}$ ).

## Chapter IV

### THE SYSTEM CoO-ZnO

#### 4.1. Introduction

This system of mixed crystals has been investigated many years ago. The green materials are well known in qualitative analysis as "Rinmann's green", and they have been used as pigments. Lately Robin<sup>24)</sup> made a thorough investigation of the phase diagram Co-Zn-O. Above 900°C two types of mixed crystals are found of the formula (Co,Zn)O. On the cobalt-rich side, the substances crystallize in the rock salt structure, and on the zinc-rich side in the wurtzite structure. The two phases are separated by a miscibility gap. At 1100°C. CoO is soluble in ZnO to approximately 20%. The wurtzite structure is a hexagonal close-packed structure of anions in which one-half of the tetrahedral interstices are occupied by the cations.

The reason why we were very interested in the magnetic properties of these cobalt-zinc oxides is this surrounding of cations by 4 oxygen ions. The substances are perhaps the only ones in which Co<sup>2+</sup> ions occupy exclusively tetrahedral interstices. As far as we know, magnetic susceptibility measurements have not yet been carried out.

#### 4.2. Experimental part

The substances made are listed in table 4.1 together with conditions of preparation, deviation of final weight from calculated value in % ( $\Delta w$ ), structure, molecular weight per cobalt atom, diamagnetic correction (own values) and other noteworthy remarks.

Of the nine substances, four have been used for magnetic measurements at high temperature, the other five for measurements at room temperature only, partly because they had not the proper quality and partly as a consequence of the high dilution of the Co ions which made the  $\chi_g$  too small for measurements at high temperature.

The magnetic data are collected in table 4.2 and fig. 4.1. In table 4.2  $\chi_A$  (exp.) is the susceptibility per gram atom of Co expressed in e. m. u.; the values are corrected for diamagnetism. In the columns  $\chi_A \cdot 10^3$  (calc.) the values were calculated with the formula  $\chi_A = A + \frac{C}{T - \theta}$  in which the constants A, C and  $\theta$  are as completely as possible adapted to the experimental data. The values of A, C and  $\theta$  and other figures which are interesting to compare are given in table 4.3.

In the discussion of the results (following section) data on the substances Co<sub>0.20</sub>Zn<sub>0.80</sub>O (IIA) and Co<sub>0.105</sub>Zn<sub>0.895</sub>O (IIA) are not



Table 4.1.

Substance	Prepared from:	Method	Firing	Atm.	$\Delta w$ in %	Structure	$M_A$	$X_D \cdot 10^3$
$Co_{0.200}Zn_{0.800}O$ IIA	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	6h. 1100°	Air	+ 0.7	wurtzite	400	-0.13
$Co_{0.200}Zn_{0.800}O$ IIB	product IIA	-	5h. 1200°	O <sub>2</sub>	+ 0.5	wurtzite	400	-0.13
$Co_{0.110}Zn_{0.890}O$ I	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	15h. 1100°	Air	+ 0.6	wurtzite	736	-0.24
$Co_{0.105}Zn_{0.895}O$ IIA	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	20h. 870°	Vac	+ 1.0	wurtzite + rocksalt	763	-0.25
$Co_{0.105}Zn_{0.895}O$ IIB	product IIA	-	18h. 1200°	O <sub>2</sub>	+ 0.3	wurtzite	763	-0.25
$Co_{0.050}Zn_{0.950}O$	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	15h. 1100°	Air	+ 0.2	wurtzite	1622	-0.52
$Co_{0.033}Zn_{0.967}O$ I	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	8h. 1100°	Air	+ 0.7	wurtzite	2436	-0.73
$Co_{0.025}Zn_{0.975}O$ I	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	8h. 1100°	Air	+ 1.1	wurtzite	3245	-1.04
$Co_{0.025}Zn_{0.975}O$ II	$Co(NO_3)_2$ $Zn(NO_3)_2$	A	6h. 1100°	Air	+ 1.1	wurtzite	3239	-1.04

The letter in the column "method" corresponds with the description given in section 1.1.

The structure was determined with the Unicam 9 cm powdercamera.

$\Delta w = \frac{\text{final weight (exp.)} - \text{final weight (calc.)}}{\text{final weight (calc.)}} \times 100$

$M_A$  is the molecular weight per gramatom of cobalt.

$X_D$  is the diamagnetic correction per gramatom of cobalt.

Table 4.2.

Co <sub>0.20</sub> Zn <sub>0.80</sub> O. IIB			Co <sub>0.11</sub> Zn <sub>0.89</sub> O. I			Co <sub>0.105</sub> Zn <sub>0.895</sub> O. IIB		
T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.
83	12.5	14.1	83	17.1	18.9	83	16.6	18.8
289	6.22	6.22	290	7.07	7.05	293	6.84	6.84
360	5.31	5.31	291	7.02	7.02	421	5.05	5.04
421	4.69	4.71	414	5.27	5.24	582	3.87	3.86
520	4.04	4.00	519	4.34	4.35	742	3.16	3.17
581	3.68	3.67	644	3.65	3.65	889	2.75	2.76
696	3.23	3.19	779	3.13	3.14	992	2.52	2.52
736	3.07	3.05	914	2.80	2.77	1088	2.35	2.36
839	2.76	2.77	1095	2.40	2.42	1200	2.25	2.19
893	2.60	2.64	1195	2.24	2.27			
988	2.37	2.45						
993	2.40	2.43						
1054	2.36	2.33						
1081	2.27	2.29						
1081	2.29	2.29						
1180	2.17	2.14						
1191	2.16	2.13						
Co <sub>0.050</sub> Zn <sub>0.950</sub> O								
T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.						
81	22.3	26.9						
290	7.54	7.54						
430	5.30	5.24						
583	3.98	4.00						
738	3.26	3.26						
891	2.77	2.78						
989	2.58	2.56						
1093	2.35	2.36						

Substance	T	$\chi_A \cdot 10^3$ exp.
Co <sub>0.20</sub> Zn <sub>0.80</sub> O. IIA	83 288	11.9 5.90
Co <sub>0.105</sub> Zn <sub>0.895</sub> O. IIA	286	5.26
Co <sub>0.033</sub> Zn <sub>0.967</sub> O.	80 294	23.5 7.61
Co <sub>0.025</sub> Zn <sub>0.975</sub> O. I	83 290	23.9 7.66
Co <sub>0.025</sub> Zn <sub>0.975</sub> O. II	83 290	24.0 7.72

incorporated. As already mentioned in table 4.1 the latter substance consisted of two phases (rocksalt and wurtzite). This is now confirmed magnetically. The  $\chi_A$ -value at room temperature ( $5.26 \cdot 10^{-3}$ ) of the product is much smaller than that of the fired substance IIB ( $6.84 \cdot 10^{-3}$ ). The homogenizing effect of the firing procedure brings the Co atoms further apart, which causes an augmentation of the susceptibility. For the same reason the substance Co<sub>0.20</sub>Zn<sub>0.80</sub>O (IIA) is not discussed. Although the X-ray photograph gave no indication of incomplete mixing, the  $\chi$  value at room temperature increased from  $5.90 \cdot 10^{-3}$  to  $6.22 \cdot 10^{-3}$  after an extra heating period.

In fig. 4.1 we have plotted  $1/\chi_A$  for the four substances versus the absolute temperature from 80 to about 1200°K. A plot of  $\chi \cdot T$

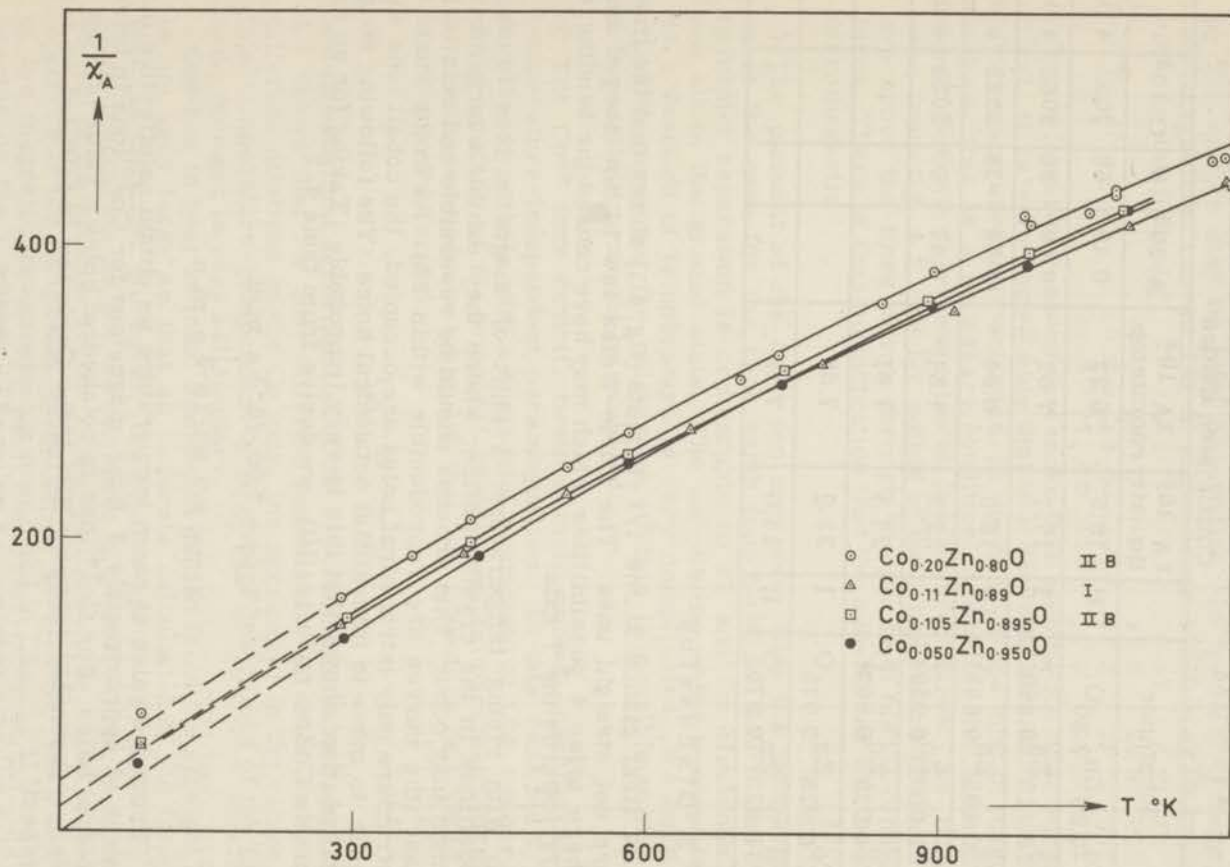


FIGURE 4.1.

against T offers no particular advantages because of the value of  $\theta$ , which is in most cases different from zero.

Table 4.3.

Cobalt-zinc oxides

Substance		$\chi_A \cdot 10^3$ liq. air	$\chi_A \cdot 10^3$ roomtemp.	A. $10^3$	$\theta$	C. $10^3$	$\mu$
$\text{Co}_{0.20}\text{Zn}_{0.80}\text{O}$ .	IIB	12.5	6.22	0.49	-68	2063	4.06
$\text{Co}_{0.110}\text{Zn}_{0.890}\text{O}$ .	I	17.1	7.02	0.58	-30	2068	4.07
$\text{Co}_{0.105}\text{Zn}_{0.895}\text{O}$ .	IIB	16.6	6.84	0.54	-28	2023	4.02
$\text{Co}_{0.050}\text{Zn}_{0.950}\text{O}$ .		22.3	7.54	0.47	0	2050	4.05
$\text{Co}_{0.033}\text{Zn}_{0.967}\text{O}$ .		23.5	7.61				
$\text{Co}_{0.025}\text{Zn}_{0.975}\text{O}$ .	I	23.9	7.66				
$\text{Co}_{0.025}\text{Zn}_{0.975}\text{O}$ .	II	24.0	7.72				

4.3. Discussion

A first glance at the  $1/\chi$ -T plots (fig. 4.1) shows that the lines are not straight ones. The Curie-Weisz law is not obeyed and there arise 4 possibilities which may have caused the bending of  $1/\chi$  towards the T axis.

a) With rising temperature, a shift of magnetic ions to other positions in the crystal lattice, where they exhibit a larger moment may occur. This process should be reversible and relatively fast (the curves are reproducible within 2%). As in the wurtzite structure only tetrahedral holes are occupied, the cobalt ions will have to move to interstitial octahedral holes. The following rough calculation shows that this is very improbable. Taking for an example  $\text{CoZn}_{8.12}\text{O}_{9.12}$  (IIB), we derive from table 4.2.

$$\chi_{290} = 7.00 \cdot 10^{-3} \text{ e. m. u.}$$

$$\chi_{1095} = 2.33 \cdot 10^{-3} \text{ e. m. u.}$$

From the value at room temperature we obtain an effective moment of approximately 4 Bohr magnetons for  $\text{Co}^{2+}$  ions in tetrahedral holes. For  $\text{Co}^{2+}$  ions in octahedral holes a value of  $5 \mu_B$  is very reasonable (chapter III). If the Curie law is fulfilled we may expect

$$\chi_A = 1.86 \cdot 10^{-3} \text{ at } 1095^\circ\text{K.}$$

To explain the much higher value of  $2.33 \cdot 10^{-3}$ , some 40 - 50% of the cobalt ions should have occupied the interstitial octahedral

holes. Although the effect of occupation of interstitial holes is quite common in ionic crystals, in general this does not happen to a greater extent than a few percent. We may thus exclude this possibility.

b) The curves may be Néel hyperbolae. In the Néel <sup>5)</sup> theory of ferrimagnetism curved  $1/\chi$ - $T$  plots occur which may be represented by the formula

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{S}{T-\theta}$$

There are two reasons that make this assumption unacceptable. First, it is very improbable that in a wurtzite structure two sublattices are unequally occupied. In the case of one kind of magnetic ions, this is a necessary condition. Secondly, the substances should become ferromagnetic at low temperatures. As may be seen from fig. 4.1, the  $1/\chi$  points at the temperature of liquid air are above the lines drawn through the points at higher temperatures. There is thus no indication that the substances will become ferromagnetic.

c) The moment of the  $\text{Co}^{2+}$  ion may vary with the temperature as is the case for the rare earth ions  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ . Here the multiplet separation is comparable to  $kT$  and the electrons are not all in the ground state. The calculation of the susceptibility as a function of temperature is very complicated. We have not tried to carry out the calculation (if this is possible at all), so this possibility can not be excluded.

d) The  $\text{Co}^{2+}$  ions exhibit, besides their normal paramagnetism temperature-independent paramagnetism. In this case the  $1/\chi$ - $T$  plot is a hyperbola with a horizontal asymptote at  $1/A$ , where  $A$  is the magnitude of the temperature-independent paramagnetism. It is readily seen from table 4.2 that the  $\chi_A$  values calculated according to the formula

$$\chi_A = A + \frac{C}{T-\theta}$$

are in excellent agreement with the experimental values, and table 4.3 shows that for four different substances, of which three have different dilutions of the Co ions, the agreement in the values for this temperature-independent term and for the values of the magnetic moment is very satisfactory.

One has to bear in mind that the deviation from the straight line is not very large so that an accurate calculation of the constant term is difficult. Moreover, the measurements become more and more inaccurate as the temperature is raised, which is a consequence of the smaller forces acting on the sample. A third source of errors is the molecular weight of the substances. The accuracy of the magnetic measurements mentioned in Chapter II have their bearing on the  $\chi_g$  values. The value  $\chi_A$  contains also the error in the cobalt content of the substances, which may be considerable in the case of high dilution.

The diamagnetic correction may cause, as we have seen in

chapter III, considerable errors, especially in the highly-diluted substances. We have used  $\chi_D = -0.026 \cdot 10^{-3}$  for ZnO. This value has been determined by direct measurement on ZnO (Merck *p. a.*) and shows an appreciable difference from that calculated according to Klemm <sup>12</sup>), namely  $-0.019 \cdot 10^{-3}$ .

Several measurements on ZnO can be found in the literature. The values  $-0.027 \cdot 10^{-3}$  obtained by Chevenau <sup>25</sup>) and  $-0.026 \cdot 10^{-3}$  by Pascal <sup>26</sup>) are in excellent agreement with our value, while  $-0.021 \cdot 10^{-3}$  obtained by St. Meyer <sup>27</sup>) agrees better with the value calculated according to Klemm. Any error in the diamagnetic correction appears only in the value of the constant term A. However,  $A = 0.5 \times 10^{-3}$  will not be far beyond the true value. Although the highest diluted substances with 3.3 and 2.5% CoO are not measured at higher temperatures, no interesting developments are to be expected, as the  $\chi_A$  values at room temperature and even those at liquid air temperature do not much differ from the corresponding values for the substance with 5% CoO (see table 4.3).

The question arises whether these results are to be expected on theoretical considerations or are simply curiosities. As we have seen in the preceding chapter  $\text{Co}^{2+}$  ions in octahedral oxygen holes show a moment with an appreciable orbital contribution. This is in agreement with the moments usually found for  $\text{Co}^{2+}$  ions. The ions following  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  all show the same behaviour. The ions with less than half filled 3d shells show, together with  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ , no orbital contribution to the moment. In these ions the orbital moment is quenched by an octahedrally-shaped electric field of negative ions or water dipoles, while  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  have no orbital contribution at all, as they are in an S-state. In the second half of this group the coupling of L and S becomes stronger and the crystal fields are no longer able to quench the orbital contribution to the magnetic moment completely. The theory of this phenomenon of quenching is due to Van Vleck <sup>28</sup>).

We will now compare  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions in their normal surroundings of 6 electrical charges.

	$\text{Cr}^{3+}(4F_{3/2})$	$\text{Co}^{2+}(4F_{9/2})$
spin configuration of d electrons	↑ ↑ ↑	↑ ↑ ↑ ↑ ↑ ↓ ↓
contribution of orbital to magnetic moment	no orbital contribution	appreciable orbital contribution

The spin configurations of three unpaired electrons in  $\text{Cr}^{3+}$  and three "electron holes" in the 3d shell of  $\text{Co}^{2+}$  are very much alike. The term schemes of both ions are built up of the same levels and energy differences but in a reverse order. Gorter <sup>29</sup>) has drawn attention to the fact that a term scheme is turned upside down when the symmetry of the crystal field changes from octahedral to tetrahedral. The orbital contribution in  $\text{Co}^{2+}$  ions in octahedral interstices is not only due to a stronger L - S coupling but is also

a consequence of the fact that in a cubic field the lowest levels are split into two triplets <sup>30</sup>). If now, in tetrahedral surroundings the term scheme is turned upside down, a singlet level becomes lowest, as is the case for Cr<sup>3+</sup> ions in octahedral holes, and one of the causes of the orbital contribution to the moment disappears. We may thus expect Co<sup>2+</sup> ions in tetrahedral interstices to exhibit a  $\mu$  value much closer to the spin-only value, although as a consequence of the stronger L - S coupling, the orbital angular momentum is not completely quenched.

It is not easy to predict a temperature-independent term for this situation. It is, however, possible that the crystal field strength in tetrahedral holes is smaller than that in octahedral ones. Consequently, the energy difference between the lowest and the highest energy levels will be smaller and temperature-independent paramagnetism, which is inversely proportional to this energy difference, will become important.

The satisfactory description of the data by the formula

$$\chi = A + \frac{C}{T-\theta}$$

and the support which can be found from the theory make it very improbable that the magnitude of the magnetic moment of Co<sup>2+</sup> in tetrahedral surrounding is a function of temperature. It remains possible, however, that in the higher temperature region this effect might become of importance.

#### Summary of Chapter IV

Mixed crystals of CoO and ZnO with wurtzite structure were made with up to 20% CoO, and magnetic susceptibility measurements were carried out from 100 to 1200°K to investigate the magnetic behaviour of Co<sup>2+</sup> ions in the tetrahedral interstices of an oxygen lattice. The temperature dependence of the susceptibility could be described by the formula  $\chi = A + \frac{C}{T-\theta}$ . The temperature-independent term varied from 0.47 - 0.58 · 10<sup>-3</sup> e.m.u. per gram atom Co and the magnetic moment calculated from the formula  $\mu = \sqrt{8C}\mu_B$  varied from 4.02 to 4.07 Bohr magnetons.

The occurrence of temperature-independent paramagnetism and the nearly spin-only value of the moment could be accounted for by theoretical considerations of Gorter <sup>29, 30</sup>).

## Chapter V

### THE SYSTEM $\text{CoAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$

#### 5.1. Introduction

The cobalt-zinc aluminates have been investigated by Romeyn<sup>31)</sup>. This author concluded, from X-ray intensities determined very carefully with a Norelco spectrometer, that  $\text{CoAl}_2\text{O}_4$  and the mixed crystals with  $\text{ZnAl}_2\text{O}_4$  are normal spinels. The intensities were not influenced by the heat treatment of the samples. Heating at  $1300^\circ\text{C}$ . and quenching made no difference. In contrast to the observation of Romeyn<sup>31)</sup>, Greenwald, Pickart and Grannis<sup>32)</sup> assumed on the basis of their X-ray intensity measurements that  $\text{CoAl}_2\text{O}_4$  is a partially inverse spinel with 19%  $\text{Co}^{2+}$  situated at octahedral interstices. A sample heated to  $1400^\circ\text{C}$ . and quenched appeared to contain 31% of the  $\text{Co}^{2+}$  ions at the octahedral sites. The susceptibility measurements on these  $\text{CoAl}_2\text{O}_4$  samples up to  $1200^\circ\text{K}$  gave as a result a low temperature slope of the  $1/\chi$ -T plot corresponding to a Curie constant  $C = 3.07$  and a high temperature slope corresponding to  $C = 3.86$ .

Assuming for  $\text{Co}^{2+}$  in the tetrahedral holes a g factor of 2, they calculated for  $\text{Co}^{2+}$  in the octahedral holes a g factor of 4.30 from the high temperature Curie constant and the ionic distribution of the quenched samples, and a g factor of 4.26 from the low temperature Curie constant combined with the ionic distribution of the tempered sample. The agreement between these two values for the g factor in octahedral interstices seemed to be a support of the view that the  $\text{CoAl}_2\text{O}_4$  spinels are partially inverse.

#### 5.2. Experimental part

All the experimental data concerning this group of substances are collected in table 5.1 and figure 5.1. Of all the substances Debye-Scherrer diagrams were made. No deviations from the spinel structure could be observed. The error in the final weight of the substances  $\Delta w$  is not given in the table as for most of them it was not determined.

We have used our own diamagnetic corrections based on a direct measurement of the susceptibility of  $\text{ZnAl}_2\text{O}_4$ . The most dilute substances have not been subjected to high temperature measurements as the effects became too small. As the curves of these mixed crystals were so much alike, not all the  $1/\chi$ -T plots are drawn in fig. 5.1.



Table 5.1.

Substance	CoAl <sub>2</sub> O <sub>4</sub> ·(Al <sub>2</sub> O <sub>3</sub> ) <sub>0.03</sub>			CoAl <sub>2</sub> O <sub>4</sub> ·II.			Co <sub>0.75</sub> Zn <sub>0.25</sub> Al <sub>2</sub> O <sub>4</sub>			Co <sub>0.503</sub> Zn <sub>0.497</sub> Al <sub>2</sub> O <sub>4</sub>		
Prepared from:	Co oxalate + Al(NO <sub>3</sub> ) <sub>3</sub>			Co(NO <sub>3</sub> ) <sub>2</sub> + Al(NO <sub>3</sub> ) <sub>3</sub>			Co oxalate + Zn(NO <sub>3</sub> ) <sub>2</sub> + Al(NO <sub>3</sub> ) <sub>3</sub>			Co oxalate + Zn oxalate + Al(NO <sub>3</sub> ) <sub>3</sub>		
Method	AC			A			ACB			AC		
Firing	9h. 1100° - 7h. 700°			15h. 1100°			30h. 1100°			4h. 1100° - 7h. 700°		
Atm.	air			O <sub>2</sub>			O <sub>2</sub>			O <sub>2</sub>		
M <sub>A</sub>	180			177			237			358		
χ <sub>D</sub> ·10 <sup>3</sup>	-0.08			-0.08			-0.10			-0.15		
Magnetic data	T	χ <sub>A</sub> ·10 <sup>3</sup> exp.	χ <sub>A</sub> ·10 <sup>3</sup> calc.	T	χ <sub>A</sub> ·10 <sup>3</sup> exp.	χ <sub>A</sub> ·10 <sup>3</sup> calc.	T	χ <sub>A</sub> ·10 <sup>3</sup> exp.	χ <sub>A</sub> ·10 <sup>3</sup> calc.	T	χ <sub>A</sub> ·10 <sup>3</sup> exp.	χ <sub>A</sub> ·10 <sup>3</sup> calc.
		81	14.1	17.7	291	6.67	6.67	293	6.77	6.77	80	17.5
	195	8.59	9.04	380	5.35	5.33	439	4.75	4.77	195	9.30	9.71
	289	6.58	6.54	409	5.10	5.02	553	3.94	3.92	289	6.76	6.76
	293	6.48	6.47	530	4.04	4.04	640	3.47	3.47	293	6.63	6.67
	353	5.54	5.54	684	3.28	3.27	743	3.07	3.08	420	4.84	4.83
	398	5.03	5.01	779	2.95	2.95	868	2.71	2.72	546	3.86	3.84
	464	4.42	4.42	850	2.74	2.75	967	2.47	2.50	699	3.12	3.11
	553	3.85	3.82	996	2.40	2.42	1071	2.32	2.32	773	2.87	2.87
	631	3.41	3.43	1085	2.27	2.27	1172	2.17	2.17	808	2.76	2.76
	743	2.98	3.01	1130	2.19	2.20				926	2.50	2.48
	840	2.71	2.73	1192	2.10	2.11				1000	2.31	2.31
	935	2.50	2.51							1070	2.19	2.21
	1034	2.33	2.32							1197	2.04	2.03
	1073	2.26	2.26									
A·10 <sup>3</sup>	0.50			0.46			0.56			0.51		
θ	-33°K.			-35°K.			-14°K.			-4°K.		
C·10 <sup>3</sup>	1940			2023			1905			1830		
μ	3.94 μ <sub>B</sub>			4.02 μ <sub>B</sub>			3.88 μ <sub>B</sub>			3.83 μ <sub>B</sub>		

Table 5.1. (continued 1)

Substance	$\text{Co}_{0.40}\text{Zn}_{0.60}\text{Al}_2\text{O}_4$			$\text{Co}_{0.20}\text{Zn}_{0.80}\text{Al}_2\text{O}_4$ I.			$\text{Co}_{0.20}\text{Zn}_{0.80}\text{Al}_2\text{O}_4$ III.			$\text{Co}_{0.170}\text{Zn}_{0.830}\text{Al}_2\text{O}_4$		
Prepared from:	Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$			Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$			Co $(\text{NO}_3)_2$ + Zn $(\text{NO}_3)_2$ + $\text{Al}(\text{NO}_3)_3$			Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$		
Method	AC			AC			A			AC		
Firing	4h. 1100° - 7h. 700°			4h. 1100° - 7h. 700°			12h. 1100°			7h. 1100°		
Atm.	air			air			air			air		
$M_A$	452			913			916			1071		
$\chi_D \cdot 10^3$	-0.18			-0.38			-0.38			-0.45		
Magnetic data	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.
		83	18.0	21.7	80	20.7	27.1	83	20.9	25.5	80	24.1
	292	6.65	6.65	192	10.03	10.5	288	7.30	7.25	289	8.10	8.12
	420	4.79	4.78	289	6.99	6.99	288	7.25	7.25	418	5.67	5.67
	518	3.99	3.98	292	7.01	6.92	424	5.03	5.01	532	4.50	4.51
	635	3.35	3.33	407	5.09	5.04	575	3.78	3.78	717	3.44	3.44
	744	2.92	2.92	451	4.60	4.58	686	3.21	3.23	773	3.25	3.22
	843	2.63	2.63	523	4.06	4.00	734	3.04	3.04	939	2.69	2.72
	971	2.33	2.35	624	3.50	3.42	893	2.55	2.56	1075	2.42	2.43
	1080	2.15	2.16	638	3.35	3.35	991	2.33	2.35	1197	2.20	2.23
	1188	2.01	2.01	741	2.95	2.94	1050	2.24	2.24			
				809	2.70	2.73	1195	2.04	2.01			
				926	2.44	2.44						
				1015	2.24	2.26						
				1108	2.11	2.11						
				1194	2.03	1.99						
$A \cdot 10^3$	0.48			0.46			0.38			0.46		
$\theta$	-3°K.			+12°K.			+6°K.			+17°K.		
$C \cdot 10^3$	1820			1809			1938			2090		
$\mu$	3.82 $\mu_B$			3.80 $\mu_B$			3.94 $\mu_B$			4.08 $\mu_B$		

Table 5.1. (continued 2)

Substance	$\text{Co}_{0.100}\text{Zn}_{0.900}\text{Al}_2\text{O}_4$			$\text{Co}_{0.055}\text{Zn}_{0.945}\text{Al}_2\text{O}_4$			$\text{Co}_{0.032}\text{Zn}_{0.968}\text{Al}_2\text{O}_4 \cdot \text{I.}$			$\text{Co}_{0.033}\text{Zn}_{0.967}\text{Al}_2\text{O}_4 \cdot \text{II.}$		
Prepared from:	Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$			Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$			Co oxalate + Zn oxalate + $\text{Al}(\text{NO}_3)_3$			$\text{Co}(\text{NO}_3)_2 + \text{Zn}(\text{NO}_3)_2 +$ $\text{Al}(\text{NO}_3)_3$		
Method	AC			AC			AC			A		
Firing	4h. 1100° - 7h. 700°			4h. 1100° - 7h. 700°			4h. 1100° - 7h. 700°			8h. 1100°		
Atm.	air			air			air			air		
$M_A$	1814			3330			5660			5490		
$\chi_D \cdot 10^3$	-0.76			-1.38			-2.34			-2.27		
Magnetic data	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	T	$\chi_A \cdot 10^3$	T	$\chi_A \cdot 10^3$ exp.			
	84	23.4	30.3	84	23.0	83	22.9	81	22.4			
	290	7.97	7.97	289	7.44	288	7.3	292	7.1			
	296	7.84	7.81	294	7.45	293	7.2					
	419	5.55	5.58									
	523	4.58	4.53									
	633	3.82	3.81									
	738	3.29	3.33									
	810	3.10	3.07									
	972	2.61	2.63									
	1090	2.44	2.40									
$A \cdot 10^3$	0.48			For meaning of letters and symbols see tables 3.1. and 4.1.								
$\theta$	+15°K.											
$C \cdot 10^3$	2059											
$\mu$	4.06 $\mu_B$											

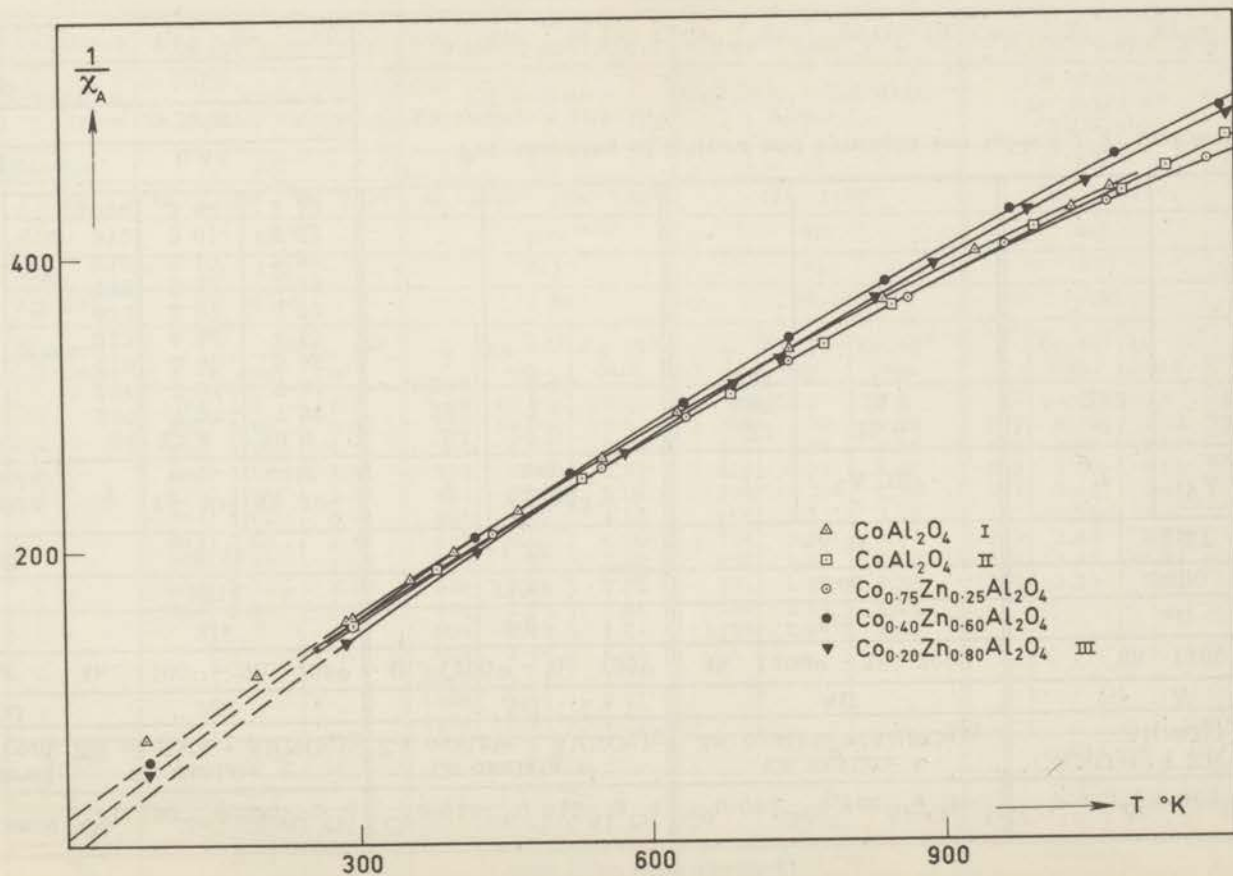


FIGURE 5.1.

### 5.3. Discussion

From fig. 5.1 it may be seen that all the mixed crystals of  $\text{CoAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  behave in the same manner as  $\text{CoAl}_2\text{O}_4$  itself. We discussed in chapter IV the four possibilities which may cause the bending of the  $1/\chi$ -T plots of the mixed crystals  $(\text{Co}, \text{Zn})\text{O}$ . The assumption that the curves may be Néel hyperbolae can be excluded beforehand (see section 4.3). The hypothesis that  $\text{Co}^{2+}$  ions shift to other crystallographic positions is a more probable possibility in a spinel than in a wurtzite structure. In fact, this supposition is made by Greenwald, Pickart and Granis<sup>32)</sup>. They have drawn two different straight lines through a series of  $1/\chi$  points which actually lie on a smooth curve. Table 5.1 shows how excellent the susceptibilities of all our substances can be represented by the formula  $\chi = A + \frac{C}{T-\theta}$ , where A as well as C are fairly constant throughout the whole series of dilutions and are practically the same as the constants A and C found for the mixed crystals  $(\text{Co}, \text{Zn})\text{O}$ , as may be observed by comparing the tables 4.3 and 5.1.

From all our experimental data, it is evident that in the Co-Zn aluminates the  $\text{Co}^{2+}$  ions occupy the tetrahedral interstices of the spinel structure. This observation is in excellent agreement with the conclusion of Romeyn<sup>31)</sup> that  $\text{CoAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  both are normal spinels. As for the observations of Greenwald *et al.*, we may notice that the experimental data agree in so far as the shapes of the  $1/\chi$ -T curves are compared, although our  $\chi$  values are somewhat lower. We must conclude, however, that these authors have made a wrong interpretation of the experimental facts, as they have neglected the temperature-independent paramagnetism of  $\text{Co}^{2+}$  ions in tetrahedral interstices.

We did not observe any influence within the experimental errors of the heat treatment of the sample on its magnetic behaviour. The substances quenched from  $1100^\circ\text{C}$ . and those tempered at  $700^\circ\text{C}$ . show no important difference in the values of A and C. As we have not quenched our samples from a higher temperature than  $1100^\circ\text{C}$ ., we cannot exclude the possibility that at more elevated temperatures a partial inversion occurs. This might be the reason that Greenwald *et al.* observe a difference in X-ray intensities between a sample quenched from  $1400^\circ\text{C}$ . and a tempered one. We must make the same remarks as in chapter IV concerning the temperature dependence of the magnetic moment of the  $\text{Co}^{2+}$  ions. In the higher temperature region, the influence of a slight temperature dependence remains possible.

We will now mention briefly two points which might be of interest.

a) The values of  $\theta$  are in some cases positive. We cannot say whether this is an effect of a wrong calculation of the constants from the experimental data or a real indication of some positive coupling effects when the  $\text{Co}^{2+}$  ions become further apart. The occurrence of the temperature-independent term, however, makes

the calculation of the Curie temperature too inaccurate to be able to decide if such an effect exists.

b) As already mentioned in the experimental part, we used our own diamagnetic correction. We found for  $ZnAl_2O_4$  a diamagnetism of  $-0.076 \cdot 10^{-3}$  e.m.u./mol. and used the same value for  $CoAl_2O_4$ . Greenwald, Pickart and Grannis 32) mention exactly the same value. No measurements on pure synthetic  $ZnAl_2O_4$  are known in the literature. Originally we used the correction tables of Klemm 12). The result was a value of A decreasing from  $-0.50 \cdot 10^{-3}$  to  $-0.20 \cdot 10^{-3}$  e.m.u. with increasing dilution of cobalt ions. The  $\chi_A$  values at room temperature showed a similar decrease beyond the dilution of 10% Co. Both effects were strong evidence for a wrongly-introduced diamagnetic correction, which was confirmed by the determination of the susceptibility of  $ZnAl_2O_4$ . The same effect has been discussed already for  $ZnO$  (see section 4.3).

### Summary of Chapter V

$CoAl_2O_4$  and mixed crystals of this compound with  $ZnAl_2O_4$  were subjected to susceptibility measurements up to  $1200^\circ K$ . The experimental data could be represented by the formula  $\chi = A + \frac{C}{T-\theta}$ . The temperature-independent term A ranged from  $0.46 - 0.56 \cdot 10^{-3}$  with one deviating value of  $0.38 \cdot 10^{-3}$  e.m.u., and the magnetic moment of  $Co^{2+}$  calculated from the Curie constants with the aid of the formula  $\mu = \sqrt{8C} \mu_B$  was found to be 3.80 to 4.08 Bohr magnetons. The values of A and  $\mu$  are in excellent agreement with those found for  $(Co,Zn)O$ . We concluded that  $CoAl_2O_4$  is a normal spinel in agreement with the X-ray measurements of Romeyn 31), and contrary to the conclusion of Greenwald *et al.* 32) from X-ray work and magnetic measurements.

## Chapter VI

### THE SYSTEM $\text{CoAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$

#### 6.1. Introduction

This series of mixed crystals has not, as far as we know, been investigated. Romeyn <sup>31</sup>), who did an extensive X-ray analysis of a series of mixed aluminates, investigated, in the case of  $\text{CoAl}_2\text{O}_4$ , only the effects of dilution with  $\text{ZnAl}_2\text{O}_4$  already discussed in chapter V. Although this system of mixed crystals is not of direct importance in relation to  $\text{Co}_3\text{O}_4$ , it seemed interesting to see whether there exists any difference in the effects of diluting  $\text{CoAl}_2\text{O}_4$ , with  $\text{MgAl}_2\text{O}_4$  or  $\text{ZnAl}_2\text{O}_4$ . Romeyn assumed  $\text{MgAl}_2\text{O}_4$  to be a normal spinel and our conclusion from the preceding chapter is that  $\text{CoAl}_2\text{O}_4$  is also a normal spinel. The latter conclusion is in agreement with the observation of Romeyn <sup>31</sup>) and contrary to the conclusions of Greenwald, Pickart and Grannis <sup>32</sup>).

#### 6.2. Experimental part

Three substances with the general formula  $(\text{Co,Mg})\text{Al}_2\text{O}_4$  were prepared according to the methods described in chapter I. Details of the preparations are given in table 6.1. The lattice constants of two of the substances were determined by means of the Unicam 9 cm powder camera. The extrapolation method of van Arkel <sup>33</sup>) was applied to five high angle reflections. The diamagnetic corrections are calculated according to own measurements on  $\text{MgAl}_2\text{O}_4$ . The results of the magnetic measurements are collected in table 6.2 and fig. 6.1. In table 6.3 the values are given of the constants A, C and  $\theta$  used to calculate  $\chi_A$  according to the formula

$$\chi_A = A + \frac{C}{T-\theta}$$

The constants for the compounds  $\text{CoAl}_2\text{O}_4$  I and II are given in the same table for comparison.

#### 6.3. Discussion

In the same way as with the cobalt-zinc oxides and the cobalt-zinc aluminates, the cobalt-magnesium aluminates show a temperature-independent paramagnetism and a temperature-dependent magnetism which can be described by a Curie-Weisz law. Actually, the calculated  $1/\chi$ -T curve fits the experimental data better than for any other substance so far discussed, as may be seen from table 6.2.

Table 6.1.

Substance	Prepared from	Method	Firing	Atm.	$\Delta w$ in %	Structure	MA	$\chi_D \cdot 10^3$
$\text{Co}_{0.503}\text{Mg}_{0.497}\text{Al}_2\text{O}_4$	Co-oxalate MgO and $\text{Al}(\text{NO}_3)_3$	AC	4h. 1100° 7h. 700°	air	-	Spinel $a = 8.093 \text{ \AA}$	318	-0.10
$\text{Co}_{0.20}\text{Mg}_{0.80}\text{Al}_2\text{O}_4$	$\text{Co}(\text{NO}_3)_2$ $\text{Mg}(\text{NO}_3)_2$ $\text{Al}(\text{NO}_3)_3$	A	7h. 1100°	air	-0.15	Spinel $a = 8.089 \text{ \AA}$	745	-0.24
$\text{Co}_{0.10}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$	$\text{Co}(\text{NO}_3)_2$ $\text{Mg}(\text{NO}_3)_2$ $\text{Al}(\text{NO}_3)_3$	A	12h. 1100°	air	-0.15	Spinel	1460	-0.48

Table 6.2.

$\text{Co}_{0.503}\text{Mg}_{0.497}\text{Al}_2\text{O}_4$			$\text{Co}_{0.20}\text{Mg}_{0.80}\text{Al}_2\text{O}_4$			$\text{Co}_{0.10}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$		
T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.	T	$\chi_A \cdot 10^3$ exp.	$\chi_A \cdot 10^3$ calc.
81	19.5	20.9	82	23.4	25.2	82	25.2	27.8
290	7.62	7.62	292	7.88	7.88	288	8.17	8.17
408	5.79	5.69	412	5.73	5.72	407	5.85	5.86
519	4.63	4.62	568	4.28	4.26	516	4.66	4.67
645	3.84	3.84	702	3.51	3.51	645	3.81	3.79
779	3.27	3.27	862	2.92	2.92	747	3.27	3.30
907	2.89	2.88	990	2.57	2.58	885	2.80	2.83
997	2.67	2.67	1096	2.36	2.36	1014	2.48	2.50
1097	2.47	2.47	1193	2.20	2.20	1150	2.26	2.23
1196	2.30	2.30						

For meaning of letters and symbols see tables 3.1. and 4.1.



Table 6.3.

Substance	Firing	A. $10^3$	$\theta$	C. $10^3$	$\mu$
$\text{CoAl}_2\text{O}_4$ I	1100° - 700°	0.50	-33	1942	3.94
$\text{CoAl}_2\text{O}_4$ II	1100° - quenched	0.46	-35	2023	4.02
$\text{Co}_{0.503}\text{Mg}_{0.497}\text{Al}_2\text{O}_4$	1100° - 700°	0.41	-32	2321	4.31
$\text{Co}_{0.20}\text{Mg}_{0.80}\text{Al}_2\text{O}_4$	1100° - quenched	0.29	-10	2292	4.28
$\text{Co}_{0.10}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$	1100° - quenched	0.24	-1	2291	4.28

Three important aspects of the magnetic behaviour of these substances need some comment.

a) The values found for the magnetic moment of the Co ions are larger than those found in the Co-Zn oxides and the Co-Zn aluminates, the difference being approximately 0.3 Bohr magnetons. This value of  $4.3 \mu_B$  lies between the spin-only value and the value found for  $\text{Co}^{2+}$  ions in octahedral interstices. Our assumption is that in the Co-Mg aluminates the  $\text{Co}^{2+}$  ions partially occupy the octahedral interstices; in other words these spinels are partially inverse.

Perhaps the colour difference between the Co-Zn aluminates and the Co-Mg aluminates (a more bright blue in the latter case) is a consequence of this difference in ionic distribution. The red colour of  $\text{Co}^{2+}$  ions in octahedral interstices may cause a shift to a more violet blue.

This conclusion seems rather surprising, for if  $\text{MgAl}_2\text{O}_4$  is indeed a normal spinel there is no reason why the system  $(\text{Co}, \text{Mg})\text{Al}_2\text{O}_4$  should behave a different way than  $(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$ . It is now interesting to note that from the neutron diffraction work of Bacon<sup>34)</sup> it does not necessarily follow that  $\text{MgAl}_2\text{O}_4$  is a 100% normal spinel. We will therefore take the following table from Bacon's paper, in which the calculated intensities for the normal and the inverse structure are obtained for a value of the  $u$  parameter of 0.387 which is well-established by the neutron diffraction experiments of Bacon himself as well as by earlier X-ray work by Barth and Posnjak<sup>35)</sup>. The  $u$  parameter in a spinel lattice determines the position of the anions; for  $u = 0.375$  the anions form a ideal close-packed lattice; for  $u > 0.375$  the tetrahedral holes become bigger and the octahedral holes become smaller and slightly distorted.

As may be seen from table 6.4, all the values of the experimental intensities (except one) lie between those calculated for the two different arrangements of cations, although the values for the normal structure are best approximated. On the basis of these data it is not permissible to exclude a partly inverse structure.

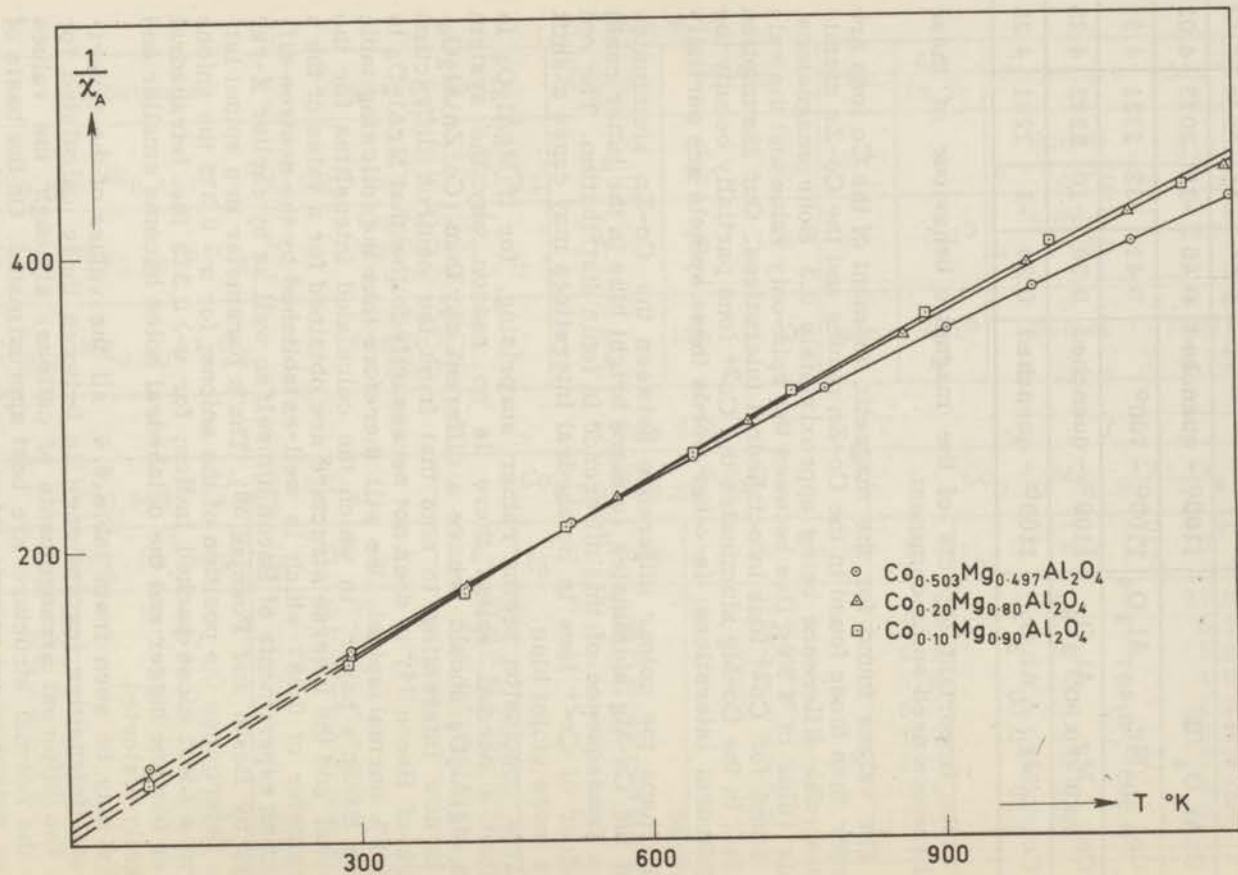


FIGURE 6.1.

Table 6.4.

Reflections	Intensity calc. for normal arrangement	Intensity exp.	Intensity calc. for inverse arrangement
111	11	11 + 3	41
220	41	36 + 4	21
311 + 222	202	194 + 5	163
400	176	188 + 5	230
511 + 333	138	226 + 8	130
440 + 531	369	352 + 6	384
Ratio $\frac{311 + 222}{220}$	4.9	5.4	7.8
Ratio $\frac{311 + 222}{111}$	18.3	17.5	4.0
Ratio $\frac{220}{111}$	3.7	3.3	0.5
Ratio $\frac{311 + 222}{400}$	1.15	1.03	0.71

We determined, as already mentioned in the experimental part, the lattice constants of two of the mixed crystals and compared them with the values calculated according to Vegard's law, which states that the lattice constants of mixed crystals shall be linear functions of their compositions. We used in the calculation Romeyn's values for  $\text{CoAl}_2\text{O}_4$ :  $a = 8.105 \text{ \AA}$ , for  $\text{MgAl}_2\text{O}_4$ :  $a = 8.086 \text{ \AA}$ . The results are as follows:  $\text{Co}_{0.503}\text{Mg}_{0.497}\text{Al}_2\text{O}_4$ :  $a_{\text{exp.}} = 8.093 \text{ \AA}$ ,  $a_{\text{calc.}} = 8.096 \text{ \AA}$ ;  $\text{Co}_{0.200}\text{Mg}_{0.800}\text{Al}_2\text{O}_4$ :  $a_{\text{exp.}} = 8.089 \text{ \AA}$ ,  $a_{\text{calc.}} = 8.090 \text{ \AA}$ . If there exists any deviation from Vegard's law it is very small, and from the observed data we may not conclude with certainty that such a deviation exists.

From the mean magnetic moment we are able to estimate the percentage of inversion in the following way:

$$(1 - \delta)(\mu_{\text{tetr.}})^2 + \delta(\mu_{\text{oct.}})^2 = (\bar{\mu})^2;$$

$$(1 - \delta)4^2 + \delta 5^2 = (4.3)^2;$$

$$\delta = 0.3$$

We have used in this calculation 4 and 5 Bohr magnetons for

$\mu_{\text{tet.}}$  and  $\mu_{\text{oct.}}$ , respectively. Thus, about 70% of the  $\text{Co}^{2+}$  ions must occupy the tetrahedral and about 30% the octahedral holes to account for the experimental moment. We must remark that this value of 30% is probably the maximum that is required. If the moment in tetrahedra is  $4.1 \mu_B$  and the moment in octahedra is larger than  $5 \mu_B$  a much smaller percentage of inversion is sufficient.

b) As may be seen from table 6.3, quenching or annealing the sample has no influence on the magnitude of the mean magnetic moment.

c) The constant A decreases with increasing dilution, although we have used our own diamagnetic correction, determined from a direct measurement on  $\text{MgAl}_2\text{O}_4$ . No good measurement on pure synthetic  $\text{MgAl}_2\text{O}_4$  could be found in the literature.

We have seen that the use of the corrections of Klemm 12) resulted in a similar decrease in A for the cobalt-zinc aluminates. A direct measurement on  $\text{ZnAl}_2\text{O}_4$  revealed that these corrections were too small. We must conclude from this decrease in A that for  $\text{MgAl}_2\text{O}_4$  our own diamagnetic correction is probably also too small. A comparison of the differences between our values and those of Klemm for both  $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  supports this view.

	$\chi_D \cdot 10^3$ (Klemm)	$\chi_D \cdot 10^3$ (own value)
$\text{ZnAl}_2\text{O}_4$	-0.050	-0.076
$\text{MgAl}_2\text{O}_4$	-0.043	-0.048

Introducing a value for  $\text{MgAl}_2\text{O}_4$  of  $-0.065 \cdot 10^{-3}$ , based on the value of Klemm and the difference found for  $\text{ZnAl}_2\text{O}_4$  we obtain A values of 0.45, 0.38 and  $0.41 \cdot 10^{-3}$  e.m.u. for the three different substances, which are very satisfactory magnitudes.

Comparing the results of chapters III, IV, V and VI we notice the remarkable fact that the diamagnetic corrections determined for  $\text{ZnO}$  and  $\text{ZnAl}_2\text{O}_4$  appear to be much better than those obtained for  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ . The measurements on such very weakly magnetic substances are very inaccurate and the slightest paramagnetic impurity may cause appreciable errors.

## Summary of Chapter VI

Mixed crystals of  $\text{CoAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  were made in the ratios 1 : 1, 1 : 4 and 1 : 9.

Susceptibility measurements were carried out from 80-1200°K to investigate the influence of dilution with  $\text{MgAl}_2\text{O}_4$  on the magnetic behaviour of  $\text{CoAl}_2\text{O}_4$ .

The magnetic data could be represented by the formula

$$\chi = A + \frac{C}{T - \theta}$$

The value of A (temperature-independent paramagnetism) varied from  $0.41 \cdot 10^{-3}$  to  $0.24 \cdot 10^{-3}$  e.m.u. per Co atom. This decrease in A on increasing dilution is perhaps a consequence of a wrong diamagnetic correction.

For the mean magnetic moment a value of  $4.3 \mu_B$  was found. The conclusion was drawn that the mixed crystals  $(Co, Mg)Al_2O_4$  are partially inverse spinels to a maximum of 30%.  $MgAl_2O_4$  itself was also suggested to be partially inverse. Neutron diffraction experiments of Bacon <sup>4</sup>) tend to the same conclusion. A deviation from Vegard's law could not be detected with certainty.

## Chapter VII

### THE SYSTEMS $\text{ZnAl}_2\text{O}_4$ - $\text{ZnCo}_2\text{O}_4$ , $\text{ZnCo}_2\text{O}_4$ AND $\text{ZnCo}_2\text{O}_4$ - $\text{Co}_3\text{O}_4$

#### 7.1. Introduction

The investigation of these systems was undertaken in direct connection with  $\text{Co}_3\text{O}_4$ . Indeed, the successive substitution of all the cations in  $\text{ZnAl}_2\text{O}_4$  by cobalt has led to a final elucidation of the problems concerning  $\text{Co}_3\text{O}_4$ . As far as we know these mixed crystals have not yet been investigated magnetically. Crystallographic work has been done on the three pure components, which turned out to be spinels.

The work on  $\text{ZnAl}_2\text{O}_4$  has already been discussed in chapter V. For the present purpose it is important to know that this substance is a normal 2-3 spinel.

Holgerson and Karlsson<sup>36)</sup> prepared for the first time a series of cobaltites, among them  $\text{ZnCo}_2\text{O}_4$ , and determined the crystal structure. The mixed crystals of  $\text{ZnCo}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  were investigated by Robin<sup>3)</sup>. These mixed crystals and  $\text{ZnCo}_2\text{O}_4$  itself can only be prepared from a mixture of the nitrates, and the temperature of firing must be lower than 550-650°C. A mixture of  $\text{ZnO}$  and  $\text{Co}_3\text{O}_4$  is obtained when a mixture of the oxalates is fired or when the mixture of nitrates is heated at too high a temperature. Mixed crystals with spinel structure and a Zn-Co ratio higher than 1 : 2 could not be prepared. For this reason Robin assumes  $\text{ZnCo}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  to be normal 2-3 spinels. The pure substance  $\text{Co}_3\text{O}_4$  is discussed separately in chapter VIII.

#### 7.2. Experimental part

For most of the details we may refer to the tables 7.1, 7.2 and 7.3, and to fig. 7.1. All the data concerning the mixed crystals  $\text{Zn}(\text{Co}, \text{Al})_2\text{O}_4$  are collected in table 7.1. As may be seen from this table, the Debye-Scherrer diagrams were not very good and in most cases the strongest ZnO reflections were just visible. Apparently the substances are not homogeneous. For our purpose however, the quality appeared to be sufficient. Magnetic measurements were performed only at liquid air and room temperature, as the substances were so weakly magnetic that even at room temperature the  $\chi_g$  value was comparable with that of the empty quartz vessels.

The data for the pure zinc cobaltites and two zinc cobaltites with 5% excess ZnO are given in table 7.2. Here too the Debye-Scherrer diagrams were poor, but became better when the original substances were fired at higher temperatures, mostly in sealed tubes

Table 7.1.

Substance	Prepared from	Firing	Atm.	$\Delta w$ in %	Structure	M	$\chi_D \cdot 10^3$	Magnetic data	
$Zn[Co_{0.3}Al_{1.7}]O_4$	Zn(NO <sub>3</sub> ) <sub>2</sub> Co(NO <sub>3</sub> ) <sub>2</sub> Al(NO <sub>3</sub> ) <sub>3</sub>	1h. 600°C 24-36h. 325°C	O <sub>2</sub>	+4.1	spinel faint D. S. diagram ZnO lines present	193	-0.053	T	$\chi_M \cdot 10^3$
								82 287	0.46 0.16
$Zn[Co_{0.3}Al_{1.7}]O_4$ H	$Zn[Co_{0.3}Al_{1.7}]O_4$	3h. 620°C	O <sub>2</sub>	+1.0	spinel faint D. S. diagram ZnO lines present	193	-0.053	T	$\chi_M \cdot 10^3$
								80 291	0.52 0.16
$Zn[Co_{0.5}Al_{1.5}]O_4$	Zn(NO <sub>3</sub> ) <sub>2</sub> Co(NO <sub>3</sub> ) <sub>2</sub> Al(NO <sub>3</sub> ) <sub>3</sub>	1h. 600°C 24-36h. 325°C	O <sub>2</sub>	+3.0	spinel faint D. S. diagram ZnO lines present	199	-0.054	T	$\chi_M \cdot 10^3$
								80 287	0.75 0.28
$Zn[Co_{0.5}Al_{1.5}]O_4$ H	$Zn[Co_{0.5}Al_{1.5}]O_4$	3h. 620°C	O <sub>2</sub>	+1.0	spinel faint D. S. diagram ZnO lines present	199	-0.054	T	$\chi_M \cdot 10^3$
								80 291	0.79 0.28
$Zn[Co_{0.67}Al_{1.33}]O_4$	Zn(NO <sub>3</sub> ) <sub>2</sub> Co(NO <sub>3</sub> ) <sub>2</sub> Al(NO <sub>3</sub> ) <sub>3</sub>	24h. 350°C 3h. 650°C	air O <sub>2</sub>	+3.0	spinel faint D. S. diagram no ZnO detectable	205	-0.055	T	$\chi_M \cdot 10^3$
								80 291	0.81 0.29

M = molecular weight per formula unit AB<sub>2</sub>O<sub>4</sub>

$\chi_D$  = diamagnetic correction per formula unit AB<sub>2</sub>O<sub>4</sub>

$\chi_M$  = susceptibility per formula unit AB<sub>2</sub>O<sub>4</sub> corrected for diamagnetism.

The other symbols have the same meaning as in table 4.1.

Table 7.2.

Substance	Prepared from	Method	Structure	M	$\chi_D \cdot 10^3$	Other remarks									
ZnCo <sub>2</sub> O <sub>4</sub> series A4	Co-oxalate Zn-oxalate	C	spinel, faint D. S. diagram, becomes better on further heating	247	-0.066										
ZnCo <sub>2</sub> O <sub>4</sub> series A7	Co-oxalate Zn-oxalate	C	spinel, rather sharp D. S. diagram, ZnO lines not visible	247	-0.066										
ZnCo <sub>2</sub> O <sub>4</sub> · 0.05ZnO A9	Co-oxalate Zn-oxalate	C	spinel, faint D. S. diagram	251	-0.067	firing: 3h. 350°C 4h. 680°C in O <sub>2</sub>									
ZnCo <sub>2</sub> O <sub>4</sub> · 0.05ZnO A10	Co-oxalate Zn-oxalate	C	spinel	251	-0.067	firing: 3h. 610°C									
Substance	ZnCo <sub>2</sub> O <sub>4</sub> · A4	ZnCo <sub>2</sub> O <sub>4</sub> · A4A	ZnCo <sub>2</sub> O <sub>4</sub> · A4B	ZnCo <sub>2</sub> O <sub>4</sub> · A4C	ZnCo <sub>2</sub> O <sub>4</sub> · A4D	ZnCo <sub>2</sub> O <sub>4</sub> · A7	ZnCo <sub>2</sub> O <sub>4</sub> · A7A								
Firing	9h. 350°C	20h. 420°C	16h. 510°C	1h. 500-600°C	3h. 700°C	2h. 350°C 4h. 620°C	3h. 700°C								
Atm.	O <sub>2</sub>	sealed tube O <sub>2</sub>	sealed tube O <sub>2</sub>	sealed tube O <sub>2</sub>	sealed tube O <sub>2</sub>	O <sub>2</sub>	O <sub>2</sub>								
Magnetic data	T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$			
ZnCo <sub>2</sub> O <sub>4</sub> · A9	80	5.74	80	4.49	80	4.20	81	4.12	80	4.07	82	2.70	83	2.30	
	291	2.32	294	1.90 <sup>7</sup>	295	1.81	292	1.75	293	1.59	294	1.07 <sup>3</sup>	291	0.89 <sup>4</sup>	
T	$\chi_M \cdot 10^3$	397	1.83	388	1.52 <sup>5</sup>	289	1.85	457	1.27	288	1.64	293	1.08 <sup>7</sup>	492	0.62 <sup>5</sup>
		457	1.66	510	1.25	375	1.51 <sup>5</sup>	529	1.15	374	1.32 <sup>5</sup>	375	0.90 <sup>9</sup>	641	0.54 <sup>7</sup>
81	5.33	552	1.43	599	1.12	529	1.17	646	1.00	513	1.04 <sup>8</sup>	506	0.74 <sup>4</sup>	417	0.70 <sup>1</sup>
290	2.36	773	0.90	691	1.02	675	1.00 <sup>6</sup>			631	0.91 <sup>3</sup>	635	0.65 <sup>0</sup>	745	0.51 <sup>5</sup>
						764	0.95			826	0.78 <sup>3</sup>	744	0.60 <sup>0</sup>	865	0.49 <sup>2</sup>
ZnCo <sub>2</sub> O <sub>4</sub> · A10														981	0.51 <sup>1</sup>
														1068	0.62 <sup>2</sup>
T	$\chi_M \cdot 10^3$														
287	2.10														

For meaning of symbols see table 7.1.



Tables 7.3.

$\text{Co}_{0.125}\text{Zn}_{0.875}\text{Co}_2\text{O}_4$ A5		$\text{Co}_{0.125}\text{Zn}_{0.875}\text{Co}_2\text{O}_4$ A5A		$\text{Co}_{0.033}\text{Zn}_{0.967}\text{Co}_2\text{O}_4$ series MI				
Prepared from: Co-oxalate Zn-oxalate		Prepared from: product A5		Prepared from: Co-oxalate Zn-oxalate		firing	T	$\chi_M \cdot 10^3$
Method: C M = 247 $\chi_D \cdot 10^3 = -0.066$		M = 247 $\chi_D \cdot 10^3 = -0.066$		Method: C M = 247 $\chi_D \cdot 10^3 = -0.066$	MIA	3h. 620°C, O <sub>2</sub>	292	2.27
Structure: spinel		Structure: spinel			MIB	3h. 670°C, O <sub>2</sub>	291	1.93
firing: 3h. 350°C in O <sub>2</sub>		firing: 3h. 650-700°C sealed tube O <sub>2</sub>			MIC	12h. 670°C, O <sub>2</sub>	291	1.72
Magnetic data		Magnetic data		$\text{Co}_{0.095}\text{Zn}_{0.905}\text{Co}_2\text{O}_4$ series MII				
T	$\chi_M \cdot 10^3$	T	$\chi_M \cdot 10^3$	Prepared from: Co-oxalate Zn-oxalate		firing	T	$\chi_M \cdot 10^3$
80	5.60	82	4.16	Method: C	MIIA	3h. 670°C, O <sub>2</sub>	291	1.95
295	2.10	294	1.57	M = 247	MIIB	3h. 700°C, O <sub>2</sub>	291	1.85
291	2.18 <sup>8</sup>	292	1.59	$\chi_D \cdot 10^3 = -0.066$	MIIIC	6h. 700°C, O <sub>2</sub>	290	1.82
372	1.73 <sup>7</sup>	374	1.30 <sup>5</sup>	$\text{Co}_{0.193}\text{Zn}_{0.807}\text{Co}_2\text{O}_4$ series MIII				
507	1.35 <sup>2</sup>	519	1.02 <sup>7</sup>	Prepared from: Co-oxalate Zn-oxalate		firing	T	$\chi_M \cdot 10^3$
634	1.11 <sup>4</sup>	628	0.90 <sup>4</sup>	Method: C	MIIIA	3h. 670°C, O <sub>2</sub>	290	2.32
782	0.87 <sup>8</sup>	718	0.83 <sup>5</sup>	M = 246	MIIIB	3h. 700°C, O <sub>2</sub>	291	2.24
872	0.79 <sup>4</sup>	805	0.80 <sup>8</sup>	$\chi_D \cdot 10^3 = -0.066$	MIIIC	6h. 700°C, O <sub>2</sub>	291	2.18

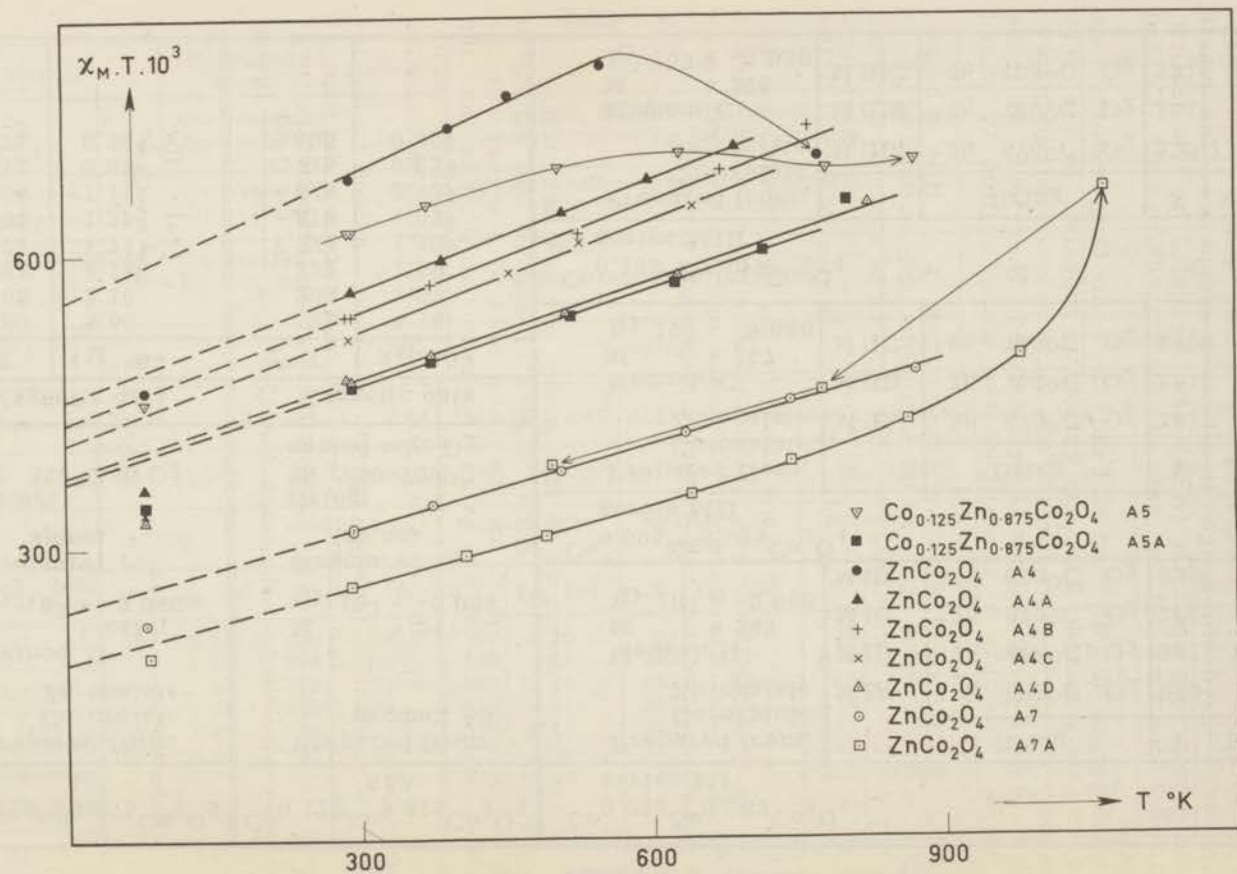


FIGURE 7.1.

under oxygen. We will now draw attention to the remarkable fact that at the same time the paramagnetism of these substances decreased, sometimes to extremely low values.

The samples were measured in sealed quartz containers, which were filled with oxygen in all cases except one. The quartz vessel containing  $\text{ZnCo}_2\text{O}_4$  (A7A) was evacuated before sealing. Table 7.3 contains all the data on the mixed crystals (Co,Zn)  $\text{Co}_2\text{O}_4$ .

In the series MI, MII, and MIII only the room temperature value of  $\chi$  was determined. The susceptibility appeared to be very dependent on the heat treatment, and there are reasons to believe that none of the substances is well-defined. Therefore, we made no further attempts to investigate the whole system of mixed crystals of  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ .

In fig. 7.1 we used a plot of  $\chi_{\text{MT}}$  versus  $T$ . If it is to be expected that the value of  $\theta$  will be negligible, this method of plotting can be applied with success. The bending of some of the lines in fig. 7.1 is not caused by a finite value of  $\theta$ , but is caused by a chemical change in the sample. We will discuss this point in the following sections.

The diamagnetic corrections used for all the substances discussed in this chapter, are calculated according to the data of Klemm 12). An eventual error in these corrections will only affect the values of the temperature-independent term A.

### 7.3. Discussion of the system $\text{Zn}(\text{Co}, \text{Al})_2\text{O}_4$

Although the substances in this group are not completely homogeneous (most of the X-ray diagrams showed the strongest ZnO lines), they consist for the most part of a spinel with the general formula  $\text{ZnCo}_x\text{Al}_{2-x}\text{O}_4$ . The only condition is that the mean valence of the cobalt ions must be three and the possibility of an equal amount of  $\text{Co}^{2+}$  and  $\text{Co}^{4+}$  may not be excluded beforehand.

The susceptibility measurements, however, enabled us to decide between the two possibilities. We will compare the experimental values of the Curie constants at room temperature (neglecting  $\theta$ ) with those calculated for  $\text{Co}^{3+}$  and  $\frac{\text{Co}^{2+} + \text{Co}^{4+}}{2}$  (using spin-only values).

Substance with:	C (exp.) per Co	C (calc.) for $\text{Co}^{3+}$	C (calc.) for $\frac{\text{Co}^{2+} + \text{Co}^{4+}}{2}$
0.3 Co	0.16	3.0	3.1
0.5 Co	0.16	3.0	3.1
0.67 Co	0.125	3.0	3.1

Neither of the two possibilities seems to be a good approximation. The extremely low magnetism of these substances can only be explained by the assumption that the valence of cobalt is three,

but that the metal ion does not exhibit the normal paramagnetism of four unpaired electrons. Indeed, a practically non-magnetic cobalt is found in the numerous complex compounds in which Co is trivalent and surrounded by 6 NH<sub>3</sub>, 3 ethylenediamine, 6NO<sub>2</sub><sup>-</sup>, 3(COOH)<sub>2</sub><sup>-</sup> or other groups to which it is covalently bonded.

It is important to know that this non-magnetic state is only possible if Co is surrounded by six groups. The simplest way to explain this situation is with the aid of Pauling's d<sup>2</sup>sp<sup>3</sup> hybrids. Co<sup>3+</sup> has six 3d electrons. If this ion shares an electron pair with each of the six surrounding groups, the total number of electrons becomes 18. Then the 3d and the following 4s and 4p shells are completely occupied which causes an extra stability. At the same time the permanent magnetic moment disappears since all electrons are paired. Pauling proved that these d<sup>2</sup>sp<sup>3</sup> bonds point to the corners of a regular octahedron.

In the general discussion we will consider Pauling's method, its disadvantages in coordination lattices and the other methods which may be used for treatment of the problems. For the moment it is sufficient to note that in the octahedral interstices all the requirements are fulfilled for the occurrence of this binding mechanism.

We have yet to explain the small positive magnetism which is observed. The assumption is made that the magnetism is caused by the inhomogeneity of the samples. If ZnO can be detected by X-ray analysis a part of the cobalt must be in the divalent state, since in a spinel structure with only di- and trivalent ions the ratio of these ions has to be one to two.

In the following section, we shall see that although Co<sup>III</sup> in octahedral holes has no permanent moment, it is not completely diamagnetic. A small temperature-independent paramagnetism is found of about 0.1 · 10<sup>-3</sup> e. m. u. per Co<sup>III</sup>. Applying this correction to the Curie constants already mentioned, we obtain for ZnCo<sub>x</sub>Al<sub>2-x</sub>O<sub>4</sub>:

x = 0.3	C <sub>290°C</sub> = 0.12	C <sub>80°C</sub> = 0.12
x = 0.5	C <sub>290°C</sub> = 0.12	C <sub>80°C</sub> = 0.11
x = 0.67	C <sub>290°C</sub> = 0.09	C <sub>80°C</sub> = 0.08

From the agreement between the Curie constants at liquid air and room temperature, we may conclude that the neglect of  $\theta$  was admissible. As a second result of the calculation it follows that the observed weak paramagnetism can be explained with less than 6% of the total amount of cobalt in the divalent state. This estimation is based on a Curie constant for Co<sup>2+</sup> of 2.0, a value which is found in tetrahedral interstices.

All the experimental data can thus be explained by the assumption of the occurrence of Co<sup>III</sup>, which has no permanent magnetic moment.

#### 7.4. Discussion of the zinc cobaltites

After the discussion of the mixed crystals  $\text{Zn}(\text{Co}, \text{Al})_2\text{O}_4$ , the interpretation of the experimental results obtained with  $\text{ZnCo}_2\text{O}_4$  will be much easier. The very low value of the susceptibility is again a striking feature. The magnetic behaviour of these substances can be described by the general formula  $\chi = A + \frac{C}{T}$ . The assumption that  $\theta = 0$  is confirmed by the linearity of the  $\chi_M \cdot T$  versus  $T$  plots from which we can derive the constants  $A_M$  and  $C_M$  (per mol.  $\text{ZnCo}_2\text{O}_4$ ).

$\text{ZnCo}_2\text{O}_4$	$A_M \cdot 10^3$	$C_M$
A 4 A	0.37	0.450
A 4 B	0.37	0.426
A 4 C	0.37	0.405
A 4 D	0.33	0.372
A 7	0.28	0.237
A 7 A	0.26	0.183

The temperature-independent term  $A_M$  is attributed to the "covalent  $\text{Co}^{\text{III}}$  atoms", and the Curie constant to the occurrence of  $\text{Co}^{2+}$  ions. It appears, that  $A_M$  as well as  $C_M$  are very dependent on the heat treatment. Apparently the successive firings of the original substance  $\text{ZnCo}_2\text{O}_4(\text{A}4)$  had a different influence on the amount of  $\text{Co}^{2+}$  ions.

In general, the amount of  $\text{Co}^{2+}$  ions decreases as the firing temperature is raised. It seemed interesting to investigate whether a  $\text{ZnCo}_2\text{O}_4$  sample could be prepared without any  $\text{Co}^{2+}$  ions. The substances A7 and A 7 A approximate much better an "ideal"  $\text{ZnCo}_2\text{O}_4$ .

We did not succeed in making a better zinc cobaltite than the product A 7 A. As may be seen from table 7.2, the products A 9 and A 10 containing an excess ZnO are as bad as the substance A 4. Perhaps the excess ZnO is an extra stimulation for cobalt to become divalent by the possibility of forming mixed crystals (Co, Zn)O.

It is still an open question if it will be possible at all to prepare pure  $\text{ZnCo}_2\text{O}_4$  which will exhibit only temperature-independent paramagnetism.

We will finally discuss six points which require some comment.

a) The question may arise how it is possible that the oxidation from  $\text{Co}^{2+}$  to  $\text{Co}^{\text{III}}$  continues in sealed tubes. Apparently the substance A 4 with which this procedure is carried out to prepare A 4 A, A 4 B, A 4 C and A 4 D is not completely free from nitrate. If the hot tubes were taken out of the furnace a brown gas was visible above the solid substance. Actually the black substances obtained when the nitrates were preheated at  $350^\circ\text{C}$  in air lost their last small amounts of nitrous gases only on heating at more elevated temperatures.

b) The dependence on the heat treatment of the constant  $A_M$  is a consequence of the  $Co^{2+}$  ions present. We have seen in chapters IV and V that  $Co^{2+}$  ions in tetrahedral interstices exhibit besides their normal paramagnetism a temperature-independent paramagnetism of approximately 0.5 e. m. u. per Co. As the Curie constant  $C_M$  decreases from A 4 to A 7 A, the amount of  $Co^{2+}$  ions decreases and consequently the contribution of the temperature-independent paramagnetism of  $Co^{2+}$  must decrease. It is very reasonable to assume that the  $Co^{2+}$  ions in excess are situated in tetrahedral interstices. They may occupy the sites of the wurtzite structure of ZnO or the tetrahedral sites in a spinel of composition  $(Co, Zn)Co_2O_4$ .

A rough extrapolation of the constants  $A_M$  to pure  $ZnCo_2O_4$  indicates that the two  $Co^{III}$  atoms contribute  $0.2 \cdot 10^{-3}$  e. m. u. to  $\chi_M$ . Thus, per  $Co^{III}$ , a temperature-independent paramagnetism of  $0.1 \cdot 10^{-3}$  e. m. u. is found. This magnitude agrees well with that found for  $Co^{III}$  in complex compounds. Rosenbohm (37) obtained values from 0.055 to  $0.073 \cdot 10^{-3}$  for what he called a "paramagnetic increment". Asmussen (38) mentioned values of 0.070, 0.081, 0.090, 0.117, 0.060 and  $0.029 \cdot 10^{-3}$  in the series hexammine to hexacid complexes, and recently Kernahan and Sienko (39) investigated  $Co(NH_3)_5HCO_2I_2$  and  $Co(NH_3)_5NO_2I_2$  and found 0.141 and  $0.165 \cdot 10^{-3}$ , respectively.

c) A further support for the assumption of  $Co^{2+}$  ions in these substances is the deviation of the liquid air points in fig. 7.1. This deviation becomes smaller with decreasing  $C_M$  values, a consequence of the greater dilution of the  $Co^{2+}$  ions. Actually, the difference between the calculated and experimental value of  $\chi_{800K}$  for  $ZnCo_2O_4$  (A 7 A) is no more than 7.5%.

d) We are able to estimate the percentage  $Co^{2+}$  which must be present to account for the observed paramagnetism. Taking for the Curie constant of  $Co^{2+}$  in tetrahedral holes approximately 2.0, we obtain for the substance A 7 6% and for A 7 A 4.5%  $Co^{2+}$ , in excellent agreement with the value estimated for the  $Zn(Co, Al)_2O_4$  mixed crystals.

e) The occurrence of  $Co^{2+}$  ions in the zinc cobaltites must be accompanied by a deficiency in the oxidizing power. Two determinations carried out according to the description in chapter I (section 1.2) gave as a result 1.94 and 1.95 Eq/mol. The theoretical value for pure  $ZnCo_2O_4$  is 2.00 Eq/mol. The titrations, however, were not performed in a nitrogen atmosphere but in an open flask.  $NaHCO_3$  was added to the solution to fill the vessel with  $CO_2$  and to prevent oxidation of the liquid by air.  $Co_3O_4$  samples titrated in this way showed oxidizing powers of 1.98 and 1.99 Eq/mol., while the titrations under nitrogen atmosphere of the same samples showed these values to be 1.93 and 1.94 (see chapter VIII). It is quite certain that the determinations in open flasks result in a too high value of the oxidizing power. We may thus conclude that for  $ZnCo_2O_4$  (A 7) a lack in the oxidizing power of more than 3% is found.

Of the other substances, only  $\text{ZnCo}_2\text{O}_4$  (A 4 B) and (A 4 D) were subjected to one titration, since not enough material of the others was available. The oxidizing power was found to be 1.83 and 1.84 Eq/mol, respectively, which indicates a  $\text{Co}^{2+}$  content of more than 8%. Although the absolute values of the percentage  $\text{Co}^{2+}$  determined magnetically and chemically do not agree very well, the comparative values of two substances are satisfactory as may be seen as follows.

Substance	% $\text{Co}^{2+}$ estimated magnetically	% $\text{Co}^{2+}$ determined by titration
$\text{ZnCo}_2\text{O}_4$ A 7	6%	3%
$\text{ZnCo}_2\text{O}_4$ A 4 D	9.5%	8%
$\text{ZnCo}_2\text{O}_4$ A 4 B	10.5%	8.5%

f) The behaviour of the curves for  $\text{ZnCo}_2\text{O}_4$  (A 4) and (A 7 A) at high temperatures is quite different from the others and rather unexpected. Both phenomena can be very simply explained. The substance A 4 changed during the measurements (in sealed quartz vessel) into substance A 4 C. Actually, at this time the influence of an extra heat treatment on the magnetic susceptibility was discovered.

The substance A 7 A was measured in an evacuated quartz container. The sudden rise in the  $\chi$  value between 700 and 800°C is a consequence of a partial decomposition of the substance. This process appeared to be partly reversible, as may be seen from the  $\chi_M$  values which were determined afterwards.

$$T = 497 \quad \chi_M = 0.76^4$$

$$T = 778 \quad \chi_M = 0.58^5$$

It is, of course, fortuitous that the substance A 7 is almost formed again (fig. 7.1). We may only guess about the nature of the decomposition process. It is very probable, however, that the substance loses oxygen.

## 7.5. Discussion of the system $(\text{Co}, \text{Zn})\text{Co}_2\text{O}_4$

The only important substance in this system is the product  $\text{Co}_{0.125}\text{Zn}_{0.875}\text{Co}_2\text{O}_4$  (A 5 A). As may be seen from fig. 7.1, this substance fits exactly in the series of  $\text{ZnCo}_2\text{O}_4$  already discussed in the preceding section.  $\chi_M$  is given by the formula

$$\chi_M = A_M + \frac{C_M}{T} \quad \text{in which } A_M = 0.32^5 \cdot 10^{-3} \text{ e.m.u. and } C_M = 0.366.$$

The estimated amount of  $\text{Co}^{2+}$  ions is approximately 0.185 per mol. As 0.125  $\text{Co}^{2+}$  is already present at the tetrahedral interstices, only 3% of the cobalt from the  $\text{Co}_2\text{O}_4$  group is in the divalent state. The determination of the oxidizing power (titrated in open flask) showed an oxygen deficiency of 2% (1.96 Eq/mol).

The identical behaviour of this mixed crystal and the  $\text{ZnCo}_2\text{O}_4$  samples is an extra confirmation of our assumption that in the latter substances the weak paramagnetism is a consequence of the inhomogeneity of the products. The other products may be discussed very briefly. Our attempts to prepare more members of the series were not very successful.

The  $\chi$  values at room temperature of the substances MI, MII and MIII decreased after every new firing procedure. It seems very difficult to find the proper conditions for the preparation of good zinc cobaltites.

This failure to obtain data for the whole series of mixed crystals between  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$  causes no serious lack in our knowledge since no other important facts are to be expected and all the problems can be solved without this series.

Finally, we will only draw attention to the substance  $\text{Co}_{0.125}\text{Zn}_{0.875}\text{Co}_2\text{O}_4$  (A 5). Its magnetic behaviour is completely comparable to that of  $\text{ZnCo}_2\text{O}_4$  (A 4) (see section 7.4 f). Both substances were prepared by heating the nitrates at  $350^\circ\text{C}$  in oxygen. The assumption already made (section 7.4 a) that such substances are not completely free of nitrate is confirmed by the determination of the oxidizing power of A 5, which was found to be 2.09 Eq/mol.

## Summary of Chapter VII

Mixed crystals of  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ , a series of  $\text{ZnCo}_2\text{O}_4$  samples and some mixed crystals of  $\text{ZnCo}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  were prepared. The magnetic susceptibility of all the substances could be described by the formula  $\chi = A + \frac{C}{T}$ . Cobalt in the trivalent state in octahedral interstices appears to exhibit a temperature-independent paramagnetism of about  $0.1 \cdot 10^{-3}$  e. m. u.

The weak normal paramagnetism which is observed in all the substances is attributed to a small amount of  $\text{Co}^{2+}$  ions in tetrahedral interstices. None of the substances is homogeneous. The determination of oxidizing powers showed in all the cases an oxygen deficiency. Most of the X-ray diagrams showed the strongest ZnO lines. The attempts to prepare a pure  $\text{ZnCo}_2\text{O}_4$  were not successful.

The spinel structures, as far they are present in the substances, are normal 2-3 spinels.

No further attempts were made to prepare the whole series of mixed crystals between  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ , since the magnetic behaviour of these substances was too much dependent on the heat treatment.



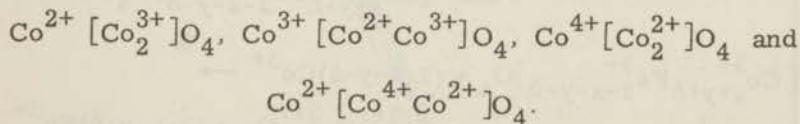
## Chapter VIII

### $\text{Co}_3\text{O}_4$

#### 8.1. Introduction

Although many different cobalt oxides are mentioned in the literature <sup>40)</sup>  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  are the only compounds in this system which have been shown to exist with certainty.  $\text{CoO}$  crystallizes in the rock salt structure; its magnetic behaviour, already discussed in chapter III, shows, apart from a strong antiferromagnetism, no surprising aspects.  $\text{Co}_3\text{O}_4$  crystallizes in the spinel structure and exhibits a rather low magnetic susceptibility, as we mentioned briefly in the introduction to this thesis.

Verwey and de Boer <sup>2)</sup> were the first to consider the four structures which are possible for the ionic distribution in  $\text{Co}_3\text{O}_4$ , namely:

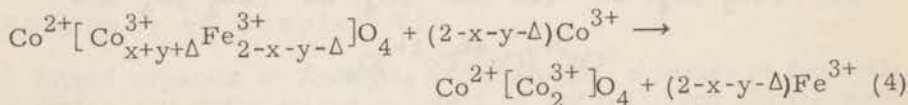
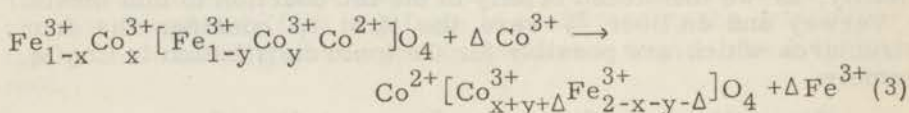
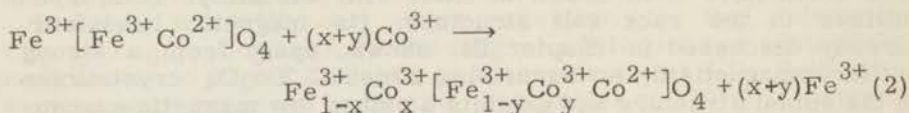
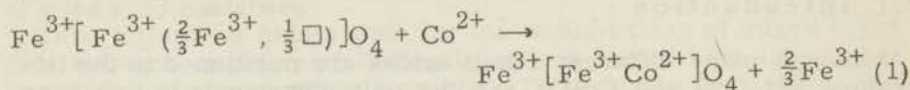


On account of the low conductivity of  $\text{Co}_3\text{O}_4$ , the small parameter  $u$  which was determined as  $0.380 \pm 0.005$  and the intensity ratio of the Debye-Scherrer lines 111 and 222, they concluded that this compound could be a normal 4-2 spinel.

We will give an elucidation of their reasoning. The low conductivity excluded the structure  $\text{Co}^{3+} [\text{Co}^{2+} \text{Co}^{3+}] \text{O}_4$ , since the presence at crystallographic equivalent positions of ions of the same element differing only one charge unit will cause the substance to be a good conductor, as electrons may pass from one ion to another leaving the total number of both kinds of ions constant. The structures  $\text{Co}^{2+} [\text{Co}_2^{3+}] \text{O}_4$  and  $\text{Co}^{2+} [\text{Co}^{4+} \text{Co}^{2+}] \text{O}_4$  were less probable because of the low value of the  $u$  parameter. Since a small  $u$  parameter corresponds to a relatively small tetrahedral hole, the  $\text{Co}^{2+}$  ions (supposed to be larger than  $\text{Co}^{3+}$  or  $\text{Co}^{4+}$ ) were assumed to be too large to fit in the tetrahedral holes. The remaining structure  $\text{Co}^{4+} [\text{Co}_2^{2+}] \text{O}_4$  could be accounted for by the observed intensity ratio of the 111 and 222 reflections, and offered the further advantage of a half-filled 3d shell in the  $\text{Co}^{4+}$  ion (as in  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ ), which appears to be an energetically favourable electronic configuration.

Recently Robin <sup>3)</sup> and Robin and Benard <sup>41)</sup> made an extensive X-ray study on oxides containing Co and other transition group elements. It appeared impossible to replace more than one Co in  $\text{Co}_3\text{O}_4$  by a divalent ion such as  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$ , which was a reason

to assume that only one  $\text{Co}^{2+}$  ion is present in this compound. In the substances obtained by gradual replacement of Fe in  $\gamma\text{-Fe}_2\text{O}_3$  by Co, an irregularity in the cell dimensions occurs not far beyond a Co content of  $33\frac{1}{3}\%$ .  $\gamma\text{-Fe}_2\text{O}_3$  has a spinel like structure which may be written as  $\text{Fe}^{3+}[\text{Fe}^{3+}(\frac{2}{3}\text{Fe}^{3+}\frac{1}{3}\square)]\text{O}_4$  ( $\square$  means an unoccupied octahedral hole). The replacements of Fe by Co now proceed in the following way:



Replacement (1) is accompanied by a linear increase of the cell constant. The maximum is reached for a composition  $\text{CoFe}_2\text{O}_4$  which is an inverse spinel. The gradual decrease of the cell constant which accompanies replacement (2) is interrupted at 39% Co and the following increase is accomplished at 41.7% Co. In this short interval, rearrangement (3) is supposed to take place, which is actually a relatively sudden change from an inverse to a normal spinel initiated by the addition of a small quantity ( $\Delta$ ) of  $\text{Co}^{3+}$  ions.

The following replacement (4) proceeds in the regular way accompanied by a linear decrease of the cell constant. The failure to replace more than one Co by Zn or Ni and the irregularity in the cell constants of the mixed crystals of  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  both were reasons to assume that  $\text{Co}_3\text{O}_4$  is a normal 2-3 spinel.

The magnetic measurements on  $\text{Co}_3\text{O}_4$  (and " $\text{Co}_2\text{O}_3$ ") of Bhatnagar, Prakash and Qayyum<sup>4</sup>) gave as a result the very low Bohr magneton number of about 3.0 per cobalt ion. Their measurements ranged from 300 to 500°K. The  $\chi_g$  values at room temperature were approximately  $31 \cdot 10^{-6}$  e.m.u. for  $\text{Co}_3\text{O}_4$  and 28 to 29  $\cdot 10^{-6}$  e.m.u. for " $\text{Co}_2\text{O}_3$ ". From these data it is quite clear that they did not obtain  $\text{Co}_2\text{O}_3$  but only  $\text{Co}_3\text{O}_4$ . The  $\Theta$  values were rather large and were measured from -150 to -180°K. From the present knowledge concerning  $\text{Co}_3\text{O}_4$  two basic problems arise, namely, the uncertainty as to whether this compound con-

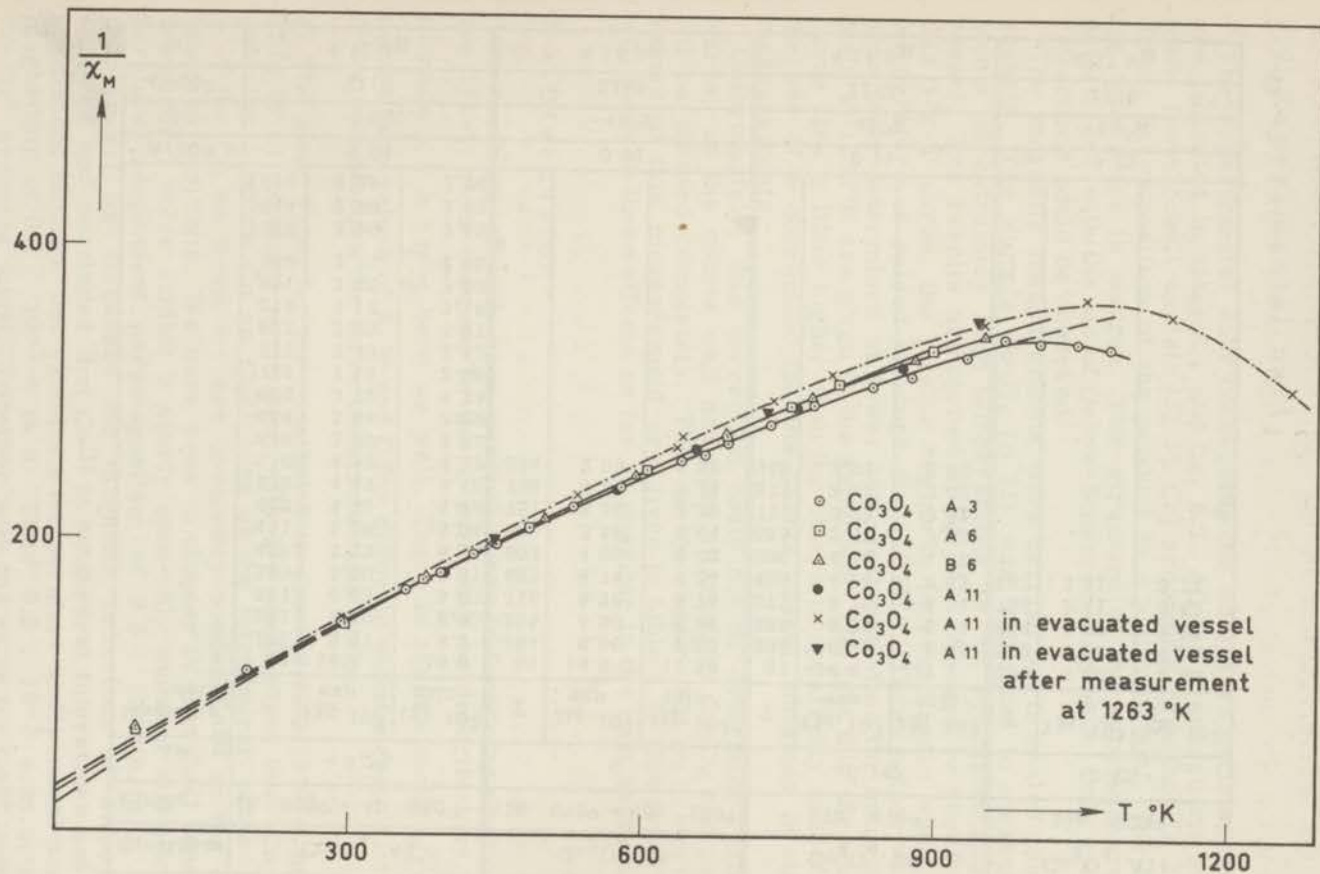


FIGURE 8.1.

Table 8.1.

Substance	Co <sub>3</sub> O <sub>4</sub> . A3			Co <sub>3</sub> O <sub>4</sub> . A6			Co <sub>3</sub> O <sub>4</sub> . B6			Co <sub>3</sub> O <sub>4</sub> . A11		
Firing	1h. 600° - 4h. 350°			12h. 670° - 60h. 250°			17h. 670°			20h. 900°		
Δw	+0.2%			0			-0.1%			-0.4%		
Magnetic data	T	χ <sub>M</sub> · 10 <sup>3</sup> exp.	χ <sub>M</sub> · 10 <sup>3</sup> calc.	T	χ <sub>M</sub> · 10 <sup>3</sup> exp.	χ <sub>M</sub> · 10 <sup>3</sup> calc.	T	χ <sub>M</sub> · 10 <sup>3</sup> exp.	χ <sub>M</sub> · 10 <sup>3</sup> calc.	T	χ <sub>M</sub> · 10 <sup>3</sup> exp.	χ <sub>M</sub> · 10 <sup>3</sup> calc.
		81	14.4	16.0	81	14.6	17.19	81	14.4	17.2	395	5.62
	195	9.07	9.2	294	6.96	6.96	295	6.95	6.94	572	4.25	4.23
	291	6.89	6.93	295	6.90	6.94	295	6.98	6.94	654	3.78	3.82
	357	6.02	5.97	375	5.76	5.76	377	5.72	5.74	755	3.41	3.43
	393	5.60	5.57	483	4.74	4.74	498	4.64	4.63	683	3.11	3.11
	427	5.23	5.24	603	4.00	4.00	590	4.06	4.06			
	451	5.06	5.04	683	3.66	3.64	685	3.63	3.63			
	483	4.78	4.79	751	3.39	3.39	771	3.33	3.32			
	528	4.47	4.49	798	3.23	3.24	877	3.05	3.02			
	576	4.19	4.22	894	2.99	2.98	948	2.91	2.86			
	640	3.90	3.92									
	664	3.84	3.82									
	686	3.72	3.73									
	728	3.55	3.58									
	773	3.39	3.43									
	833	3.25	3.27									
	874	3.17	3.16									
	931	3.05	3.03									
	969	2.93	2.95									
	1006	2.96	2.88									
	1044	2.96	2.82									
	1078	2.98	2.76									
A · 10 <sup>3</sup>	0.90			0.71			0.71			0.73		
θ	-59°K.			-49°K.			-49°K.			-50°K.		
C · 10 <sup>3</sup>	2110			2143			2143			2176		
μ	4.11 μ <sub>B</sub>			4.14 μ <sub>B</sub>			4.14 μ <sub>B</sub>			4.17 μ <sub>B</sub>		

sists of di- and tri- or di- and tetravalent cobalt, and the unusually low magnetic susceptibility.

## 8.2. Experimental part

The experimental data concerning the different  $\text{Co}_3\text{O}_4$  samples are collected in table 8.1 and fig. 8.1. All the preparations were made from cobalt oxalate (32.0% Co) according to method D, *i. e.* direct decomposition of the product in a platinum boat. The firing took place in oxygen. The structure of the substances was determined with the aid of Debye-Scherrer diagrams. Only spinel reflections could be observed.

The magnetic measurements were carried out in sealed quartz vessels. The sample  $\text{Co}_3\text{O}_4$  (A 11) was subjected to measurements at extremely high temperatures in an evacuated quartz vessel. The results are plotted in fig. 8.1. As may be seen from this  $1/\chi$ -T curve, the  $\chi$  value begins to increase again when the temperature is raised to more than  $1050^\circ\text{K}$ . Three points which have been determined at lower temperatures after the measurement at  $1263^\circ\text{K}$  are given in the same plot. The fact that the whole curve lies a little higher than the others is apparently caused by the use of a correction for the quartz vessel, obtained in older measurements.

Unfortunately, this correction could not be determined afterwards, as the quartz wall had been attacked by  $\text{Co}_3\text{O}_4$  and could not be cleaned completely. This is the reason that no numerical values of this measurement are given in table 8.1. However, we will discuss these effects as far as possible in the next section.

## 8.3. Discussion

As we have already seen several times in foregoing chapters, the  $1/\chi$ -T plots concave to the T axis may be described by the formula  $\chi = A + \frac{C}{T-\Theta}$  here as well. There is again a close agreement in the values of A,  $\Theta$  and C for different substances.

We will discuss the three constants separately:

a) The mean value for the constant A is about  $0.75 \cdot 10^{-3}$  e. m. u. This is in excellent agreement with the assumption that  $\text{Co}_3\text{O}_4$  contains  $\frac{1}{3}$  of its Co as  $\text{Co}^{2+}$  ions at the tetrahedral sites and  $\frac{2}{3}$  of the Co as more or less covalently-bonded  $\text{Co}^{\text{III}}$  in the octahedral positions. We have seen in chapter IV that  $\text{Co}^{2+}$  ions in tetrahedral holes exhibit a nearly spin-only moment and a temperature-independent paramagnetism of  $0.5 \cdot 10^{-3}$  e. m. u. In chapter VII we discussed the magnetic behaviour of  $\text{ZnCo}_2\text{O}_4$  samples and concluded that  $\text{Co}^{\text{III}}$  in octahedral interstices has no permanent moment but exhibits a temperature-independent paramagnetism of  $0.1 \cdot 10^{-3}$  e. m. u. Thus  $0.2 \cdot 10^{-3}$  e. m. u. per  $\text{Co}_2\text{O}_4$  group is found. Together with the value for  $\text{Co}^{2+}$  ions in

tetrahedral interstices, we calculate a temperature-independent term for  $\text{Co}_3\text{O}_4$  of about  $0.7 \cdot 10^{-3}$ .

b) The value of  $\theta$  of about  $-50^\circ\text{K}$ , is in good agreement with  $-35^\circ\text{K}$  found for  $\text{CoAl}_2\text{O}_4$ , which is a confirmation of the similarity of the two compounds. From chapter V we know that  $\text{CoAl}_2\text{O}_4$  is a normal spinel, *i. e.*, with  $\text{Co}^{2+}$  ions at the tetrahedral interstices and diamagnetic material at the octahedral interstices.

c) The value of the moment of the  $\text{Co}^{2+}$  ions is found to be  $4.14 \mu_B$ . This is a somewhat larger value than that found for  $(\text{Co}, \text{Zn})\text{O}$ , namely,  $4.05 \mu_B$ . At this point we must recall the behaviour of  $\text{ZnCo}_2\text{O}_4$ . We found in chapter VII that this substance could not be prepared completely stoichiometrically. The question arises if the higher moment found in  $\text{Co}_3\text{O}_4$  is perhaps due to a slight oxygen deficiency and consequently a larger ratio between di- and trivalent cobalt than 1:3. We have made determinations of the oxidizing power of  $\text{Co}_3\text{O}_4$  samples made at different temperatures. Unfortunately the substances of which the susceptibility was measured have been lost in failures. We have therefore made a series of 5 new samples, determined the exact formula by means of their final weight and determined the oxidizing power according to the method described in chapter I. The results are given in table 8.2. All the firings took place in oxygen. The formula in the last column was calculated from two determinations of the oxidizing power. The mutual difference between two determinations was never larger than 1%.

Table 8.2.  
Preparation and analyses of  $\text{Co}_3\text{O}_4$  from cobalt oxalate

Firing procedure	Formula based on final weight	Formula based on oxidizing power
5h. 600°C	$\text{Co}_3\text{O}_{3.94}$	$\text{Co}_3\text{O}_{3.97}$
5h. 700°C	$\text{Co}_3\text{O}_{3.96}$	$\text{Co}_3\text{O}_{3.965}$
6h. 800°C	$\text{Co}_3\text{O}_{3.96}$	$\text{Co}_3\text{O}_{3.97}$
6h. 900°C	$\text{Co}_3\text{O}_{3.97}$	$\text{Co}_3\text{O}_{3.965}$
6h. 1150°C	$\text{Co}_3\text{O}_{3.69}$	$\text{Co}_3\text{O}_{3.76}$

As may be seen from this table, a slight oxygen deficiency of 3% is indeed found for all the substances except for that fired at  $1150^\circ\text{C}$ . This means that one formula unit contains  $1.06 \text{Co}^{2+}$  instead of 1.00. The mean Bohr magneton number now becomes 4.02 instead of 4.14. The agreement with the value found for the mixed crystals  $(\text{Co}, \text{Zn})\text{O}$ , which was 4.05, is much better. We are not able to give an elucidation of the problem where the extra  $0.02 \text{Co}^{2+}$  in  $\text{Co}_3.02\text{O}_4$  must be placed in the spinel lattice.

It is however possible that some systematic error has occurred in the determinations of the oxidizing power so that actually  $\text{Co}_3\text{O}_4$  is a real stoichiometric compound. In this case we must

assume that the value of  $4.14 \mu_B$  for  $\text{Co}^{2+}$  ions in the tetrahedral holes of this substance is the real value. Then the differences between the values found for  $\text{Co}_3\text{O}_4$  and those found for  $(\text{Co}, \text{Zn})\text{O}$  and  $(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$  may be caused either by systematic errors in the Co content of the latter substances or by slight differences between the electric crystal field in the three types of lattices. We think the latter assumption to be the best one since the final weights are not completely reproducible (see the values for the samples A3, A6, B6 and A11 in table 8.1) and the values of the oxidizing powers appear to be independent of the firing temperature.

We will now discuss the effects observed at very high temperatures for  $\text{Co}_3\text{O}_4$  (A 11) and to a slight extent also for  $\text{Co}_3\text{O}_4$  (A 3). As may be seen from fig. 8.1 the curves for both substances show a maximum between 900 and 1000°K. This means that the values beyond this temperature increase with increasing temperature.

a) Trivalent Co begins to contribute to the magnetization because of a higher energy level which will be occupied successively with rising temperature.

b) Decomposition of  $\text{Co}_3\text{O}_4$  into  $\text{CoO}$  and  $\text{O}_2$  takes place.

Since we know that in one atmosphere above 900°C (that is, about 1200°K),  $\text{Co}_3\text{O}_4$  loses oxygen to form a product with more  $\text{Co}^{2+}$  ions and finally gives  $\text{CoO}$ , the latter assumption seems the more probable. A rough calculation shows that, as the temperature is raised, the observed  $\chi$  value of  $\text{Co}_3\text{O}_4$  (A 11) starts to deviate from the calculated value at a temperature as low as 950°K. We have seen a similar decomposition of  $\text{ZnCo}_2\text{O}_4$  which was not completely reversible.  $\chi$  measurements showed, however, that for  $\text{Co}_3\text{O}_4$  this decomposition is almost reversible.

We are convinced of the fact that our investigation of  $\text{Co}_3\text{O}_4$  at elevated temperatures is not complete enough to be able to give any conclusion with certainty.

It would be interesting to carry out the following investigations:

1) Preparation, careful X-ray analysis (also intensity measurements) and  $\chi$  measurements in a wide temperature range of samples of cobalt oxide with an oxygen content between that of  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ .

2) high temperature  $\chi$  measurements on  $\text{Co}_3\text{O}_4$  samples in closed quartz vessels under different pressures.

Both investigations should be helpful in solving the problem whether  $\text{Co}_3\text{O}_4$  is stoichiometric or not, the behaviour of trivalent cobalt at high temperature, the problem whether the products between  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  are mono- or bi-phase systems and the mechanism of the decomposition of  $\text{Co}_3\text{O}_4$  into  $\text{CoO}$  and  $\text{O}_2$ .

## Summary of Chapter VIII

Four different samples of  $\text{Co}_3\text{O}_4$  made at different temperatures up to 900°C were subjected to susceptibility measurements.

The results could be described by the formula  $\chi = A + \frac{C}{T-\theta}$ . The mean value of A was about  $0.75 \cdot 10^{-3}$  e.m.u. and the mean magnetic moment for the  $\text{Co}^{2+}$  ion at the tetrahedral position was found to be  $4.14 \mu_B$ . The temperature-independent term was assumed to consist of a contribution of about  $0.5 \cdot 10^{-3}$  from the  $\text{Co}^{2+}$  ions in the tetrahedral holes of the spinel lattice and about  $0.2 \cdot 10^{-3}$  e.m.u. from the  $\text{Co}_2\text{O}_4^-$  group. The trivalent cobalt at the octahedral position exhibits no permanent magnetic moment. The assumption is in agreement with the results found for the mixed crystals  $(\text{Co,Zn})\text{O}$  and the  $\text{ZnCo}_2\text{O}_4$  samples discussed in the chapters IV and VII. The value of  $4.14 \mu_B$  which is somewhat different from that found for  $\text{Co}^{2+}$  ions in the tetrahedral interstices of  $(\text{Co,Zn})\text{O}$  or  $(\text{Co,Zn})\text{Al}_2\text{O}_4$  is perhaps caused by a slight oxygen deficiency of the samples. Another assumption is that this cobalt oxide is exactly  $\text{Co}_3\text{O}_4$ . The difference in the  $\mu$  values may then be explained either by dilution errors in the Zn oxides and the aluminates or by small differences in the electric crystal fields.



## GENERAL CONCLUSION

In order to draw general conclusions, we will compare the results of chapters III to VIII. For this purpose we have made fig. C.1 in which the  $1/\chi$ -T plots have been drawn for a representative of each group of substances. The mean values of the constants A and  $\mu$  found for each group are given in table C.1.

Table C.1

Substance or group of substances	$\bar{A} \cdot 10^3$ per formula unit	$\bar{\mu}$ in $\mu_B$ per $\text{Co}^{2+}$ ion
Co - Mg oxides	0	4.8 litt. 21) 22) 5.0
Co - Zn oxides	0.52	4.05
Co - Zn aluminates	0.48	3.93
Co - Mg aluminates	0.24 - 0.41 (0.41 with other diamagnetic correction)	4.29
$\text{CoAl}_2\text{O}_4$ (2 samples)	0.48	3.98
$\text{Co}_3\text{O}_4$ (4 samples)	0.75	4.14 (4.02 when corrected for oxygen deficiency)
$\text{ZnCo}_2\text{O}_4$ (extrapolated to stoichiometric subst.)	0.2	

The magnetic behaviour of all these substances is similar, which is readily seen from the table and the figure, where all the values refer to formula units containing one  $\text{Co}^{2+}$  ion. The cobalt-magnesium oxides show a deviation such that no temperature-independent paramagnetism is found and that the moment is some 20 to 25% larger than for the other substances. They are the only representatives in this thesis of the large group of substances in which the  $\text{Co}^{2+}$  ions occupy octahedral interstices. Abragam and Pryce<sup>42)</sup> have given a satisfactory theoretical interpretation of the magnetic behaviour of  $\text{Co}^{2+}$  ions in octahedral surroundings, based on the crystal field theory of Van Vleck<sup>28)</sup> and Penney and Schlapp<sup>43)</sup>. The ground state of a  $\text{Co}^{2+}$  ion is, according to the Hund rule, a  $4F$  term. This ground level is split by a cubic field into a triplet. If the octahedron is tetragonally distorted, as is the case in many hydrated Co salts, this triplet is split further into several doublets, the lowest of which is again split into two triplets by the L - S coupling which is rather strong in the second

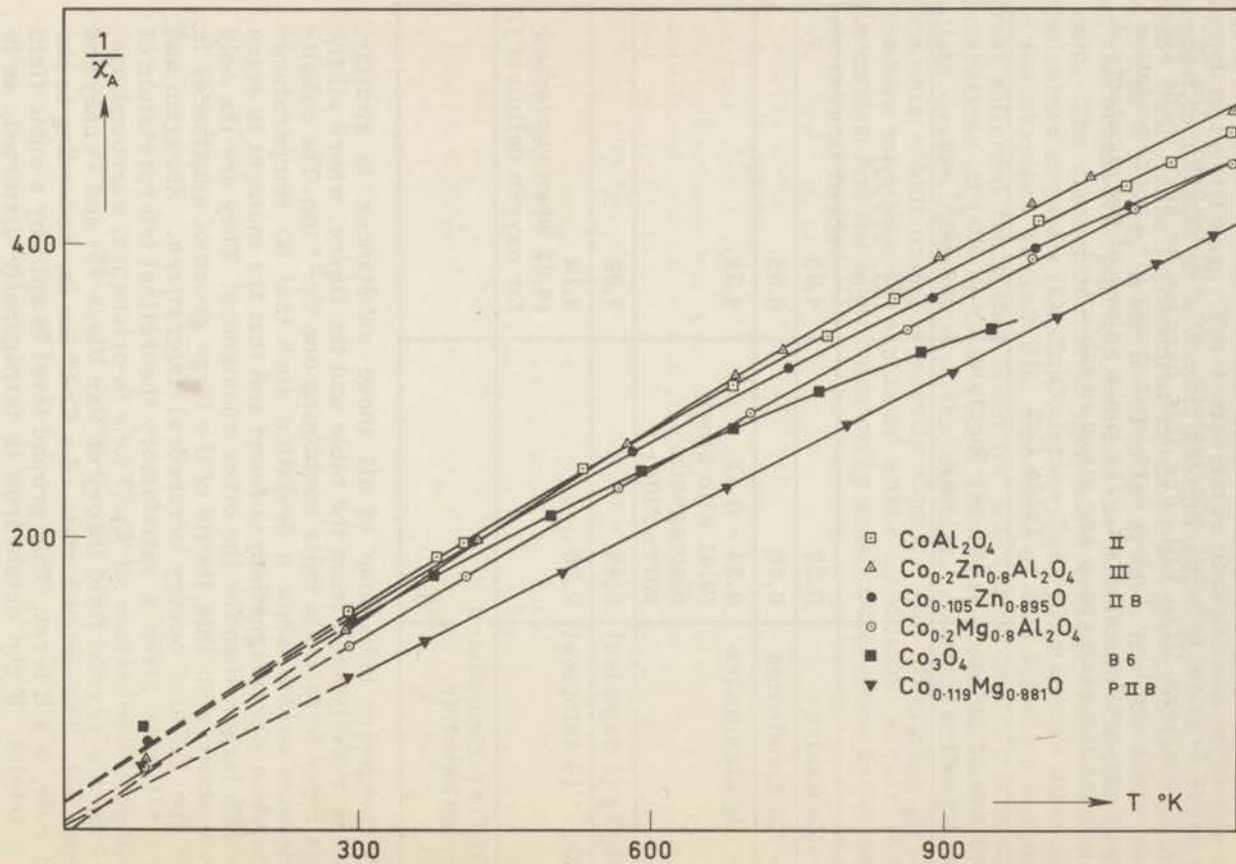


FIGURE C.1.

half of the transition group elements. Together with a rather low-lying 4 P term, a very complex system of energy levels is formed. The number and distances of these energy levels are very dependent on the crystal field. This is the reason that the g factors, which are closely related to the term scheme and consequently to the  $\mu$  values determined from susceptibility measurements, may be different from one compound to the other. According to tables which may be found in the books of Van Vleck (*Electric and Magnetic Susceptibilities*) and Bates (*Modern Magnetism*), the Bohr magneton numbers for  $\text{Co}^{2+}$  ions in different compounds range from 4.4 to 5.3. The crystal field theory is confirmed by paramagnetic resonance experiments which allow a direct measurement of the anisotropy of g factors in single crystals. Extensive reviews on resonance data are given by Bleaney and Stevens <sup>44</sup>) and by Bowers and Owen <sup>45</sup>). According to the latter authors, a dependence of the g factors on the dilution of the  $\text{Co}^{2+}$  ions may not be excluded, although such an effect does not appear from the resonance data so far available. The different values for  $\mu$  found in our cobalt-magnesium oxides of different Co content are not very surprising from a theoretical point of view. We will mention one other point in relation to the cobalt-magnesium oxides. In chapter III, we discussed the diamagnetic correction which had to be chosen for MgO to avoid  $1/\chi$ -T curves convex to the T axis. The question arises if the observed deviation from the Curie-Weisz law, when Klemm's ion susceptibilities are used, may be caused by this complicated character of the low-lying energy levels in  $\text{Co}^{2+}$  ions. The possibility may not be excluded, but the fact that CoO shows no deviation, together with the observation that the effects become more pronounced with increasing dilution, make our assumption of a wrongly-introduced diamagnetic correction all the more probable.

Another, although much smaller, deviation is found in the cobalt-magnesium aluminates. They show a temperature-independent paramagnetism of  $0.4 \cdot 10^{-3}$  e.m.u. and a permanent moment for  $\text{Co}^{2+}$  of about  $4.3 \mu_B$ . The suggestion was made that we have here representatives of a group of substances in which both octahedral and tetrahedral interstices are occupied. This led to the assumption that  $\text{MgAl}_2\text{O}_4$  could be a partially inverse spinel. In all the other substances discussed in this thesis the  $\text{Co}^{2+}$  ions occupy tetrahedral interstices.

Not very much is known about  $\text{Co}^{2+}$  ions in tetrahedra. The reason is that in most substances the  $\text{Co}^{2+}$  ions are situated in octahedral positions. No theoretical treatment of  $\text{Co}^{2+}$  ions in tetrahedral surroundings exists, as it does for the case of  $\text{Co}^{2+}$  ions surrounded by six water molecules <sup>42</sup>). Again, the crystal field theory of Van Vleck <sup>28</sup>), extended by Gorter <sup>29</sup>), gives a satisfactory theoretical basis for the magnetic behaviour. The tetrahedrally shaped crystal field, opposite in sign to the octahedral one, causes a singlet level to be lowest. The only contribution of orbital magnetic moment to  $\mu$  now comes from the L - S coupling which is rather strong in the second half of the transition group. Our values found for  $(\text{Co}, \text{Zn})\text{O}$ ,  $(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$ , which are, respectively, 4.05, 3.93, 3.98

and  $4.14 \mu_B$ , are indeed somewhat higher than the spin-only value for a  $3d^7$  configuration, namely  $3.87 \mu_B$ . The differences in these  $\mu$  values may be caused by slight differences in the magnitudes of the crystal fields, small errors in the dilution of the  $\text{Co}^{2+}$  ions or in the case of  $\text{Co}_3\text{O}_4$ , by a slight oxygen deficiency. If in the latter substance the  $\mu$  value is corrected on the basis of our determinations of the oxidizing power, a value of  $4.02 \mu_B$  is found. With the aid of the present experimental data, we are not able to decide among the three possibilities. Paramagnetic resonance experiments have been performed by Owen on  $\text{Cs}_3\text{CoCl}_5$  in which the  $\text{Co}^{2+}$  ions are situated in tetrahedra of  $\text{Cl}^-$  ions. As far as we know, this work has not yet been published, but the results are given in the review on resonance data by Bowers and Owen<sup>45</sup>). They report  $g_{\parallel} = 2.32 \pm 0.04$  and  $g_{\perp} = 2.27 \pm 0.04$  much lower than usually found for  $\text{Co}^{2+}$  ions.

As no other experimental work is available with which to compare our results, we must accept a permanent moment of 4.0 to  $4.1 \mu_B$  and a temperature-independent paramagnetism of  $0.5 \cdot 10^{-3}$  e.m.u. per  $\text{Co}^{2+}$  ion in the tetrahedral holes of a wurtzite lattice. A better comparison with other work is possible for trivalent cobalt in octahedral interstices.

In chapter VII we have already mentioned the extensive investigations of Rosenbohm<sup>37</sup>), Asmussen<sup>38</sup>) and Kernahan and Sienko<sup>39</sup>) on numerous  $\text{Co}^{\text{III}}$  complexes in which cobalt is surrounded by six monovalent or three divalent groups. All the substances were diamagnetic, but a temperature-independent paramagnetism varying from  $0.029$  to  $0.165 \cdot 10^{-3}$  e.m.u. had to be assigned to the central cobalt atom. Our value of  $0.1 \cdot 10^{-3}$  e.m.u. per  $\text{Co}^{\text{III}}$  agrees very well with the above mentioned values.

Investigations of Bommer<sup>46</sup>) and Zernike<sup>47</sup>) on cobalt-alums and of Friedman *et al.*<sup>48</sup>) on cobaltperchlorate solutions in  $\text{HClO}_4$  leave no doubt about the diamagnetic nature of the  $\text{Co}(\text{H}_2\text{O})_6^{3+}$  complex ion.

According to Pauling<sup>49</sup>),  $\text{Co}(\text{NH}_3)_3 \cdot \text{F}$  is diamagnetic and  $\text{CoF}_3$  shows an antiferromagnetic behaviour with  $\mu$  values much lower than the theoretical ones<sup>50</sup>).  $\text{K}_3\text{CoF}_6$  appears to be the only complex compound with isolated groups in which  $\text{Co}^{3+}$  ions exhibit the normal value of the magnetic moment of  $5.3 \mu_B$ <sup>49</sup>)<sup>51</sup>). Actually, fluorides are the most heteropolar compounds which may be prepared. The paramagnetism found for  $\text{K}_3\text{CoF}_6$  is thus not very surprising. It is now interesting that for the oxidic compounds described in this thesis the diamagnetic form of trivalent cobalt is found, since oxides may be considered to follow the fluorides in heteropolarity. In a preliminary report on  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ <sup>52</sup>), the suggestion was made that the energy difference between the paramagnetic and diamagnetic states of trivalent cobalt might be small in order to be able to explain the curved character of the  $1/\chi$ - $T$  plots of  $\text{ZnCo}_2\text{O}_4$ . The more extensive study we made after this publication revealed that this curvature is due to a temperature-independent paramagnetic term, but the idea of a small energy difference between the paramagnetic and diamagnetic states of trivalent cobalt remains valuable, as may

be shown from the following. Apart from our investigation on  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$ , two more studies on oxides containing trivalent cobalt are known. Merck and Wedekind<sup>53)</sup> tried to prepare pure  $\text{Co}_2\text{O}_3$ , but obtained either anhydrous  $\text{Co}_3\text{O}_4$  only or samples with an appreciable water content and still containing some divalent cobalt. Extrapolation of the  $\chi$  values at room temperature from pure  $\text{Co}_3\text{O}_4$  to pure  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  led to a value of practically zero for the latter compound. This is in complete agreement with our observations for spinels containing trivalent cobalt. The other investigation is by Jonker and van Santen<sup>54)</sup>. They determined the magnetic behaviour of  $\text{LaCoO}_3$  and mixed crystals of this compound with the hypothetical  $\text{SrCoO}_3$ . The mixed crystals are ferromagnetic and are supposed to contain  $\text{Co}^{4+}$  ions.  $\text{LaCoO}_3$ , however, is a normal paramagnetic substance with a moment for  $\text{Co}^{3+}$  slightly less than the spin-only value.

The fact that trivalent cobalt in this Perovskite structure, where it occupies also the octahedral positions, behaves in a quite different manner to trivalent cobalt in spinels, might be explained by the assumption of a small energy difference between the paramagnetic and the diamagnetic states. If this energy difference is small, slight modifications in the electric field of the surrounding ions may cause in one case the paramagnetic state to have the lowest energy and in the other case the diamagnetic one.

In chapter VIII we have already briefly given Pauling's method of describing this diamagnetic state. The nine electrons of a cobalt atom are divided among the five 3d- the one 4s- and three 4p-orbitals. Then two of the 3d-orbitals ( $3d_{x^2-y^2}$  and  $3d_{3z^2-r^2}$ ), the 4s- and the 4p-orbitals ( $4p_x$ ,  $4p_y$  and  $4p_z$ ) are hybridized, to yield six  $d^2sp^3$  hybrids which point to the corners of a regular octahedron. If now, for example, a substance like  $\text{K}_3\text{Co}(\text{CN})_6$  is formed, this central cobalt atom shares the nine available electrons with the three valence electrons from the K atom and the six electrons of the 6 CN groups. In this way all electrons are shared and the  $\text{Co}(\text{CN})_6^{3-}$  ion is diamagnetic. For trivalent cobalt in a lattice of negative oxygen ions this description leads to an unsatisfactory charge distribution with an electric charge of plus one on all the oxygens in the lattice.

A better description is possible by means of Mulliken's M.O. method or by the method of Penney and Schlapp. Mulliken's approach to the problem is the linear combination of the  $3d_{x^2-y^2}$ ,  $3d_{3z^2-r^2}$ , 4s and 4p orbitals of the central atom with  $2p_\sigma$  or  $2p_\pi$  orbitals of the surrounding oxygen atoms and it turns out that the lowest energy of the complex is obtained when twelve of the eighteen electrons occupy the 6 molecular orbitals while the other six occupy the  $3d_{xy}$ ,  $3d_{xz}$  and  $3d_{yz}$  orbitals of the central Co atom. All electrons are shared and the complex is again diamagnetic. Penney and Schlapp assume that the electric potential field at the position of the Co atom is so large that the Russell-Saunders coupling between the  $d^5$  electrons is broken by the crystal field.

The energy levels of the d shell are then split into an upper doublet and a lower triplet with so large an energy separation that effectively two sub-shells are formed. The lower  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals are then first occupied by 3 pairs of electrons. This  $\text{Co}^{3+}$  ion is again diamagnetic. The three methods are discussed by Van Vleck <sup>55</sup>).

The difference between the magnetic behaviour of trivalent Co in a spinel and a perovskite like  $\text{LaCoO}_3$  is also easier to understand by the method of Mulliken or that of Penney and Schlapp, while Pauling's method fails also with respect to this problem, although it may not be said that the other two ways of description give a real solution. Following Mulliken, it may be said that the field in which the electrons travel is influenced by the 8  $\text{La}^{3+}$  ions surrounding the  $\text{CoO}_6$  group in such a way that the oxygen orbitals have the greater coefficients, causing a practically ionic behaviour. Similarly, according to Penney and Schlapp, the 8  $\text{La}^{3+}$  ions weaken the electric field of the surrounding oxygen ions to such an extent that the Hund rule is still valid for the central  $\text{Co}^{3+}$  ion.

From the comparison of our results on trivalent cobalt with those obtained by other investigators, we may conclude that in most cases the diamagnetic state is favoured. It is, however, not easy to predict when the paramagnetic state will occur. So far only one fluoride and one oxide have been found to be paramagnetic. It would be interesting to investigate if there are other compounds behaving in the same way.

## SUMMARY

The main object of this investigation has been the elucidation of some of the problems concerning  $\text{Co}_3\text{O}_4$ . The magnetic behaviour of divalent cobalt in octahedral and tetrahedral interstices and of trivalent cobalt in octahedral interstices could be studied separately.

From the measurements on mixed crystals of  $\text{CoO}$  and  $\text{MgO}$ , which crystallize in the rock salt structure, the moment of  $\text{Co}^{2+}$  ions in octahedral interstices of an oxygen lattice was determined to be 4.7 to 5.0 Bohr magnetons (chapter III). The moment of  $\text{Co}^{2+}$  ions in tetrahedral interstices was found from measurements on mixed crystals of  $\text{CoO}$  and  $\text{ZnO}$  crystallizing in the wurtzite structure. Values of 4.0 to 4.1 Bohr magnetons were observed together with a temperature-independent paramagnetism of approximately  $0.5 \cdot 10^{-3}$  e.m.u. per  $\text{Co}^{2+}$  (chapter IV). The different behaviour of  $\text{Co}^{2+}$  ions in octahedral and tetrahedral interstices could be accounted for on the basis of the crystal field theory of Van Vleck.

The behaviour of trivalent cobalt in octahedral interstices was studied in  $\text{ZnCo}_2\text{O}_4$  and mixed crystals of  $\text{ZnCo}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  (chapter VII). No permanent moment for this trivalent Co was found. A small temperature-independent paramagnetism of approximately  $0.1 \cdot 10^{-3}$  per  $\text{Co}^{3+}$  was observed. The zinc cobaltites and the mixed crystals with zinc aluminates have not been obtained completely free from  $\text{Co}^{2+}$  ions. The magnetic behaviour of  $\text{Co}_3\text{O}_4$  could be represented by the formula  $\chi = A + \frac{C}{T-\theta}$

(chapter VIII). The temperature-independent term was found to be approximately  $0.7 \cdot 10^{-3}$  e.m.u. per mol, of which  $0.5 \cdot 10^{-3}$  was assumed to be due to one  $\text{Co}^{2+}$  ion in tetrahedral surroundings and  $0.2 \cdot 10^{-3}$  to the two trivalent cobalt atoms at the octahedral interstices. The moment of the  $\text{Co}^{2+}$  ion in the tetrahedral hole was found to be 4.1 to 4.2 Bohr magnetons. An oxygen deficiency of about 3% was found for  $\text{Co}_3\text{O}_4$  but some systematic error in the determination of the oxidizing power could be possible. We could conclude from the experimental data with certainty that  $\text{Co}_3\text{O}_4$  is a normal 2-3 spinel.

In addition to this, the mixed crystals of  $\text{CoAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  were investigated (chapter V). A temperature-independent term of about  $0.5 \cdot 10^{-3}$  was again observed. The moment of the  $\text{Co}^{2+}$  ions appeared to be 3.9 to 4.0  $\mu_B$ . We concluded that  $\text{CoAl}_2\text{O}_4$  and the mixed crystals with  $\text{ZnAl}_2\text{O}_4$  are normal spinels. For the dilutions of  $\text{CoAl}_2\text{O}_4$  with  $\text{MgAl}_2\text{O}_4$  we obtained the rather surprising value of 4.3  $\mu_B$  for the  $\text{Co}^{2+}$  ions, and a temperature-independent term of about  $0.4 \cdot 10^{-3}$  e.m.u. (chapter VI). These mixed spinels ( $\text{Co, Mg} \text{Al}_2\text{O}_4$ ) were assumed to be partially inverse. All the experimental data are collected in tables and figures. A comparison with other experimental work and theoretical

considerations are given in a general conclusion. Preparative and analytical procedures are described separately (chapter I). All the magnetic measurements were carried out with a sensitive torsion balance (Faraday method) in a temperature range from 80 to 1200°K. A schematic description of the apparatus and an extensive series of calibration experiments with different substances are given in chapter II. On account of the latter experiments,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  was chosen as a standard substance.

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Op verzoek van de faculteit der Wis- en Natuurkunde volgt hier een korte levensbeschrijving.

Ik werd geboren op 13 Juni 1926 te Leiden, alwaar het lager en middelbaar onderwijs genoten werd. Na het eindexamen H. B. S. B te hebben afgelegd in 1943, volgde in 1944 het analysexamen eerste gedeelte der Ned. Chem. Ver.

In 1945 kon met de studie te Leiden een begin worden gemaakt. In 1948 werd het candidaatsexamen F afgelegd en in 1952 volgde cum laude het doctoraal examen scheikunde, hoofdrichting anorganische chemie, bijvak kristallografie.

In 1948 werd mij door de B. P. M. een van haar studieprijzen toegekend, waarvoor ik de directie van deze maatschappij veel dank verschuldigd ben.

Een jaar voor mijn candidaatsexamen werd ik assistent op het Laboratorium voor Anorganische en Fysische Chemie, waar ik betrokken was bij de voor-candidaats practica. Gedurende het studiejaar 1949/'50 werd een assistentschap vervuld op het Laboratorium voor Organische Chemie. Vanaf October 1950 ben ik verbonden geweest aan de afdeling voor Anorganische Chemie, eerst als assistent, na het doctoraalexamen achtereenvolgens als hoofdassistent, wetenschappelijk ambtenaar en sinds 1 Januari 1956 als wetenschappelijk ambtenaar 1e klas. Behalve organisatorische werkzaamheden heb ik in deze periode wetenschappelijk werk verricht onder leiding van Prof. Dr A. E. van Arkel. De resultaten hiervan zijn neergelegd in dit proefschrift. Een klein deel van het onderzoek verscheen in een voorlopige publicatie (P. Cossee, Structure and magnetic properties of  $\text{Co}_3\text{O}_4$  and  $\text{ZnCo}_2\text{O}_2$ , Rec. Trav. Chim. 75, 1089 (1956)).

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