II. Magnetic compounds with spg nel structure

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An important part of the research on the oxides of the transition elements is concerned with the relation between their crystal structure and chemical composition and their magnetic properties. By giving the oxides the appropriate chemical composition it is possible, within certain limits, to predetermine their magnetic properties. In this article we shall give a number of examples to illustrate this procedure, often referred to as "ionic engineering". We shall confine ourselves to materials with spg nel structure, because many magnetic materials in use have this structure. To obtain scientific insight it is often necessary to study compounds with a simpler structure, such as the perovskite or rock salt structure. These compounds, however, show no magnetic properties that can be put to use. There are other materials, on the other hand, that have highly complex crystal structures (e.g. garnets and hexagonal ferrites), but with these the relation between properties and chemical composition is much more difficult to understand [1].

A typical example of the influence of composition on magnetic properties is the following. Zinc ferrite (ZnFe$_2$O$_4$) and magnesium ferrite (MgFe$_2$O$_4$) are similar compounds of the form Me$^{2+}$Fe$^{3+}$O$_4$ (Me = metal). Both have the spg nel structure, and the constituent ions of the one are magnetically equivalent to those of the other: Fe$^{3+}$ is paramagnetic, Mg$^{2+}$ and Zn$^{2+}$ are both diamagnetic. The magnetic properties, however, are widely different. Magnesium ferrite exhibits a spontaneous magnetic moment and has a very high Curie temperature (715 °K), whereas zinc ferrite has no magnetic moment, even at low temperature. These differences are apparently due to the choice of the bivalent diamagnetic ion in the composition Me$^{2+}$Fe$_2$O$_4$.

The spg nel structure

It is not possible to build up a magnetic material properly if the crystal structure is unknown. First, therefore, we shall give a description of the spg nel structure.

Compounds with spg nel structure have the general chemical formula AB$_2$X$_4$. In this formula X represents an anion (in most cases the O$^{2-}$ ion). These anions form a cubic close-packed structure. In this structure the smaller cations fit into the interstices, which are surrounded by four or by six anions arranged in a regular tetrahedron or octahedron (see fig. 1). A represents a cation at a tetrahedral site (or A site) and B a cation at an octahedral site (or B site). We see that there are therefore two possible sites in the structure for the cations. It is because of this structural peculiarity that spg nel structure ferrites can have a magnetic moment. This means however that the properties of

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Fig. 1. The spg nel structure. The positions of the ions in two octants of the unit cell are shown. The large circles represent anions, the small hatched circles octahedrally surrounded cations (B sites) and the small open circles tetrahedrally surrounded cations (A sites).
energy. The cation distribution is determined by a large number of energy terms, which are to some extent conflicting. While some terms favour the normal distribution, other terms will oppose it because they favour the inverse distribution. It is therefore difficult, and usually in fact impossible, to predict which distribution will materialize. The following are some of the energy terms involved [3]:

a) The Madelung energy, which originates from the electrostatic attraction and repulsion between the positive and negative ions. It follows from electrostatic considerations, for example, that lower energies result with large ions of low charge at A sites or small ions of high charge at A sites.

b) The Born energy, which is related to the repulsion between the electron clouds of the ions.

c) The ordering energy, where cations of different charge are located on one type of lattice site: the effect of ordering is to minimize electrostatic repulsion between the cations (the highly charged cations surround themselves as far as possible with ions of low charge). Calculations of these three energy terms were carried out in the forties by members of our laboratory [3].

d) The energy connected with the preference of particular ions for occupying tetrahedral or octahedral sites (see part I of this article). Familiar examples are the preference of the Zn$^{2+}$ ion (3d$^{10}$ configuration) for tetrahedral sites and of the Cr$^{3+}$ ion (3d$^3$ configuration) for octahedral sites. The crystal field theory discussed in part I shows that in general ions of configuration d$^1$, d$^2$, d$^4$, d$^6$, d$^7$ and d$^9$ have some preference for octahedral sites, and ions with configuration d$^3$ and d$^8$ a strong preference for octahedral sites, while ions with configuration d$^5$, d$^6$ and d$^{10}$ show no preference. The crystal field theory does not, however, take account of deviations from the ionic bonding model, which certainly occur (cf. part I). We have therefore attempted to approach this preferential energy with the aid of the more general but more complicated ligand field theory [10]. Quite a number of simplifications have to be introduced, however, in order to obtain a result, and this will therefore not be much more reliable than that obtained with crystal field theory. We found that ions with configuration d$^3$, d$^5$, d$^7$, d$^9$ and d$^{10}$ have a preference for tetrahedral sites, ions with configuration d$^0$, d$^1$, d$^3$, d$^4$ and d$^8$ have no preference, and ions with configuration d$^2$ have a preference for octahedral sites.

e) The polarization energy of the anion. The anion is surrounded more or less tetrahedrally by one cation at an A site and three cations at B sites. By making an extreme distribution of the positive charges, for example low-charged ions at A sites and highly charged ions at B sites, a strong electric field is produced around the anion, causing it to become polarized.

A detailed study of cation distribution in the spinel structure has shown that the last two energy terms are often critical, as the first three roughly compensate one another in various distributions. This is no more than a rule of thumb, however.

We shall now consider a few examples.

The spinel MgAl$_2$O$_4$, which contains exclusively ions with the inert gas configuration, is normal: Mg$^{2+}$[Al$^{3+}$]O$_4$. If the Mg$^{2+}$ ion is replaced by other bivalent ions, for example Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$ or Cu$^{2+}$ (the electron configurations being 3d$^5$, 3d$^6$, 3d$^7$, 3d$^8$, 3d$^9$ respectively), then the normal distribution remains, except with NiAl$_2$O$_4$, which is almost entirely inverse. This indicates that the Ni$^{2+}$ ion has a greater preference for B sites — or at any rate less preference for A sites — than the other bivalent ions mentioned, in agreement with the two rules given under (d), so that the inverse distribution of NiAl$_2$O$_4$ must be attributed to the preference energy.

If the Al$^{3+}$ ion in MgAl$_2$O$_4$ is replaced by other trivalent ions, for example Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$ or Ga$^{3+}$ (electronic configurations 3d$^1$, 3d$^2$, 3d$^3$, 3d$^4$, 3d$^{5}$, 3d$^{10}$ respectively), a normal distribution is again found, except with Fe$^{3+}$ and Ga$^{3+}$. The latter ions drive out the Mg$^{2+}$ ion from the A sites. This is in agreement with the second rule of preference under (d).

The effect of the polarization energy is well illustrated by the cation distribution of spinels containing lithium, for example LiMe$^{2+}$Me$^{6+}$O$_4$ and LiMe$^{3+}$Me$^{4+}$O$_4$. In these spinels the Li$^+$ ion is always found at A sites, so that the ions of low and high charge are grouped symmetrically around the anion and the polarization energy is high. There is a deviation from this distribution only if cations are present which have a strong preference for A sites, as in the case of LiFeTiO$_4$ and LiGaTiO$_4$.

Insight into the factors determining the distribution of cations can best be obtained by studying a series of compounds in which only one cation is varied. This method has been followed in our work.

**Magnetic properties**

The magnetic properties of compounds with spinel structure, in particular of ferrites, have been explained by Néel [4]. In a spinel A[B$_2$]O$_4$ with paramagnetic ions A and B the following magnetic interactions may be distinguished:

a) AB interaction, a magnetic interaction between cations at tetrahedral and cations at octahedral sites;

b) BB interaction, a magnetic interaction between the cations at octahedral sites. (The analogous interaction between cations at tetrahedral sites — AA interaction — is very weak owing to the considerable distance be-
between the cations on A sites. This interaction is therefore disregarded.

Néel assumed that the AB interaction is negative and strong compared with the BB interaction. The magnetic structure of a spinel, that is the manner in which the magnetic moments in the crystal lattice are oriented with respect to one another, can then be represented symbolically as \( \bar{A}(\bar{B} \bar{B})\)O4. The sign of the BB interaction is not relevant here. The AB interaction orients the moments at all the A sites antiparallel to those at all the B sites. Since, generally speaking, the magnetic moment of two B ions will not be identical with that of one A ion, the result is a magnetic moment which is equal to the difference between the magnetic moments at A and at B sites. This phenomenon is known as ferrimagnetism.

An actual example is nickel ferrite with the cation distribution \( \text{Fe}[\text{NiFe}]_2\text{O}_4 \). The Fe\(^{3+}\) ion (3d\(^8\)) has a magnetic moment of 5 \( \mu_B \), the Ni\(^{2+}\) ion (3d\(^{8}\)) a magnetic moment of about 2.3 \( \mu_B \) \([2]\). The resultant magnetic moment is thus:

\[
m = m_B - m_A = (5 \mu_B + 2.3 \mu_B) - 5 \mu_B = 2.3 \mu_B.
\]

Values have been found experimentally between 2.2 \( \mu_B \) and 2.3 \( \mu_B \) (see, for example, reference \([2]\)) so that the agreement between theory and experiment is good.

The difference between the magnetic properties of magnesium ferrite and zinc ferrite, referred to in the introduction are thus explained. Whereas magnesium ferrite is almost inverse (MgO.1Fe\(_{0.9}\)MgO.9Fe\(_{1.1}\)O4), zinc ferrite is normal (Zn\(_{2}\)[Fe\(_{2}\)O\(_4\)]) because Zn\(^{2+}\) has a preference for A sites. Magnesium ferrite therefore has a magnetic moment (1.1 - 0.9) \times 5 \( \mu_B = 1 \mu_B \), owing to the negative interaction between unequal numbers of Fe\(^{3+}\) ions at A and at B sites. In zinc ferrite, however, there is no AB interaction (Zn\(^{2+}\) is diamagnetic). In fact, zinc ferrite shows paramagnetic behaviour down to a very low temperature. This also proves that the BB interaction between Fe\(^{3+}\) ions must be very weak.

It is interesting to note that the magnetic moment of magnesium ferrite differs from zero owing to the slight deviation from the inverse cation distribution. For the hypothetical completely inverse Fe[MgFe]O4 one would expect a magnetic moment equal to zero.

Néel's hypothesis implies the possibility of anomalous magnetization-temperature curves \((M-T)\) curves.

The saturation magnetization of a ferromagnetic material decreases with increasing temperature and vanishes at the Curie temperature; this is the Brillouin curve, shown in fig. 2. Under certain conditions, completely different \(M-T\) curves may be expected for a ferrimagnetic material. This is because the magnetization of a ferrimagnetic compound represents the difference between two or more sub-lattice magnetizations. Now if the temperature-dependence is not the same for these sub-lattice magnetizations, anomalous \(M-T\) curves may be found. This is illustrated diagrammatically in fig. 3, where two dissimilar sub-lattice magnetizations, \(M_A\) and \(M_B\), are shown as a function of temperature. The difference \(M_B-M_A\) is the magnetization \(M\) of the compound. If \(|M_B| > |M_A|\) at 0 °K, the difference \(M_B-M_A\) is the magnetization \(M\) of the compound. If \(|M_B| > |M_A|\) at 0 °K,

\[
\text{Fig. 2. Magnetization } M \text{ of a ferromagnetic material as a function of temperature } T.
\]

\[
\text{Fig. 3. How anomalous magnetization-temperature curves } (M-T) \text{ curves for a ferrimagnetic material can arise. The sub-lattice magnetizations } M_A \text{ and } M_B \text{ (negative and positive respectively) are shown as functions of temperature. These disappear at the same temperature (the Curie temperature) because they owe their existence to their exchange interaction (AB interaction). The difference } M_B-M_A \text{ is the magnetization } M \text{ of the compound. This is measured experimentally } (M_A \text{ and } M_B \text{ are not directly measurable).}
\]

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\text{It is assumed in the figure that } M_B \text{ decreases faster with increasing } T \text{ than } M_A. \text{ If now } |M_B| > |M_A| \text{ at } 0 \degree \text{ K, an } M-T \text{ curve with a compensation point may be found (a); if } |M_B| < |M_A|, \text{ the result may be a curve showing a maximum (b). Néel called the first a type } N \text{ curve and the second a type } P \text{ curve.}
\]

\([2]\) For further details, see G. Blasse, Philips Res. Repts., Suppl. 1964, No. 3.


\([5]\) The spin moment of Ni\(^{2+}\)(3d\(^8\)) is 2 \( \mu_B \), but there is also a contribution from the orbital momentum.
and $M_B$ decreases faster with temperature than $M_A$, an $M-T$ curve is found with a compensation point at which north and south poles change sign (type $N$ magnetization curve, fig. 3a). If, however, $|M_B| < |M_A|$ at 0 °K, the resultant curve has a maximum (type $P$ magnetization curve, fig. 3b). Both anomalous magnetization curves were found experimentally after Néel had predicted them: the type $N$ curve was found in our laboratory by Gorter and Schulkes [6], the type $P$ curve by Maxwell and Pickart [7]. This phenomenon clearly indicates that there must be more than one magnetic lattice present in a ferrimagnetic compound. The effect revealed by the type $P$ magnetization curve opens up the possibility of making magnetic materials whose magnetization is independent of temperature in a particular temperature range.

The magnetic sub-lattices can be given a widely different temperature dependence by introducing in one way or another a strongly negative BB interaction. This interaction as it were disturbs the parallel orientation of the moments of the B cations, so that the magnetic moment of the B lattice decreases rapidly. This situation is assumed in fig. 3a and b.

We shall now show how certain magnetic properties can be produced by chemical substitutions.

The nickel ferrite-vanadite system (NiFe$_2$-$t$V$_t$O$_4$)

If the Fe$^{3+}$ ion in nickel ferrite, Fe[NiFe]O$_4$, is replaced by the V$^{3+}$ ion (configuration $3d^5$), the magnetic properties are drastically changed. With increasing vanadium content the magnetic moment and the Curie temperature decrease, and the shape of the $M-T$ curve undergoes marked variation. In order to be able to interpret these effects, it is necessary first of all to know the cation distribution of this system. For the time being, we shall consider only low vanadium concentrations, i.e. $0 \leq t \leq 1$. The cation distribution then proves to be Fe[NiFe$_{1-t}$V$_t$]O$_4$ [8]. This means that the vanadium introduced takes the place of only the ferric ions on B sites. Since the V$^{3+}$ ion has two unpaired electrons, the magnetic moment of this ion will be roughly $2 \mu_B$. This means therefore that the total magnetic moment decreases as the vanadium content increases, the reason being that the V$^{3+}$ ion has a smaller moment than the Fe$^{3+}$ ion it replaces. At a particular vanadium concentration ($t \approx 0.75$) the magnetizations of A and B sites become identical, so that the total magnetic moment (at 0 °K) is zero (see fig. 4).

At a higher vanadium concentration ($1 \leq t \leq 2$) the magnetization values differ considerably from those that can be calculated for any reasonable cation distribution on the basis of Néel's hypothesis. This means that the BB interaction is no longer weak compared with the AB interaction. An asymptotic Curie temperature equal to $-750$ °K has indeed been found for the spinel Mg[V$_2$]O$_4$, a compound in which the only possible magnetic interaction is BB interaction between V$^{3+}$ ions. Evidently, therefore, this BB interaction must be strongly negative. Because of this

![Fig. 4. Magnetic moment $m$ (in Bohr magnetons) of the system nickel ferrite-vanadite (NiFe$_{2-t}$V$_t$O$_4$) as a function of vanadium content $t$. The crosses indicate values found experimentally. The straight line was calculated for the cation distribution Fe[NiFe$_{1-t}$V$_t$]O$_4$ on the basis of Néel's hypothesis and using the following values for the magnetic moments of the ions: Ni$^{2+}$ 2.3 $\mu_B$; Fe$^{3+}$ 5 $\mu_B$; V$^{3+}$ 2 $\mu_B$.](image)

![Fig. 5. The Curie temperature $T_c$ for the system NiFe$_{2-t}$V$_t$O$_4$ as a function of the vanadium content $t$.](image)
strongly negative BB interaction between V$^{3+}$ ions the magnetic moments at B sites will no longer be parallel at a particular vanadium concentration (probably $t > 1$) but will align themselves at a particular angle to each other, thus making concessions to both the AB and the BB interaction. This may explain why the experimentally determined magnetizations differ so much from those predicted on the basis of Néel's hypothesis.

We have already stated that strong BB interactions would give rise to anomalous $M$-$T$ curves. These have in fact been found for certain values of $t$ (see fig. 6). The $M$-$T$ curve for compositions with $t < 0.75$ is of type $N$, and for compositions with $t > 0.75$ it is of type $P$. This agrees well with the theory, since the magnetization of the B ions is greater than that of the A ions for $t < 0.75$, so that we have the situation of fig. 3a, while the magnetization of the A ions is greater than that of the B ions when $t > 0.75$, giving the situation in fig. 3b. The assumption here, then, is that the average BB interaction is strongly negative, and this is easily demonstrated by experiments on the spinel Mg[V$_2$]O$_4$ (see above).

We have succeeded in making a ferrite which has a low temperature-independent magnetization at about room temperature (NiFeVO$_4$, the composition with $t = 1$; see fig. 6). This property is particularly desirable for microwave ferrites. Unfortunately, the ferrite with this composition has certain other properties which make it less suitable for application, namely a relatively low electrical resistivity (about 100 $\Omega$cm) and a high anisotropy.

By introducing a strongly negative BB interaction in this case we have made the normal $M$-$T$ curve of nickel ferrite change into anomalous curves. The curve with the compensation point, type $N$, was first obtained, and then the one with the maximum, type $P$. It may now be asked whether it is also possible to introduce a positive BB interaction into nickel ferrite, thus causing the normal $M$-$T$ curve to change first into a curve of type $P$ and only afterwards into a curve of type $N$.

**The Ni ferrite-antimonate system** (Ni$_{1+2t}$Fe$_{2-3t}$Sb$_t$O$_4$)

The inverse sequence of $M$-$T$ curves (first type $P$ and then type $N$) has been obtained by replacing an increasing number of the Fe$^{3+}$ ions in nickel ferrite by a combination of Ni$^{2+}$ and Sb$^{5+}$ ions, in accordance with the rule $3$Fe$^{3+}$ $\rightarrow$ $2$Ni$^{2+}$ $+$ Sb$^{5+}$. This results in materials that have the general composition Ni$_{1+2t}$Fe$_{2-3t}$Sb$_t$O$_4$. The maximum attainable value of $t$ is about 1/3. At values of $t > 1/3$ single-phase spinels can no longer be obtained (NiSb$_2$O$_6$ forms a second phase). The magnetization and the $M$-$T$ curve as a function of $t$ are shown in figs. 7 and 8.

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[8] The ways in which the cation distribution can be determined experimentally are discussed and commented upon in reference [3].
The cation distribution is seen to be as follows. The Sb\(^{3+}\) ions are located solely at B sites. The Ni\(^{2+}\) ions are for the greater part at B sites. The percentage of Ni\(^{2+}\) ions at A sites increases with increasing value of \(t\).

By way of illustration we give the distribution for the two extreme compositions, i.e. for NiFe\(_2\)O\(_4\) (\(t = 0\)) and for Ni\(_{3/2}\)FeSb\(_{1/3}\)O\(_4\) (\(t = 1/3\)): these are Fe[NiFe]O\(_4\) and Ni\(_{1/3}\)FeSb\(_{1/3}\)O\(_4\) respectively.

It can be seen from fig. 8 that the \(M-T\) curve in this system changes from normal to type \(P\). The type \(N\) is not found here. This is attributable to the fact that the state in which the magnetization of the A ions is greater than that of the B ions is not attained. The occurrence of a type \(P\) curve points to a positive BB interaction. Since the mutual BB interactions between Ni\(^{2+}\) ions and between Fe\(^{3+}\) ions are extremely weak, it can obviously be assumed that the BB interaction between Ni\(^{2+}\) and Fe\(^{3+}\) is positive. Further evidence supporting this assumption was later found independently.

As fig. 8 shows, the introduction of a positive BB interaction has enabled a \(P\)-type \(M-T\) curve to be obtained. The maximum in the curve, however, is between 200 and 250 °K, and this makes the material less suitable for application. Moreover, the shape of the curve at the maximum is rather sharp.

Nevertheless, the existence of positive BB interaction raises the question of whether it might be possible to make a ferromagnetic instead of a ferrimagnetic spinel. In a ferromagnetic spinel all the magnetic moments would be parallel, making it possible to achieve a very high magnetization.

**Ferromagnetic oxides with spinel structure**

Since it is very improbable on theoretical grounds that the AB interaction between any ions could ever be positive, a ferromagnetic spinel can only be obtained by locating diamagnetic cations at A sites and paramagnetic cations, between which there must be a positive interaction, at B sites. Materials have recently been found in which this situation occurs. An example is Cu\(^{+}\)[Mg\(_{0.5}\)Mn\(_{1.5}\)]O\(_4\) \([9]\. The Cu\(^{+}\) ion (3d\(^{10}\)), like the Mg\(^{2+}\) ion, is diamagnetic. The Mn\(^{4+}\) ion is the only paramagnetic ion present. The magnetic interaction proves to be positive, so that the material becomes ferromagnetic. The Curie temperature is however rather low at 57 °K.

**The nickel ferrite-rhodite and cobalt ferrite-rhodite systems** (NiFe\(_{2-t}\)Rht\(_t\)O\(_4\) and CoFe\(_{2-t}\)Rht\(_t\)O\(_4\))

Finally, we shall show how a diamagnetic ion can affect the cation distribution of paramagnetic ions, and hence also the magnetic properties, in an entirely different manner. This we shall do by considering the replacement of Fe\(^{3+}\) ions by Rh\(^{3+}\) ions in nickel ferrite and cobalt ferrite.

The Rh\(^{3+}\) ion (4d\(^6\)) is in the low-spin state, i.e. the six d electrons are paired. This means that this ion is diamagnetic in spite of the presence of an incompletely filled d shell. (We disregard here a weak temperature independent paramagnetism.)

It proves to be possible to make spinels that have the composition NiFe\(_{2-t}\)Rh\(_t\)O\(_4\) and CoFe\(_{2-t}\)Rh\(_t\)O\(_4\). In figs. 9 and 10 the magnetic moment in these systems is shown as a function of composition. The diamagnetic Rh\(^{3+}\) ions are found to occupy octahedral sites only. Whereas nickel and cobalt ferrite are inverse spinels (Fe[FeNi]O\(_4\) and Fe[CoFe]O\(_4\) respectively), nickel rhodite (Ni[Rh\(_2\)]O\(_4\)) and cobalt rhodite (Co[Rh\(_2\)]O\(_4\)) are normal. In the systems under consideration a transition must therefore take place from an inverse to a normal cation distribution.

In addition to the experimental magnetization values fig. 9 also shows the values calculated for the distribution Fe[NiFe\(_{2-t}\)Rh\(_t\)]O\(_4\) on the basis of Néel's hypothesis. It can be seen that fairly good agreement exists in the concentration region 0<\(t<1\). The fact...
that the experimental values are somewhat higher than
the calculated ones may be explained in a simple way
by assuming that a few of the nickel ions are located at
tetrahedral sites. In the concentration region $1 < t < 2$
there must be a transition from inverse to normal
distribution. Since there is then a very high concentration
of diamagnetic ions at B sites, Néel’s hypothesis should
no longer be expected to apply: some of the paramagnetic
ions on A sites are then surrounded by so many
diamagnetic B ions that the A ion is no longer magnetically
coupled to the other paramagnetic ions [10].

In the system CoFe$_2$-$\text{Rh}_2$O$_4$ the transition from
inverse to normal spinel takes place in an entirely
different way. This can at once be seen by comparing
the experimentally determined magnetizations with
those calculated for the distribution Fe[CoFe$_2$-$\text{Rh}_2$]O$_4$
(line a in fig. 10). We have also calculated the
magnetizations to be expected for the distribution
Co[Fe$_2$-$\text{Rh}_2$]O$_4$, i.e. for a normal distribution; this
calculation gives the straight line b in fig. 10. It can be
seen that in quite a wide range of concentrations there
is good agreement between these calculated values and
those found in experiments. The conclusion can therefore
be drawn that the inverse cobalt ferrite quickly
becomes normal if rhodium ions are substituted for
the ferric ions.

Summarizing, we arrive at the following result. The
system NiFe$_2$-$\text{Rh}_2$O$_4$ is inverse from $t = 0$ to $t = 1$
and becomes normal between $t = 1$ and $t = 2$. The system CoFe$_2$-$\text{Rh}_2$O$_4$, on the other hand, becomes
normal between $t = 0$ and $t = 1$ and remains so for
$t > 1$. The Rh$^{3+}$ ion therefore has a different effect
on the Ni$^{2+}$-Fe$^{3+}$ cation distribution than on the
Co$^{2+}$-Fe$^{3+}$ distribution. This demonstrates once again
how complicated the question of cation distribution is.

We have observed a similar difference when the
Fe$^{3+}$ ion in nickel ferrite and cobalt ferrite was replaced
by trivalent ions other than Rh$^{3+}$, namely Al$^{3+}$, V$^{3+}$
or Cr$^{3+}$ [2].

Not only is the variation of the magnetization as a
function of composition (figs. 9 and 10) dependent on
the manner in which the cation distribution goes from
inverse to normal in these systems, but other physical
properties also vary in different ways. In the system
NiFe$_2$-$\text{Rh}_2$O$_4$, for example, the Curie temperature for
the composition with $t = 0$ (NiFe$_2$O$_4$) is 858 K, and
for the composition with $t = 1$ (NiFeRhO$_4$) it is
540 K; in the system CoFe$_2$-$\text{Rh}_2$O$_4$ these values are
790 and 355 K respectively. A decrease in the Curie

[11] It can similarly be shown that Néel’s hypothesis ceases to be
valid at a given composition in the familiar and technically
important system nickel-zinc ferrite, a transition occurring
from ferrimagnetism (NiFe$_3$O$_4$) to weak antiferromagnetism
(ZnFe$_3$O$_4$).
temperature is not of course unexpected, since a non-magnetic ion is substituted for a magnetic one. In the cobalt system, however, this drop is much greater than in the corresponding nickel system, which is attributable to the differences in the cation distribution.

Finally, we would like to point out that the compounds Ni[Rh₂]O₄ and Co[Rh₂]O₄ are ideal materials for study of the AA interaction in the spinel structure, containing as they do only paramagnetic ions at A sites and diamagnetic ions on B sites. The AA interaction in itself is found to be weak, but not so weak as expected [11]. Further investigations have shown that the interaction concerned is not a true AA interaction but a long range interaction in which the diamagnetic Rh³⁺ ion occupying the octahedral sites also takes part. We should therefore prefer to call it an ABA interaction. There is reason to believe that this ABA interaction has little if any significance in ferrites.

The examples discussed show that it is possible to vary the magnetic properties of ferrites by chemical substitutions. In many cases it is possible to state that certain desired magnetic properties, such as specific values of magnetization and Curie temperature and a magnetization-temperature curve with the required shape, can be selectively imparted to a ferrite by “engineering” its composition.

Summary. The investigation of magnetic materials by the methods of crystal chemistry is illustrated by means of a number of examples relating purely to compounds with spinel structure. After a general introduction to the crystal chemistry (in particular the cation distribution) of spinels and a short account of Néel’s theory of ferrimagnetic compounds, it is shown with reference to the systems NiFe₂₋₁V₂O₄ (nickel ferrite-vanadite) and Ni₁₋ₓFeₓ₋₂₋₁Sb₂O₄ (nickel ferrite-antimonate) that it is possible to control the shape of the magnetization-temperature curve by chemical substitutions. Ferrites can be made whose magnetization is independent of temperature within a particular temperature range. This investigation also showed that ferromagnetic interactions are possible in spinels. On the basis of this result a ferromagnetic oxide with spinel structure was found. The Curie temperature of this material, however, is low (57 °K). Finally, by considering the systems NiFe₂₋₁Rh₂O₄ (nickel ferrite-rhodite) and CoFe₂₋₁Rh₂O₄ (cobalt ferrite-rhodite) it is demonstrated that a particular non-magnetic ion, Rh³⁺, does not necessarily affect the cation distribution of different magnetic ions in an identical way.

Measurement of the density of small particles

In the study of solid materials a fairly accurate knowledge of the density is often necessary. For measuring the density of powders and large particles pyknometric methods are available. The density of a single small particle can be measured by immersing the particle in a liquid whose density is varied by mixing with a second liquid till the particle just remains suspended. Suitable liquids are:

CCl₄ – CBr₄ 1.59–2.96 g/cm³
CCl₄ – CI₄ 1.59–3.32 ”
Thoulet’s liquid (K₂HgI₄ in water) 1 –3.19 ”
Rohrbach’s liqu. (BaHgI₄ in water) 1 –3.59 ”
Clerici’s liqu. A (TI malonate-fommate 1 : 1 and water) 1 –4 ”
Clerici’s liqu. B (TI fluoride, fommate and water) 1 –5.4 ”

Fig. 1. Basic parts of the apparatus for density measurement. A is the capillary tube containing the particle and the liquid of adjustable density. The liquid is made homogeneous by bringing it into C or D by gentle suction or blowing at P. The U-tube B contains water. From h₁ and h₂, the differences in height arising when the pressure at P is different from the atmospheric pressure, the density of the liquid is readily calculated.