

Cobalt Ions in Non-Metallic Structures

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1. — Introduction

The present communication is based on a three-year research programme performed at the Battelle Institute, Geneva, from 1960 to 1962 for the Cobalt Information Centre (CIC), Brussels, on the interactions of cobalt ions in non-metallic structures.

Before discussing some aspects of the work done and of the results obtained, we find it appropriate to evoke the problem which gave rise to these investigations.

The most widely known and most successful non-metallic magnetic materials are the ferrites (both cubic and hexagonal), and the question arises why not « cobaltites » instead of ferrites. In this respect we find the following situation [1].

- (i) Ferrites are mixed oxide compounds which contain trivalent paramagnetic iron ions (Fe^{3+}) and divalent transition metal ions (Fe^{2+} , Co^{2+} , Ni^{2+} , etc.). The cobalt analogue of a ferrite should contain trivalent cobalt ions.

Now

- Cobalt is preferentially divalent.
- If trivalent, cobalt is preferentially diamagnetic (low spin state).
- (ii) Divalent cobalt however, plays an important rôle in magnetic materials [2]. In a large number of magnetic compounds (ferrites in particular) divalent cobalt contributes to an exceptionally large extent to the magneto-crystalline anisotropy energy, and technically important magnetic parameters (such as coercivity, retentivity, initial permeability) do strongly depend on magnetic anisotropy.

Therefore, when thinking of possible new cobalt compounds, one is quite naturally led to consider the following two types of compounds :

- compounds with known magnetic characteristics in which Co^{2+} replaces Fe^{3+} ;
- compounds in which Co^{3+} is stabilized in a high spin state.

The realization of such compounds is not an easy undertaking. In order to stand some chance of success, it was necessary to achieve a deeper understanding of the rôle of cobalt in magnetic materials. The metallic state being so far much more difficult to understand than the non-metallic one, we restricted our investigations to non-metallic cobalt compounds (1). On this basis, a preliminary three-year research was undertaken devoted to the investigation of the magnetic properties of non-metallic cobalt compounds and intended to prepare a more specific investigation of certain selected classes of these [3, 4].

2. — Comparison between magnetic compounds

The particularities of cobalt compounds can be fully understood only by comparison with those of similar compounds. By similar we mean the compounds of the whole family of 3d transition metals : Ti, V, Cr, Mn, Fe, Co, Ni, and Cu.

Any comparison requires a common feature. In our case we have recognized it in the fact that most non-metallic compounds can be described, with a good approximation, in terms of a (more or less distorted) close-packed anionic structure, with partial occupation of the tetrahedral and octahedral interstitial positions by cations [5]. A substantial part of our research is based on this point of view. Most metals and alloys can

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(1) However, many of the preliminary results obtained so far can also be extended in a natural way to metallic magnetic materials.

also naturally be described in terms of close-packed structures with dilute foreign atoms in interstitial positions.

Examples of comparison between compounds having completely different X-ray symmetry, but which from the present point of view are related, may be found in reference [3].

To facilitate understanding, we first summarize some general properties of close-packed structures.

2.1. — Properties of close-packed structures

A close-packed arrangement of spheres of equal radii in a plane is fixed (to within a rotation) by the choice of a point A for the centre of one sphere. We call (A) the corresponding layer. For stacking the following layer in a close-packed way, there are two possibilities : putting the centre of a sphere either above point B or above point C of layer (A). We indicate by (B) and by (C) the respective layers (Fig. 1). The distance between the two stacking planes is about $0.817 d$, where d is the diameter of the spheres.

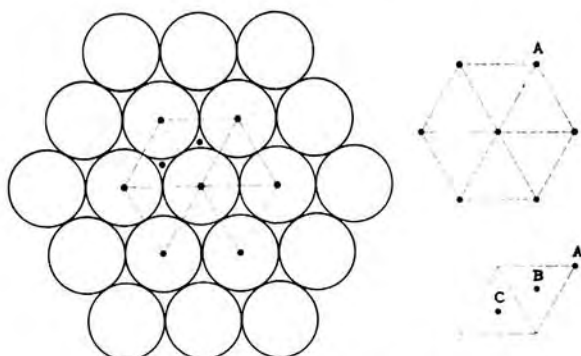


Fig. 1. — Types of close-packed layers. The centres of the spheres are indicated by dots.

In general, a close-packed structure is characterized by its stacking order, e.g. ABACBAB...

All spheres are equivalent (that is, have equal environments) only in the hexagonal or in the cubic close-packing.

In a close-packing one can distinguish three kinds of interstitial sites :

- the tetrahedral sites of the first kind,
- the octahedral sites,
- the tetrahedral sites of the second kind.

The centres of gravity of these sites have an elevation of respectively $1/4$, $1/2$, and $3/4$ of the distance between the two stacking planes.

Disregarding surfaces, there are as many sites of each kind as there are lattice points. The tetrahedral sites of one kind always form a lattice of the same close-packed type as the ori-

ginal lattice. This is also true for the octahedral sites of the cubic packing.

In most close-packed structures, small cations occupy only part of the available sites. We introduce occupation numbers n , indicating the ratio of the number of occupied to the number of available sites.

$$0 \leq n \leq 1 \quad \begin{array}{l} n = 0 \text{ means no occupation,} \\ n = 1 \text{ means full occupation.} \end{array}$$

Close-packed structures with only partial occupation of the lattice points L also occur sometimes. We therefore distinguish between n_{Δ} , n_{\square} , n_{∇} , and n_L , and we characterize each of the structures considered by means of the notation :

$$(n_{\Delta}, n_{\square}, n_{\nabla}, n_L)_{A \dots},$$

A... standing for the stacking order of the close-packing. We call such a symbol a close-packing formula.

In particular, we have :

$(0001)_h$ for the hexagonal close-packing,
 $(0001)_c$ for the cubic close-packing.

In the following tables (Tables 1 to 3) the close-packing formulas are indicated for a number of Strukturbericht types.

3. — A simple model for the investigation of Curie (or Néel) temperatures

One of the technical requirements put on a magnetic material is that it should remain ferro- (or ferri-) magnetic up to a relatively high transition temperature, its Curie or Néel temperature ⁽¹⁾.

To predict this temperature (at least its order of magnitude) for a given magnetic compound, we have elaborated a simple model for which the Curie temperature is expressed in terms of some basic structural parameters. The primitive ideas on which this approach is based are :

- that the value of the parameters depends only on the nature of the interacting ions and on the mutual positions of interacting pairs, but not on the compound considered ;
- that the contribution to the Curie temperature be additive with respect to the interacting pairs.

Our model introduces parameters which — in our opinion — should play about the same rôle as the ionic radii in the analysis of structures. Absolute structural predictions are in general not

⁽¹⁾ Throughout this communication, temperatures are indicated in degrees Kelvin.

TABLE 1
Close-packed non-metallic compounds with octahedral co-ordination of metal atoms

SB	Formula	Name	Close-packing formula	Remarks (An asterisk indicates deformations)	SB	Formula	Name	Close-packing formula	Remarks (An asterisk indicates deformations)
B1	NaCl	Rock-Salt	(0101) _c		C24	HgBr ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} hc$	
B8	NiAs	Niccolite	(0101) _h		C25	HgCl ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} hc$	
B14	FeAs		(0101) _h *	(B8)*					
B20	ε-FeSi		(0101) _c *	(B1)*					
E24	TlF		(0101) _c *	(B1)* rhomb. def.	C27	β-CdI ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} hc$	
B28	ε-FeSi		(0101) _c *	≡(B20)					
B29	SnS		(0101) _c *	(B1)*	C35	CaCl ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h^*$	(C4)*
B31	MnP		(0101) _h *	(B8)*					
C2	FeS ₂	Pyrite	(0101) _c	Close-packing of S ₂ groups	D0 ₄	CrCl ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} c$	
C4	TiO ₂	Rutile	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h^*$	Nearly close-packed	D0 ₆	BiI ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} h$	
C5	TiO ₂	Anatase	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} c$		D0 ₇	CrO ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} h$	Also called Al(OH) ₃ type (Hydrargillite)
C6	CdI ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$		D0 ₈	MoO ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} c$	
C11	CaC ₂		(0101) _c *	Close-packing of C ₂ groups (=C48)	D0 ₉	ReO ₃		$\begin{pmatrix} 1 \\ 0-0- \\ 4 \end{pmatrix} c$	
C18	FeS ₂	Marcasite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h^*$	(C4)*	D0 ₁₀	WO ₃		$\begin{pmatrix} 1 \\ 0-0- \\ 4 \end{pmatrix} c$	
C19	CdCl ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} c$		D0 ₁₂	FeF ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} h$	
C21	TiO ₂	Brookite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} hc^*$	Intermediate structure between (C4) and (C5)					

TABLE 1 (continued)

SB	Formula	Name	Close-packing formula	Remarks (An asterisk indicates deformations)	SB	Formula	Name	Close-packing formula	Remarks (An asterisk indicates deformations)
D0 ₁₃	AlCl ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} h$		E9 ₁	Ca ₃ Al ₂ O ₄	Wolframite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$	Perovskite : Ca \leftarrow \rightarrow CaII Ti \leftarrow \rightarrow CaI, Al
D0 ₁₄	AlF ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} h$	(\sim D0 ₁₂)	H0 ₆	MgWO ₄		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$	
D0 ₁₅	AlCl ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 3 \end{pmatrix} c$		UB1	LiNiO ₂		$\begin{pmatrix} 1 \\ 0-01 \\ 6 \end{pmatrix} h$	
D5 ₁	α -Al ₂ O ₃	Corundum	$\begin{pmatrix} 2 \\ 0-01 \\ 3 \end{pmatrix} h$		UD5 ₁	α -WCl ₆		$\begin{pmatrix} 1 \\ 0-01 \\ 6 \end{pmatrix} h$	
E1 ₂	α -AlOOH	Diaspore	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$		UD5 ₂	UCl ₆		$\begin{pmatrix} 1 \\ 0-01 \\ 6 \end{pmatrix} h$	(BI) : Na \leftarrow \rightarrow LiNi
E0 ₃	CdOHCl		$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} hc$		UE2 ₁	TiBaO ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 4 \end{pmatrix} hc$	
E0 ₇	FeAsS	Arsenopyrite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h^*$	(C18 where S ₂ is substituted by AsS)	UE2 ₂	LiSbO ₃		$\begin{pmatrix} 2 \\ 0-01 \\ 3 \end{pmatrix} h$	
E2 ₁	CaTiO ₃	Perovskite	$\begin{pmatrix} 1 \\ 0-01 \\ 4 \end{pmatrix} c$		UE2 ₃	NiBaO ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 4 \end{pmatrix} h$	
E2 ₂	FeTiO ₃	Ilmenite	$\begin{pmatrix} 2 \\ 0-01 \\ 3 \end{pmatrix} h$		UE2 ₄	NiCsCl ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 4 \end{pmatrix} h$	
E2 ₃	LiIO ₃		$\begin{pmatrix} 2 \\ 0-01 \\ 3 \end{pmatrix} h$		UE2 ₅	CuCsCl ₃		$\begin{pmatrix} 1 \\ 0-01 \\ 4 \end{pmatrix} h$	
E5 ₁	(FeMn)Nb ₂ O ₆	Niobite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$		UI ₁	Cu ₂ Cl(OH) ₇	Botallackite	$\begin{pmatrix} 1 \\ 0-01 \\ 2 \end{pmatrix} h$	

TABLE 2
Close-packed non-metallic compounds
with tetrahedral co-ordination of metal atoms

SB	Formula	Name	Close-packing formula
B3	ZnS	Zincblende	(1001) _c
B4	ZnS	Wurtzite	(1001) _h
C1	CaF ₂	Antifluorite	(1011) _c
C8	SiO ₂	β-quartz	—
C9	SiO ₂	β-cristobalite	$\begin{pmatrix} 1 & 1 & 1 \\ -0 & - & \\ 8 & 8 & 2 \end{pmatrix}_{hc}$
C10	SiO ₂	β-tridymite	$\begin{pmatrix} 1 & 1 & 1 \\ -0 & - & \\ 8 & 8 & 2 \end{pmatrix}_c$
C13	HgI ₂	—	$\begin{pmatrix} 1 & 1 \\ -0 & -1 \\ 4 & 4 \end{pmatrix}_c$
C42	SiS ₂	—	$\begin{pmatrix} 1 & 1 \\ -0 & -1 \\ 4 & 4 \end{pmatrix}_c$
D1 ₁	SnI ₄	—	$\begin{pmatrix} 1 & 1 \\ -0 & -1 \\ 8 & 8 \end{pmatrix}_c$
E1 ₁	CuFeS ₂	Chalcopyrite	(1001) _c

possible even if one knows the radii of the ions involved. Nevertheless number of useful rules can be formulated in terms of these radii, and they represent an expedient tool for everybody

who looks for new compounds. In fact, the use of ionic radii too is based on a few simple ideas, i.e. that compounds may be considered, in a good approximation, as packing of spheres of various radii and that, within a certain range of error (depending on co-ordination, relative electronegativity, and so on), these radii depend only on the nature of the ions, and not on the compound considered.

At the present stage of approximation of our model (we do not consider, for example, deviations from the ideal close-packing) a disagreement of 20-30 % between a predicted and an observed Curie temperature is likely to occur.

We do not intend to discuss here the relation between our model and various other approaches which also give an explicit expression for the Curie temperature as a function of some interaction parameters and which certainly have a better theoretical justification than the one suggested here for our model. The point is that our goal is the prediction of the Curie temperature of a given new magnetic compound, or at least its order of magnitude. In this respect the standard approaches are certainly inadequate. It is not sure whether the present attempt is a better one, but it has two virtues : it is very simple, and it allows the information obtained from one compound to be used for another quite different one.

TABLE 3
Some close-packed non-metallic compounds with mixed (octahedral and tetrahedral) co-ordination of metal atoms

SB	Formula	Name	Close-packing formula	Remarks
D5 ₃	Mn ₂ O ₃	—	$\begin{pmatrix} 3 & 3 \\ -0 & -1 \\ 4 & 4 \end{pmatrix}_c$	
D5 ₆	Na ₂ O.11Al ₂ O ₃	β-alumina	$\begin{pmatrix} 1 & 7 & 1 & 17 & +1 \\ 10 & 20 & 10 & 20 \end{pmatrix}$	ABCA(B-C)ACBA(C-B)
	PbO.6Fe ₂ O ₃	Magnetoplumbite	$\begin{pmatrix} 1 & 2 & 1 \\ 20 & 5 & 20 \end{pmatrix} + \begin{pmatrix} 1 \\ 20 \end{pmatrix} \diamond$	ABABCACACB
D5 ₇	γ-Al ₂ O ₃	γ-alumina	$\begin{pmatrix} 1 & 5 & 1 \\ 8 & 12 & 8 \end{pmatrix}_c$	partially-occupied spinel lattice
D7 ₂	Co ₃ S ₄	Linnaeite	$\begin{pmatrix} 1 & 1 & 1 \\ 8 & 2 & 8 \end{pmatrix}_c$	spinel lattice
D8 ₉	Co ₉ S ₈	—	$\begin{pmatrix} 1 & 1 & 1 \\ 2 & 8 & 2 \end{pmatrix}_c$	
H1 ₁	MgAl ₂ O ₄	Spinel	$\begin{pmatrix} 1 & 1 & 1 \\ 8 & 2 & 8 \end{pmatrix}_c$	
SO ₇	2Mg ₂ SiO ₄ Mg(OH, F) ₂	Chondrodite	—	contains olivine layers
S1 ₂	Mg ₂ SiO ₄	Olivine	$\begin{pmatrix} 1 & 1 & 1 \\ 8 & 2 & 8 \end{pmatrix}_h$	Forsterite

3.1. — *Definition of the model in terms of « standard superexchange parameters »*

A so-called « standard superexchange parameter » is introduced for each non-equivalent pair of magnetic ions interacting through a single anion of a given close-packing. We consider only interactions between interstitial positions (octahedral or tetrahedral) surrounding one and the same anion. It follows that the polyhedra (octahedra or tetrahedra) involved in the interaction share a face or an edge, or at least a corner. In Table 4 the standard superexchange parameters have been ordered according to this feature and to the stacking order of the close-packing. In fact, the possible relative positions are fully determined by three successive planes of the close-packing, and therefore by the hexagonal or cubic character of the layer they are imbedded in.

n_j^{kl} is the mean number of superexchange linkages of the j -type — i.e. described by the superexchange parameter I_j^{kl} — between the two interacting ions k and l .

ε_j^{kl} is : + 1 for parallel magnetic moments of the interacting ions k and l .

— 1 for antiparallel magnetic moments of the same ions k and l .

The above relation may be considered as a phenomenological ansatz defining the parameters I_j^{kl} involved : ansatz which has to be submitted to a check by comparison with experimental results. An absolute check would mean that the empirical values obtained from the above relation for the I_j^{kl} do not depend on the particular compound they have been obtained from. In practice and for most I_j^{kl} this check cannot be made. Instead of this, a relative check would be obtained if regularities are observed

TABLE 4

Standard superexchange parameters in a close-packing

Interaction between polyhedra	Octahedral type		Octahedral-tetrahedral type		Tetrahedral type	
	h	c	h	c	h	c
Close packing layer	h	c	h	c	h	c
I. Polyhedra sharing a face	I_1	—	I_5	I_6	I_9	—
II. Polyhedra sharing an edge	I_2	I_2	I_4	—	I_{10}	I_{10}
IIIa. Opposite polyhedra sharing a corner	—	I_3	I_7	—	I_{11}	I_{11}
IIIb. Non-opposite polyhedra sharing a corner (first kind)	I_4	—	—	—	I_{12}	—
IIIc. Non-opposite polyhedra sharing a corner (second kind)	—	—	I_8	I_8	I_{13}	I_{13}

We now assume that the Curie (or Néel) temperature of a non-metallic magnetic compound can be expressed in terms of our standard superexchange parameters in the following simple way :

$$T_c = \sum_{\text{all interacting pairs } (kl)} \sum_{j=1}^{13} \varepsilon_j^{kl} n_j^{kl} I_j^{kl}$$

where :

I_j^{kl} is the standard superexchange parameter of the j -type (according to Table 4) for the two magnetic ions k and l , interacting through a given single anion.

among the various numerical values. This relative check can be performed more easily, and in section 3.3 it will form the basis of our discussion.

3.2. — *Evaluation of standard superexchange parameters.*

We here give some examples of how we have evaluated the standard superexchange parameters defined in the previous section. More may be found in reference [4].

We start from cases where only one parameters is involved, so that its value may be fully determined. Using these first results, it is then possible to evaluate other parameters appearing together with those already obtained. Of course,

there are a number of cases where we get numerical values only for a given linear combination of the parameters.

As soon as several magnetic ions participate in the interaction, the distributions of these ions among the positions available become important, because within the present model the weight associated to each of the parameters depends essentially on the cationic arrangement. This fact is not in contradiction with the experimental evidence. It is well known that a thermal treatment may significantly change the Curie temperature of a given compound; in other words, this temperature is a function of the relative position of the magnetic ions. For our purpose, we need to know the effective cationic distribution in order to get the correct numerical value for the exchange parameters. Since this distribution is not always known with a sufficient degree of certainty, we evaluated in some cases the superexchange parameter for the two extreme possibilities of ordered (according to some possible symmetrical arrangement) and of completely disordered cationic arrangement. The results

parameter by the cosine of the angle made between the two interacting magnetic moments. We think, however, that it is in principle wrong to introduce such fine effects as non-collinearity into such a primitive model as ours. Non-collinearity is normally observed when the long-range interactions become competitive with the short-range ones. Our model only considers interactions occurring through a single anion; it is therefore not adapted to describing more complex spin arrangements properly. If the deviations from the collinear structure are small, then by ignoring them we still get exchange parameters within the uncertainty limits of our model.

The evaluation of standard superexchange parameters can best be illustrated by some simple examples. Let us first treat the case of some compounds having the magnetic structure type MnO (Fig. 2), as is the case for FeO, CoO, NiO or solid solutions of CoO with MgO, and of CoO with NiO. We will then also consider spinels having a magnetic structure of the NiFe_2O_4 type.

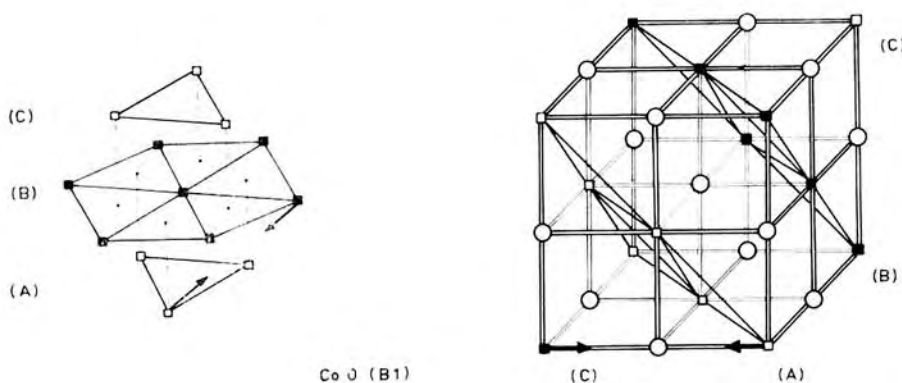


Fig. 2. — Nearest-neighbour configuration and magnetic structure of CoO, SB type B1, NaCl structure. The most important magnetic compounds with NaCl structure have the same magnetic lattice.

obtained show that we remain within the degree or accuracy expected for our rough model. As perfect order does not always correspond to a uniquely defined distribution, and as in most cases the samples had not been heat treated, we generally adopted the hypothesis of perfect disorder. If one assumes perfect disorder within a given crystallographic position, it is very easy to express the probability of finding two interacting ions, as a function of their concentration.

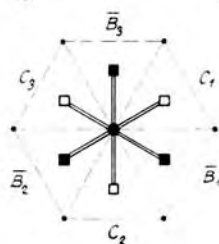
Finally, we would like to mention a last point. One knows of the existence of complex magnetic structures, in which the spins are not collinear, i.e. are not simply parallel or antiparallel with respect to a unique axis: in particular they may have a spiral or a triangular arrangement. These cases are not properly described by our simple model. One may be tempted to enlarge it in a natural way, multiplying the exchange

(a) **Magnetic structure type MnO (SB type B1, NaCl structure).**

(i) *Single cation.*

We first consider compounds in which a single type of cation appears. The relation between Curie temperature and standard superexchange parameters is easily written down, if one considers the following magnetic structure diagram and its corresponding table of linkages per unit anion.

Magnetic structure diagram Table of linkages



I_j	n_j	
	$\epsilon_j = +1$	$\epsilon_j = -1$
I_2	6	6
I_3	—	3

$$\text{Curie temperature : } \boxed{T_c = -3 I_3}$$

In our approximation, and for symmetry reasons, the Curie temperature is independent of the value of I_2 ; the values of I_3 deducible from the above relation are given in Table 6.

(ii) *Two-cation case.*

We now consider solid solutions of the same magnetic structure and which involve two different cations denoted by X and Y but a single anion (denoted by A).

The general chemical formula can be written as :

$$X_x Y_y A \quad \text{with} \quad x + y = 1$$

and we have three exchange parameters : I_3^{XX} , I_3^{XY} and I_3^{YY} .

If we assume a completely disordered distribution of the two kinds of cations among the positions available, we obtain the following expression for the Curie temperature :

$$T_c = -(3x^6 + 12x^5y + 18x^4y^2 + 12x^3y^3 + 3x^2y^4) I_3^{XX} - (6x^5y + 24x^4y^2 + 36x^3y^3 + 24x^2y^4 + 6xy^5) I_3^{XY} - (3x^4y^2 + 12x^3y^3 + 18x^2y^4 + 12xy^5 + 3y^6) I_3^{YY}.$$

System MgO-CoO.

We apply this formula to the compound $\text{Co}_{0.8}\text{Mg}_{0.2}\text{O}$. We obtain the simple relation :

$$T_c = 230^\circ = -1.92 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}),$$

because Mg^{2+} is a non-magnetic cation, and thus find for the above I_3 :

$$I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) = -120^\circ.$$

In the same way, for $\text{Co}_{0.67}\text{Mg}_{0.33}\text{O}$ we get :

$$T_c = 155^\circ = -1.36 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}),$$

giving

$$I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) = -114^\circ.$$

The two results agree fairly well.

System CoO-NiO.

Here again, we apply the same formula for $X = \text{Co}^{2+}$, $Y = \text{Ni}^{2+}$. There are now three parameters involved. For the three cases :

$$x_1 = 0.9, \quad y_1 = 0.1; \quad x_2 = \frac{2}{3}, \quad y_2 = \frac{1}{3};$$

$$x_3 = \frac{1}{3}, \quad y_3 = \frac{2}{3};$$

we obtain

$$311^\circ = -2.441 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) - 0.55 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Ni}^{2+}) - 0.03 I_3(\text{Ni}^{2+} - \text{O}^{2-} - \text{Ni}^{2+})$$

$$358^\circ = -1.336 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) - 1.468 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Ni}^{2+}) - 0.33 I_3(\text{Ni}^{2+} - \text{O}^{2-} - \text{Ni}^{2+})$$

$$425^\circ = -0.33 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) - 1.468 I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Ni}^{2+}) - 1.336 I_3(\text{Ni}^{2+} - \text{O}^{2-} - \text{Ni}^{2+})$$

giving :

$$I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+}) = -99^\circ$$

$$I_3(\text{Co}^{2+} - \text{O}^{2-} - \text{Ni}^{2+}) = -116^\circ$$

$$I_3(\text{Ni}^{2+} - \text{O}^{2-} - \text{Ni}^{2+}) = -166^\circ.$$

The results indicated above, and others as well[4], are given in Table 6.

(b) *Magnetic structure type NiFe_2O_4 (SB type Hl_1 , MgAl_2O_4 structure).*

In our model we distinguish not only between cations of different atoms, and with different ionization, but also between cations having different next-anionic surrounding. It follows that, in a normal spinel, there are at least two different types of cations and, in an inverse spinel, at least three such cation types. We recall that a spinel is called « normal » if the trivalent cations are on the tetrahedral sites only, the bivalent ones being on the octahedral positions. One has an « inverse » spinel when the trivalent cations are distributed with half of the divalent ones on the octahedral positions, the tetrahedral sites being occupied by divalent cations. For a normal spinel containing a single type of cation at the octahedral sites and a single type of cation at the tetrahedral site, the situation is the following :

Magnetic structure diagram

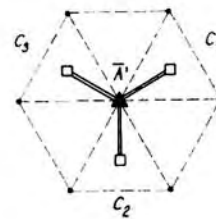


Table of linkages

I_j	n_j	
	$\epsilon_j = +1$	$\epsilon_j = -1$
I_2	3	—
I_8	—	3

$$\text{Curie temperature : } \boxed{T_c = 3 I_2 - 3 I_8}$$

For an inverse spinel, like NiFe_2O_4 , the formula for the Curie temperature becomes :

$$T_c = 3(x^3 + x^2y) I_2^{XX} + 6(x^2y + xy^2) I_2^{XY} + 3(xy^2 + y^3) I_2^{YY} - 3(x^3 + 2x^2y + xy^2) I_8^{XZ} - 3(x^2y - 2xy^2 + y^3) I_8^{YZ},$$

where X and Y denote the cations at octahedral sites, Z the cation at tetrahedral sites, and x, y, z , indicate the corresponding concentrations. In deriving the above relation, a completely disordered distribution of X and Y among the octahedral sites was assumed.

These few examples must suffice to illustrate our method. More details may be found in reference [4]. We now proceed to discuss the results yielded by our method.

3.3. — Formulation and test of some empirical rules regarding standard superexchange parameters

The set of parameters we have obtained (Tables 5 to 9) by applying our simple model in

a straightforward manner can be a useful tool for the prediction of possible Curie temperatures in non-metallic magnetic compounds. At present, however, these parameters cannot be used without great care, because of the relatively large range of error, and — the investigations being still incomplete — some parameters may be completely wrong. We believe nevertheless that an inspection of the survey Tables 5 to 9 will disclose that the set of parameters obtained is a valid one on the whole. From these tables we have tried to extract some physically plausible regularities. We have formulated such regularities in terms of «rules». For each rule, a comparative table is given, from which it is possible to gain a first impression about the reliability of the rule and of the method.

The reader then is able to draw his own conclusions. The interest of the values given here lies in the fact that they have not been manipulated in order to verify a priori hypotheses.

TABLE 5

Survey of the values obtained for I_2 superexchange parameters

□ — □	O ²⁻		S ²⁻		Sb ³⁻		Cl ⁻		Br ⁻	
Cr ³⁺ -Cr ²⁺							(-20) (-40)	CrCl ₂		
Mn ²⁺ -Mn ²⁺	-41	MnTiO ₃							(2.16)	MnBr ₂
Fe ³⁺ -Fe ²⁺	42 55/68	FeSO ₄ FeTiO ₃					8	FeCl ₂	4	FeBr ₂
Co ³⁺ -Co ²⁺	(-24)	CoSO ₄					8	CoCl ₂	6	CoBr ₂
Ni ²⁺ -Ni ²⁺	74 77	NiSO ₄ NiTiO ₃								
Ni ²⁺ -Cr ³⁺	-172	NiFeCrO ₄								
Ni ²⁺ -Fe ³⁺	-189	NiFe ₂ O ₄								
Cr ³⁺ -Cr ³⁺	-100	CrVO ₄	39 12	KCrS ₂ NaCrS ₂	118	Cr _x Mn _{1-x} Sb	16	CrCl ₃	37	CrBr ₃
Mn ³⁺ -Mn ³⁺	-200	ZnMn ₂ O ₄			270	Cr _x Mn _{1-x} Sb				
Fe ³⁺ -Fe ³⁺	-226	MgFe ₂ O ₄					(16)	FeCl ₃		
Cr ³⁺ -Mn ³⁺					-70	Cr _x Mn _{1-x} Sb				
Cr ³⁺ -Fe ³⁺	-376	Li _{0.5} Cr _{0.5} Fe ₂ O ₄								

TABLE 6

Survey of the values obtained for I_3 superexchange parameters

$\square - \square$	O^{2-}		S^{2-}		Se^{2-}		F^-	
$Cr^{2+}-Cr^{2+}$							<308	$KCrF_3$
$Mn^{2+}-Mn^{2+}$	-39/-41 -45	MnO $Mn_xCo_{1-x}O$	-43/-51 -55	α -MnS	-58 (-23.5)	MnSe $Li_xMn_{1-x}Se$	-119	$KMnF_3$
$Fe^{2+}-Fe^{2+}$	-63/-66	FeO					-153	$KFeF_3$
$Co^{2+}-Co^{2+}$	-97 -120 -114 -99 -101	CoO $Mg_{0.2}Co_{0.8}O$ $Mg_{0.33}Co_{0.77}O$ $Co_xNi_{1-x}O$ $Mn_xCo_{1-x}O$					-152/ -180	$KCoF_3$
$Ni^{2+}-Ni^{2+}$	-174/-178 -187 -166 -190	NiO NiO $Co_xNi_{1-x}O$ $Li_xNi_{1-x}O$					-326	$KNiF_3$
$Mn^{2+}-Co^{2+}$	-61	$Co_xMn_{1-x}O$						
$Co^{2+}-Ni^{2+}$	-116	$Co_xNi_{1-x}O$						
$Mn^{2+}-Mn^{2+}$					-241	$Li_xMn_{1-x}Se$		
$Ni^{2+}-Ni^{2+}$	-217	$Li_xNi_{1-x}O$						
$Cr^{3+}-Cr^{3+}$	-426	$LaCrO_3$						
$Mn^{3+}-Mn^{3+}$	350/380	$LaMnO_3$			(500)	$Li_xMn_{1-x}Se$		
$Fe^{3+}-Fe^{3+}$	-825 -920 -1000 -1010	$ErFeO_3$ $HoFeO_3$ $LaFeO_3$ $NdFeO_3$						
$Ni^{3+}-Ni^{3+}$	(-49)	$Li_xNi_{1-x}O$						
$Mn^{4+}-Mn^{4+}$	-147	$CaMnO_3$						

TABLE 7

Survey of the values obtained for I_4 superexchange parameters

$\square - \square$	$Cr^{3+} - Cr^{3+}$		$Mn^{3+} - Mn^{3+}$		$Fe^{3+} - Fe^{3+}$		$Co^{3+} - Co^{3+}$	
F^-	-80	CrF_3	129/141	MnF_3	-394	FeF_3	-460	CoF_3

TABLE 8
Survey of the values obtained
for I_8 superexchange parameters

$\Delta - \square$	O^{2-}	S^{2-}
$Mn^{2+}-Cr^{3+}$		5 $MnCr_2S_4$
$Fe^{2+}-Cr^{3+}$		-25 $FeCr_2S_4$
$Co^{2+}-Cr^{3+}$		-40 $CoCr_2S_4$
$Cu^{2+}-Cr^{3+}$	-145 $CuCr_2O_4$	
$Co^{2+}-Mn^{3+}$	-224 $Co_{1.6}Mn_{1.1}O_4$	
$Fe^{3+}-Ni^{2+}$	-244 $NiFe_2O_4$	
$Mn^{3+}-Mn^{2+}$	-315 Mn_3O_4	
$Fe^{3+}-Fe^{3+}$	-590 $MgFe_2O_4$	
$Fe^{3+}-Cr^{3+}$	-402 $Cr_{0.5}Li_{0.5}Fe_2O_4$	

TABLE 9
Survey of the values obtained
for I_{13} superexchange parameters

$\Delta - \Delta$	O^{2-}	S^{2-}
$Mn^{2+}-Mn^{3+}$		-46/-55 -50/-80/-97 γ -MnS β -MnS
$Fe^{3+}-Fe^{3+}$	-723 β -NaFeO ₂	

(a) The cationic valency rule.

« The absolute value of a given superexchange parameter for a fixed anion increases with increasing valency of the cations involved. »
(See Table 10.)

(b) The cationic sequence rule.

« The absolute value of a given superexchange parameter for a fixed anion increases with the sequence :

... Cr, Mn, Fe, Co, Ni. »

(See Tables 11 and 12.)

(c) The anionic sequence rule.

« The absolute value of a given superexchange parameter for a fixed pair of cations increases according to the sequence :

$Cl^- \sim Br^-$; $Se^{2-} \sim S^{2-}$; $O^{2-} \sim F^-$. »

We do not reproduce a new table for this rule, as its validity can easily be verified from the survey Tables 5 to 9.

TABLE 10
Comparison of standard superexchange parameters according to the cationic valency rule

Anion	Cations	Parameter	Comparative cationic valency		
			2+	3+	4+
O^{2-}	Mn-Mn	I_2 I_3	41 -39/-41/-45	-200 350/380	-147
	Fe-Fe	I_2 I_3	42/55/68 -63/-66	-226 { -825 / -920 / { -1000 / -1010	
	Ni-Ni	I_3	{ -166 / -174 / -178 { -187 / -190	(-49)	
	Ni^{2+} -Ni	I_3	-166/.../-190	-217	
	Ni^{3+} -Ni	I_3	-217	(-49)	
Se^{2-}	Mn-Mn	I_3	(-23.5)/-58	(500)	
	Mn^{2+} -Mn	I_3	(-23.5)/-58	-241	
	Mn^{3+} -Mn	I_3	-241	(500)	
Cl^-	Cr-Cr	I_2	(-20)/(-40)	16	
	Fe-Fe	I_2	8	(16)	

TABLE 11

Comparison of standard superexchange parameters according to the cationic sequence rule for a pair of identical cations

Anion	Parameter	Valency of the cation	Cr	Mn	Fe	Co	Ni
O ²⁻	I ₂	2 3	-100	-41 -200	42/55/68 -226	(-24)	74/<77
	I ₃	2 3	-426	-39/-41/-45 350/380	-63/-66 -825/.../-1010	-97/.../-120	-174/.../-190 (-49)
	I ₈	3		-315	-590		
Sb ³⁻	I ₂	3	118	270			
F ⁻	I ₃	2	<308	-119	-153	-152/-180	-326
	I ₄	3	-80	129/141	-394	-460	
Cl ⁻	I ₂	2	(-20)/(-40)		8	8	
		3	16		(16)		
Br ⁻	I ₂	2		(2.16)	4	6	

TABLE 12

Comparison of standard superexchange parameters according to the cationic sequence rule for a pair of different cations

Anion	Parameter	First cation	Valency of 2nd cation	Second cation				
				Cr	Mn	Fe	Co	Ni
O ²⁻	I ₂	Ni ²⁺	3	-172		-189		
		Fe ³⁺	3	-376		-226		
	I ₃	Co ²⁺	2		-61		-97/.../-120	-116
	I ₈	Fe ³⁺	3	-402		-590		
S ²⁻	I ₈	Cr ³⁺	2		5	-25	-40	
Sb ³⁻	I ₃	Cr ³⁺	3	118	-70			
		Mn ³⁺	3	-70	270			

4. — Oxyhalogenide cobalt compounds

The goal of obtaining cobaltites with properties comparable to those of ferrites may be attained if one succeeds in substituting Fe³⁺ by Co²⁺ in such compounds. Our idea was to consider oxyhalogenide magnetic compounds instead of oxides and, by thus lowering the anionic valency, to compensate for the charge difference between Fe³⁺ and Co²⁺. From the dissymmetry of the anionic close-packing we expected interesting electro-magnetic properties.

In the frame of the present research, experimental investigations with a view to finding possible cobalt oxyhalogenides could have only an exploratory character. We were therefore obliged to make a choice, and we restricted ourselves to the investigation of oxyfluorides. One reason for our choice was the fact that fluorine and oxygen have about the same ionic radius. A second reason was that, as a result of our phenomenological investigation on magnetic compounds reported above, we expected an enhancement of the Curie temperature from the

substitution of fluorine for oxygen, whereas the opposite effect was foreseen from the replacement by other halogenides. For this last effect, one could say qualitatively that in compact structures greater anionic radii lower the concentration of the magnetic active centres in a given compound, and therefore, in general, also reduce the Curie temperature.

We tried first to prepare cobalt oxyfluorides by sintering reactions of CoF_2 and CoO , but no cobalt oxyfluoride was obtained in this way.

We then attempted to prepare the same class of compounds by decomposition of Co(II) fluoride hydrates ($\text{CoF}_2 \cdot n\text{H}_2\text{O}$) and Co(II) hydroxyfluorides ($\text{CoF}_{2-x}(\text{OH})_x$). Here again it was not possible to obtain anhydrous oxyfluorides of divalent cobalt. Trivalent cobalt oxyfluoride (CoOF) may be obtained from $\text{CoO}(\text{OH})$: this possibility, however, was not further investigated.

During this research a number of cobalt compounds were prepared for the first time. The hydrolysis of CoF_2 -solutions, the decomposition and hydration of the hydroxyfluorides and fluoride hydrates have been investigated by orientative experiments. These results will appear in a paper by H. Schmid [6].

Let us summarize the results which are significant in the present framework.

4.1. — $\text{CoF}_2 \cdot 2\text{H}_2\text{O}$

This compound was prepared for the first time. Its structure is not yet known, but the Debye-Scherrer diagram is similar to that of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$.

4.2. — $\text{CoF}_{2-x}(\text{OH})_x$

This compound was also prepared for the first time. It has a rutile structure, and it is an example of the general property that in hydroxyfluorides the F/OH-ratio can vary within large limits without influencing the structure.

4.3. — $\text{CoF}(\text{OH})$

This compound has a $\text{ZnF}(\text{OH})$ structure. Ordered and semi-ordered modifications were obtained for the first time.

5. — β -Alumina and related magnetic compounds

Another way of reaching the goal mentioned in the previous section, i.e. obtaining cobaltites which compare favourably with ferrites, could consist in substituting Co^{3+} in its high spin state for Fe^{3+} . We know that a necessary condition for this is that the crystal field strength around a Co^{3+} cation should be lower than that normally observed in oxides. A lower field strength can be obtained in several ways, for example:

- (i) by lowering the anionic valency;
- (ii) by choosing compounds with a non close-packed anionic structure;
- (iii) by introducing large positive ions in the close-packing itself.

Approach (i) leads practically to the same type of compounds as those considered in section 4. The compounds of type (ii) are, so far as we know, easily unstable. Usually they can be stabilized by addition of large positive ions: this means (iii). Several important classes of magnetic compounds belong to this category. Let us mention the perovskite (BaTiO_3), the garnets ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$) and the magnetic compounds with hexagonal symmetry. These last compounds have been investigated in detail by the Philips Laboratories [7]. They are known principally as ferroxdure and ferroxplana, and belong to the magnetoplumbite family of structures. Substitutions of cobalt influence the magnetic properties of these crystals to a large extent.

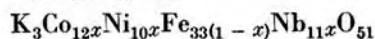
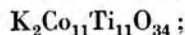
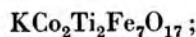
The main feature of the magnetic structures of magnetoplumbite type is that they consist of blocks of ferrite type which are coupled together so that the magnetic moment of the ferrite blocks are parallel.

The β -alumina structure of $\text{KFe}_{11}\text{O}_{17}$ is a very similar one. Again there are ferrite blocks, but this time the coupling between the blocks is such that the magnetic moments of the blocks become antiparallel (Fig. 3).

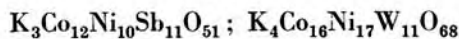
Closer inspection of the β -alumina structure shows that it should be possible to influence the coupling between the blocks (Fig. 4) and that in these compounds cobalt should have the same importance as in compounds of the magnetoplumbite type. For all these reasons, and also because the low valency of the non-magnetic cation (Na^+ for example) still allows a relatively high concentration of cations carrying a magnetic moment, we have investigated a number of possible substitutions in compounds with the β -alumina structure type.

5.1. — Replacement of Fe^{3+} by Co^{2+}

Several replacements have been carried out. Together with Co^{2+} , another high-valency cation was substituted (Ti^{4+} , Nb^{5+} , Sb^{5+} , W^{6+}). The following compositions have been prepared:



with $x = 0.1, 0.2, 0.5$, and 1 ;



and their structure examined.

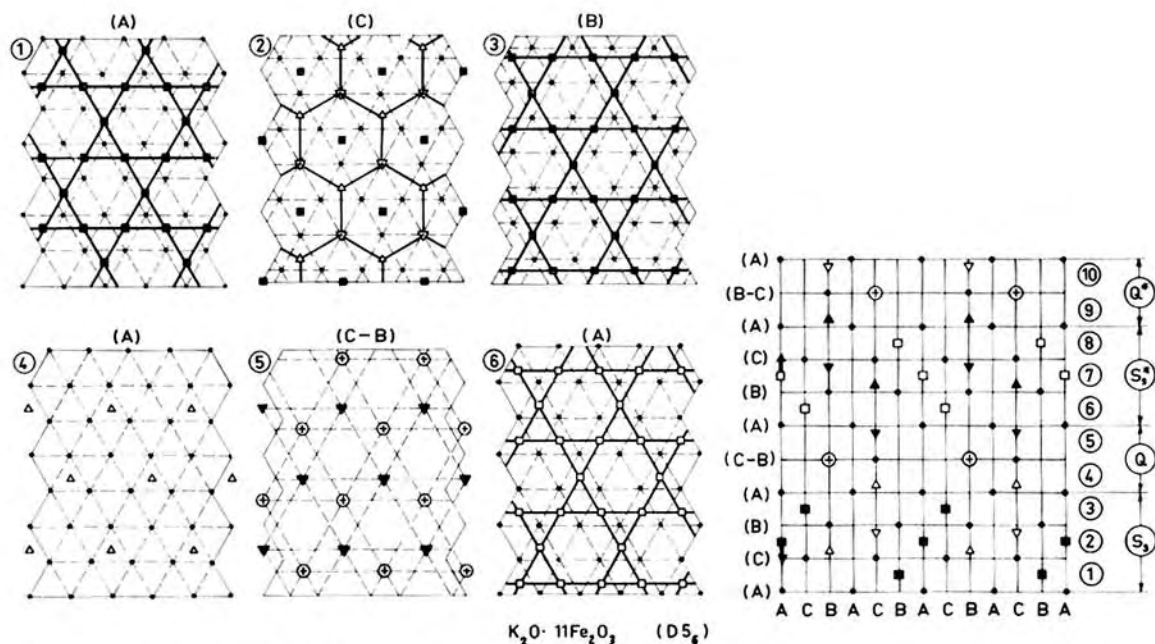


Fig. 3. — Crystallographic build-up and magnetic structure of $K_2O \cdot 11Fe_2O_3$, SB type $D5_h$ β -alumina structure.

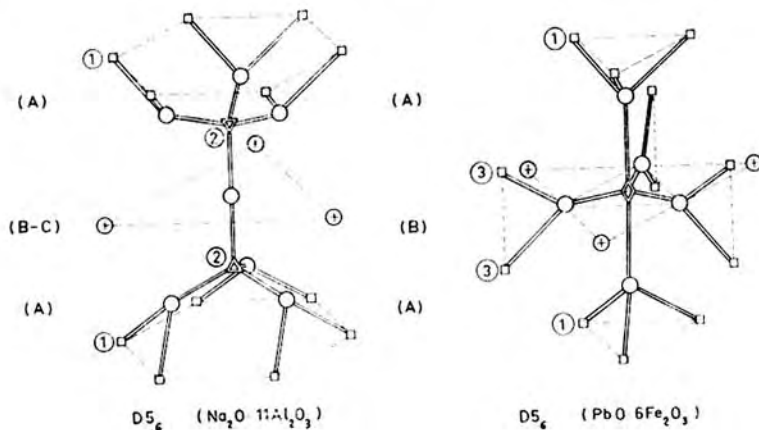
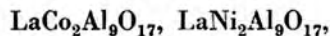


Fig. 4. — Comparison of the indirect exchange interaction nets in compounds of the SB type $D5_h$: $Na_2O \cdot 11Al_2O_3$ (β -alumina) and $PbO \cdot 6Fe_2O_3$ (magneto-plumbite) structure.

For $K_3Co_{12x}Ni_{10x}Fe_{33(1-x)}Nb_{11x}O_{51}$, with $x = 0.1$ and 0.2 , a β -alumina structure was found, together with an unidentified structure.

5.2. — Replacement of K^+ and Al^{3+} by La^{3+} and Co^{2+}

The compositions prepared were :



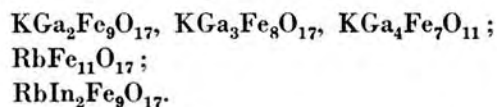
but no phase of β -alumina type was found.

5.3. — Partial replacement of Al^{3+} by Co^{3+}

The composition prepared was : $KCo_2Al_9O_{17}$. 90 % of this preparation was $CoAl_2O_4$. In addition, there were traces of unidentified substances.

5.4. — Replacement of Fe^{3+} by Ga^{3+} and In^{3+}

The compositions prepared were :



The magnetic susceptibility of these compounds has been measured between 80° and 850° . The main purpose of these substitutions was to change the magnetic coupling between the ferrite blocks.

All the compounds indicated above had β -alumina structure. The presence of impurities, however, is not excluded.

The curves of the inverse susceptibility plotted against temperature show a discontinuity of the

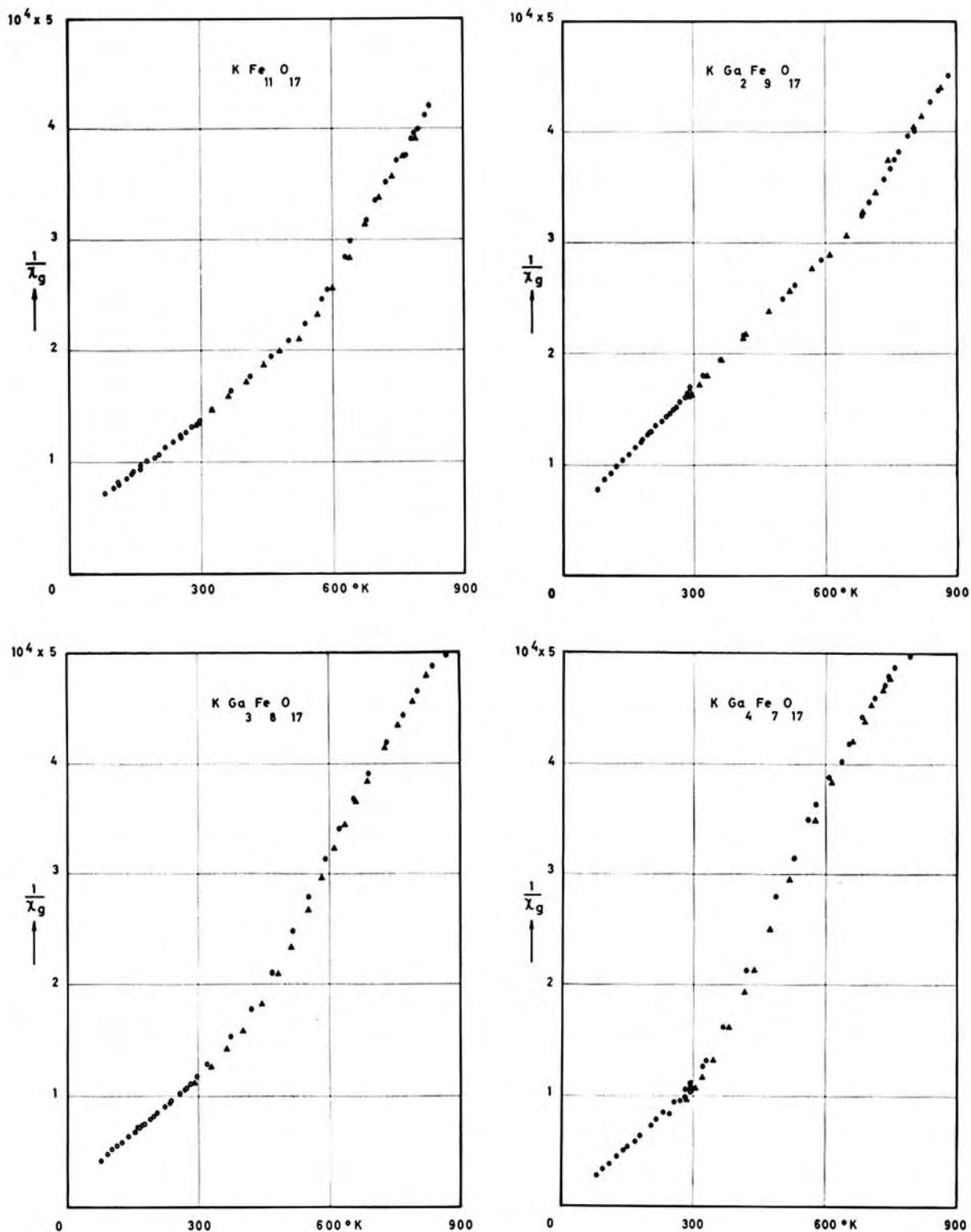


Fig. 5. — Inverse gram-susceptibility (c.g.s. units) of four compounds with the β -alumina structure (*).

(*) The kink in the $1/\chi_g$ -curve of $KFe_{11}O_{17}$ appears at a lower temperature than that indicated by Gorter (8) for single crystals. This may be due to an incorporation of more potassium than stoichiometric. We had to sinter with 100 % excess potassium (in the form of K_2CO_3) at $1200^\circ C$, with 25 %, 50 %, and 75 % excess potassium, α - Fe_2O_3 was always present because of K_2O -loss by evaporation. The samples containing gallium were also prepared with 100 % excess potassium.

slope in the case of compounds containing gallium. We have not yet explained this phenomenon, which may indicate the change in the coupling that we looked for.

Concluding remarks

The goal of the work we have reported was to prepare a research programme with a view to finding new magnetic cobalt compounds. At the same time we oriented our work in such a way that it was to make sense before any particularly interesting new compound was found. Therefore the main effort has been devoted to devising the methods for the prediction of magnetic properties of inorganic compounds. The experimental part of the work was purely exploratory.

We would be satisfied if the present research were to prove stimulating to other laboratories as well in their own research on magnetic cobalt compounds.

Acknowledgement

We wish to thank Mr. Rieder for making the susceptibility measurements.

We also express our gratitude to the Cobalt Information Centre, Brussels, for the interest and

comprehension demonstrated throughout this research. We hope that the work done will bear fruit also in more technical domains.

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