ON THE CRYSTALLINE STRUCTURE OF FERRITES AND ANALOGOUS METAL OXIDES

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Ferrites are binary oxides, the technically most important type of which is indicated by the general chemical formula MFe₂O₄ (M a bivalent metal). The ferrites of particular importance in electrotechnology are those with a crystal structure analogous to that of the mineral spinel MgAl₂O₄. These ferrites form an essential component of the new magnetic material for high frequencies, “Ferroxcube”, and also of certain resistance materials which have a large (negative) temperature coefficient of resistance. The magnetic and electrical properties of these ferrites and of the mixed crystals of which they form a part depend very closely upon certain peculiarities of their crystal structure. The latter is described in this article. It is found that the data about the ferrites in question and their mixed crystals with substances of analogous structure can be summarized in three “rules”, which considerably facilitate the preparation of materials with certain desired physical properties.

In recent years all kinds of new materials of importance in electrotechnology have been developed in the Philips Laboratories. Among these certain ferrites and the mixed crystals of ferrites occupy a special position. The ferrites are binary oxides with the formula MFe₂O₄ or MFe₂O₃, where M is respectively a monovalent or bivalent metal. In this article we shall deal exclusively with ferrites with bivalent metal. The new magnetic material for high frequencies, “Ferroxcube”, is composed of mixed crystals of these ferrites; this material has recently been discussed in detail in this periodical

The results of this crystallographic investigation will be discussed in this article; in a subsequent article we shall return to the electrical properties of the spinels and their employment as resistance materials (their magnetic properties were the subject of the article already referred to).

The spinel lattice

The structure of an ideal crystal lattice is completely given as soon as the arrangement of the atoms in the so-called elementary cell is known. The elementary cell is the smallest structural unit and in the most general case it is a paralleloiped. By placing such paralleloipeds side by side and piling them on top of each other in such a way that corresponding edges are parallel, the whole crystal is obtained.

From X-ray analysis the following is now known about the structure of an elementary cell of the spinel lattice.

The elementary cell is a cube containing 8 molecules of XY₂O₄, i.e. a total of 56 atoms. Due to the presence of such a large number of atoms per elementary cell, its structure is quite complicated. We shall first concern ourselves with the position of the oxygen ions and then with that of the metal ions.

Let us imagine for the time being that all the metal ions are removed from the spinel lattice. The lattice of the remaining oxygen ions is then relatively simple. The elementary cell of this oxygen ion lattice is then found to be twice as small linearly as that

1) Philips Techn. Rev. 8, 359, 1946.

2) For the sake of convenience we speak here of oxygen ions and metal ions. This does not mean, however, that we wish to imply that one is concerned with a pure ionic binding in the spinel lattice.
of the spinel lattice, so that it contains only four oxygen atoms. In other words, if the elementary cube of the spinel lattice is divided into eight equal cubes — which we shall call "octants" — these eight "octants" are absolutely identical as far as position of the oxygen ions is concerned.

The position of the four oxygen ions in an octant is now such that on each body diagonal of the octant there is one oxygen atom, as represented in fig. 1a; the distance of the ion to the closest corner point of the octant is the same for all four ions and amounts to $1/4$ of the length of the diagonal.

The centres of the oxygen ions in this oxygen ion lattice have the same spatial arrangement as the centres of a packing of spheres with a cubic symmetry where the empty space between the spheres is as small as possible, i.e., the so-called closest cubic packing of spheres.

Whether the oxygen ions in the spinels "touch" each other like the spheres in the cubic packing depends, of course, on the size of the metal ions which must be situated between the oxygen ions. Now in general the metal ions are considerably smaller than the oxygen ions. Therefore they can be placed in the interstices between the cubic packing of the oxygen ions without causing it to "swell" too much. Thus the oxygen ions nearly touch each other.

It should be mentioned here that actually the oxygen ion lattice of the spinels deviates somewhat from the arrangement of the closest cubic packing of spheres. The deviations are due to the fact that the metal ions do not push aside the oxygen ions directly surrounding them everywhere in the same way. These displacements, however, take place in such a way that the cubical symmetry is retained.

We shall now discuss the position of the metal ions in the interstices between the oxygen ions. There are two kinds of interstices:

Firstly, the interstices surrounded by four oxygen ions forming a tetrahedron; these interstices may be called tetrahedron spaces. Secondly, the interstices surrounded by six oxygen ions forming an octahedron and consequently called octahedron spaces. The tetrahedron and octahedron spaces are given in figs. 2a and b respectively. The arrangement of the tetrahedra and octahedra can be made somewhat clearer by choosing the elementary cell of the oxygen ion lattice differently. If one imagines all the lattice points to be displaced in the direction of a body diagonal in such a way that the oxygen ion indicated as 1 in fig. 1a lies at the lower left-hand corner, the elementary cell shown in fig. 1b is obtained. In the same way figs. 2a and b then become figs. 2c and d. By reference to these figures it may be seen that per elementary cell of the oxygen ion lattice (i.e. per octant of the elementary cell of the spinel lattice) there are 4 octahedron spaces and 8 tetrahedron spaces. Thus per elementary cell of the spinel lattice we have at our disposal 96 spaces.

Which of the 96 spaces are occupied by the 24 metal ions?

As far as the position of the metal ions is concerned the 8 octants of an elementary cell are found to fall into two groups of 4 octants, in such a way that the 4 octants of the same sort always have one edge in common (see fig. 3). In the octants of one sort only the 4 octahedron spaces are occupied (cf. fig. 2f); in the octants of the other sort all the octahedron spaces are unoccupied and only two of the tetrahedron spaces are occupied, as indicated in fig. 2e.

Fig. 4 shows the arrangement of the oxygen ions as well as of the metal ions in the elementary cell of the mineral spinel MgAl_2O_4. The illustration gives somewhat more information than follows from the above. So far we have been concerned with the position of the metal ions without
not only by the spinels which are built up of one bivalent and two trivalent metal ions (per “molecule”) (for example MgAl₂O₄), but also by the spinels which are built up of one tetravalent and two bivalent metal ions (per “molecule”) (for instance Mg₂TiO₄). We shall devote our attention to the first-mentioned possibility. Analogous considerations hold for the other case.

We have seen that in the spinel structure 8 tetrahedron spaces and 16 octahedron spaces, whose position in the elementary cell was indicated, are occupied by metal ions. In the following these 24 spaces will be indicated as those “available” for the metal ions. How are the bivalent and trivalent metal ions now distributed among the available spaces? (As already stated, the answer to this question is of great importance for determining the physical properties of the spinels.)

At first this was not considered to be any problem at all, the 8 bivalent ions being located — it was thought — in the 8 available tetrahedron spaces and the 16 trivalent ions in the 16 available octahedron spaces. In many cases this is indeed true; spinel proper, Mg₃Al₂O₄, may serve as an example of this (cf. fig. 4).

Barth and Ponsjak⁴), however, pointed out that this simple assumption is by no means correct in every case. By studying X-ray diffraction photographs of a number of spinels in which the two

The distribution of the different metal ions among the available spaces

The general chemical formula XY₃O₄ is satisfied

In Fig. 2e the centre of the cube and four corners are indicated as occupied by metal ions. It must not be forgotten, however, that each of the occupied corners must be considered as belonging to four similar octants, so that only 1/4 of it belongs to the figure in question. There are therefore, as claimed in the text, 1 + 4 × 1/₄ = 2 occupied tetrahedron spaces per octant.

Fig. 3. The cube represents symbolically the elementary cell of the spinel lattice. The four shaded and the four non-shaded octants are occupied respectively in the same way by the metal ions, namely as in figs 2e) and 2f) respectively.

⁴) T. F. W. Barth and E. Ponsjak, Z. Kristallogr. 82, 325, 1932.
kinds of metal ions have a sufficiently large difference in scattering power for X-rays, they were able to show that there are also spinels with the 8 bivalent ions in 8 of the 16 available octahedron spaces and with the 16 trivalent ions distributed equally over the remaining 8 available octahedron spaces and the 8 tetrahedron spaces. The 8 bivalent and 8 trivalent ions are at the same time distributed at random among the 16 octahedron spaces in question. In other words in the available octahedron spaces of an elementary cell one finds only on average equal numbers of bivalent and trivalent ions. This also means that the concept of "elementary cell" has here lost its significance as far as the metal ions are concerned.

The electrostatically most stable configuration of a spinel lattice

When it is seen that in some spinels the equally charged metal ions are situated only in the octahedron spaces and in others over octahedron and tetrahedron spaces, the question arises as to how this distribution is determined.

It might be assumed that it depends upon the size of the ions, so that for example the smallest ions will occur as far as possible in the tetrahedron spaces, which are considerably smaller than the octahedron spaces; but this is contrary to what has been observed.

Another factor which may determine the distribution of the metal ions among the available spaces is the electrostatic energy of the spinel lattice (in the following called "lattice energy"), i.e. the energy gained when the ions, first considered to be at an infinite distance from each other, are joined to form the spinel lattice. Because if the chemical binding in a spinel lattice is brought about only by the electrostatic (Coulomb) forces (attraction between ions of the same sign), that distribution of metal ions will be most stable where the lattice energy is greatest. In order to judge whether this is actually the case we have calculated the lattice energy for several possible distributions of metal ions. The results of these calculations are given below; the comparison with the observations will be dealt with in the following paragraph.

We consider spinels $A$), built up of bivalent and trivalent metal ions, and $B$) built up of bivalent and tetravalent metal ions. In case $(A)$ as well as in case $(B)$ there are two possibilities. In case $(A)$: $Aa)$ The bivalent ions are situated only in the tetrahedron spaces and the trivalent ions only in the octahedron spaces. The lattice energy $E$ per molecule of $XY_2O_4$ then amounts to

$$E_{Aa} = 150.3 \frac{e^2}{a},$$

where $e$ is the charge of the electron in e.s.u. and $a$ is the lattice constant in cm, i.e. the length of the edge of the elementary cell. $Ab)$ The bivalent ions are situated only in the octahedron spaces and the trivalent ions are distributed equally over the octahedron and tetrahedron spaces:

$$E_{Ab} = 143.6 \frac{e^2}{a}.$$

In case $(B)$:

$Ba)$ The tetravalent ions are situated only in the tetrahedron spaces and the bivalent ions only in the octahedron spaces:

$$E_{Ba} = 142.1 \frac{e^2}{a}.$$

$Bb)$ The tetravalent ions are situated only in the octahedron spaces and the bivalent ions are distributed equally over octahedron and tetrahedron spaces:

$$E_{Bb} = 150.3 \frac{e^2}{a}.$$

As to the calculations which led to these results, the following should be noted. In case $(Aa)$ we obtain the same value for the lattice energy as in case $(Bb)$ due to the fact that in the latter case, in which the bivalent and tetravalent ions occur
in equal numbers distributed at random in the octahedron spaces, we assumed that electrostatically this presents the same picture as a distribution of trivalent ions whose number is equal to that of the sum of the bivalent and tetravalent ions. In a similar way in the calculation in case (Ab), where the bivalent and trivalent ions occur in the octahedron spaces, we have considered them as 2.5/2 valent ions.

A comparison of the calculated values of the lattice energy now shows that the most stable state of a spinel lattice built up of bivalent and trivalent metal ions corresponds to case (Aa), where the trivalent ions are located exclusively in the octahedron spaces. On the other hand for a spinel lattice built up of bivalent and tetravalent metal ions the most stable state is found to be that where the bivalent and tetravalent ions are distributed over the octahedron spaces (case Bb). This conclusion is valid only when the lattice constant a in cases (Aa) and (Ab) (and in cases (Ba) and (Bb), respectively) has about the same value, which is quite plausible.

The fact that cases (Aa) and (Bb) must correspond to the electrostatically most stable states can also easily be understood qualitatively. It will be advantageous from the point of view of energy if the most highly charged metal ion is surrounded by as many negatively charged oxygen ions as possible. And that is exactly true in cases (Aa) and (Bb).

Checking against observations

In order to compare the above theoretical results with the actual facts we determined by X-ray analysis the distribution of the metal ions in a large number of spinels. The data thus obtained combined with those already known from the investigations of Barth and Posnjak lead to the following conclusions.

For aluminates MA12O4 and chromites MCr2O4 (M bivalent metal), where the metal ions are bivalent and trivalent, as well as for the titanates MTi2O4 and the stannates MSn2O4 (M bivalent metal), where the metal ions are bivalent and tetravalent, the actual distribution of the metal ions over the available spaces is in agreement with our calculation on the basis of the electrostatic lattice theory.

As far as the ferrites are concerned the situation is not so simple. In ZnFe2O4 and CdFe2O4 the distribution of metal ions corresponds to the electrostatic theory; in MgFe2O4 and CuFe2O4, on the other hand, it does not: here the trivalent ions (ferro ions) are divided among octahedron and tetrahedron spaces. In the other ferrites with spinel structure, for example CoFe2O4, MnFe2O4 and Fe3O4, the difference in scattering power between the bivalent and trivalent metal ions is too small to make it possible to draw any conclusions about the location of the ions from the relative intensities of the X-ray reflections. Some conclusions may, however, be drawn in this respect if we compare the values of the lattice constant for different aluminates and ferrites with each other.

Table I

<table>
<thead>
<tr>
<th>Column</th>
<th>Value</th>
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<tr>
<td>(1)</td>
<td>(2)</td>
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<tr>
<td>Ni2+</td>
<td>0.78</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.07</td>
</tr>
<tr>
<td>Mg2+</td>
<td>0.78</td>
</tr>
<tr>
<td>Cr2+</td>
<td>0.82</td>
</tr>
<tr>
<td>Ce3+</td>
<td>0.83</td>
</tr>
<tr>
<td>Fe3+</td>
<td>0.83</td>
</tr>
<tr>
<td>Mn2+</td>
<td>0.91</td>
</tr>
<tr>
<td>Cd2+</td>
<td>0.97</td>
</tr>
</tbody>
</table>

In Table I the values are given of the lattice constant for different aluminates, chromites and ferrites. Upon passing from an aluminate to the corresponding chromite the lattice constant increases, in agreement with the fact that the radius of the Cr3+ ion is larger than that of the Al3+ ion. For all pairs of corresponding chromites and aluminates this increase is approximately equal to 0.24 Å. Since the difference between the radius of the Fe3+ ion and that of the Cr3+ ion is about one half the difference between the radius of the Cr3+ ion and that of the Al3+ ion, it might be expected that the increase in the lattice constant upon passing from a chromite to the corresponding ferrite would be about 0.24 : 2 = 0.12 Å. This is indeed true in the case of Zn and Cd ferrite, i.e. for the ferrites for which the distribution of the metal ions corresponds to the electrostatic theory. For all other ferrites, however, a remark-
able fact is observed: the increase of the lattice constant is much smaller, and for all of them about equal to 0.05 Å.

Now among the ferrites which, as far as the lattice constant is concerned, show a deviating but mutually similar behaviour belong Mg and Cu ferrite, where the ferric ions are divided among the tetrahedron and octahedron spaces. From this we feel justified in concluding that the distribution of the metal ions in Co, Mn and Fe$^{3+}$ ferrites is the same as in Mg and Cu ferrite, i.e. that the ferric ions in all these ferrites are also distributed among the tetrahedron and octahedron spaces.

There are other no less important arguments for the correctness of this conclusion.

One argument, for example, is furnished by the fact that all these ferrites are ferromagnetic with the exception of Zn and Cd ferrite. This question is briefly discussed in the article referred to in footnote 1); we shall not go into it here. Another argument can be deduced from a consideration of the conductivity of the mixed crystals of ferrites, to which we shall revert in a subsequent article.

As a conclusion to the discussion of the probable distribution of the metal ions among the available spaces we should like to mention the following. The excellent agreement between the purely electrostatic theory of the spinel lattice and experiment in the case of aluminates, chromites and Zn and Cd ferrites need not suggest that the chemical binding of these spinels is almost purely electrostatic, although electrostatic forces undoubtedly play an important part. There are many indications that the binding in the spinels cannot be entirely approximated by the electrostatic conception of chemical valence and that homopolar forces (i.e. atomic binding in contrast to ionic binding) makes a significant contribution to the total picture of the binding forces. The explanation of the fact that the ferrites do not all behave in the same way, as far as the distribution of the metal ions is concerned, must be sought in certain finesses connected with these non-electrostatic forces. We shall not go further into it here because the theory is not yet able to explain the phenomenon satisfactorily.

**Rules for the distribution of metal ions in spinels**

On the basis of the results discussed above we may now set out the following rules for the structure of spinels built up of bivalent and trivalent or bivalent and tetravalent metal ions.

1) The trivalent and tetravalent metal ions occupy the octahedron spaces in agreement with the electrostatic conception of the structure of spinels.

2) Exceptions are the Fe$^{3+}$ ions, which have a preference for the tetrahedron spaces. In$^{3+}$- and Ga$^{3+}$-ions, which have not been mentioned in this article, are also exceptions to rule (1).

3) Zn$^{2+}$ and Cd$^{2+}$ have a strong preference for the tetrahedron spaces and are able to drive the ions mentioned under (2) out of these spaces.

From the measurements of intensity on X-ray diffraction photographs we were able to deduce that these rules also remain valid for the formation of mixed crystals of the spinels. Several examples are given in table II.

Although we were unsuccessful in completely solving the problem of the structure of the spinels theoretically — the preference of Fe$^{3+}$ ions for the tetrahedron spaces remains somewhat mysterious — the investigation has had the result that with the help of the above-formulated rules we can predict the position of the metal ions in any arbitrary mixed crystal with very great probability, and we can therefore also prepare materials with a desired ion distribution. As will appear from a following article, this has not unimportant practical consequences.

**Table II.**

Structure of the mixed crystals of two spinels with the components taken in a mol ratio of 1:1. The symbols of the ions situated in the octahedron spaces are placed between parentheses. Roman numerals indicate the valence of the iron ions.

<table>
<thead>
<tr>
<th>Components of the mixed crystal</th>
<th>Structure of the mixed crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$ (Fe$^{2+}$, Fe$^{3+}$) O$_4$ and Fe$^{2+}$ (Al, Al) O$_4$</td>
<td>Fe$^{3+}$ (Fe$^{2+}$ Al) O$_4$</td>
</tr>
<tr>
<td>Fe$^{3+}$ (Cu, Fe$^{3+}$) O$_4$ and Zn (Fe$^{3+}$, Fe$^{3+}$) O$_4$</td>
<td>Zn$<em>{0.5}$Fe$^{3+}$(Fe$^{2+}$)$</em>{0.5}$, Cu$_{0.5}$ O$_4$</td>
</tr>
<tr>
<td>Zn (Fe$^{3+}$, Fe$^{3+}$) O$_4$ and Zn (Cr, Cr) O$_4$</td>
<td>Zn (Fe$^{3+}$, Cr) O$_4$</td>
</tr>
<tr>
<td>Zn (Ti, Zn) O$_4$ and Fe$^{3+}$ (Mg, Fe$^{3+}$) O$_4$</td>
<td>Zn (Fe$^{3+}$, Mg) O$_4$</td>
</tr>
<tr>
<td>Mg (Ti, Mg) O$_4$ and Fe$^{3+}$ (Mg, Fe$^{3+}$) O$_4$</td>
<td>Fe$^{3+}$ (Ti$^{0.5}$, Mg$^{0.5}$) O$_4$</td>
</tr>
<tr>
<td>Zn (Fe$^{3+}$, Fe$^{3+}$) O$_4$ and Fe$^{3+}$ (Fe$^{2+}$,M$^{2+}$) O$_4$</td>
<td>Zn$<em>{0.5}$Fe$^{3+}$(Fe$^{2+}$)$</em>{0.5}$ O$_4$</td>
</tr>
</tbody>
</table>
(The measurement of impedance at h.f. and applications of the standing wave indicator).

In this article a survey is given of the different methods used in measuring impedances.

For frequencies below about 300 Mc/s the method used most frequently is that which employs a tuned circuit and in which the impedance is determined from its damping and detuning influence on the circuit.

For higher frequencies the lumped circuit can be replaced by a tuned transmission line but in that case some difficulties arise and it is preferable to use an untuned transmission line and to determine the impedance from the voltage distribution along the line.

The voltage distribution is characterised by the standing wave ratio and the position of the voltage minimum. A new diagram has been designed, which enables one to determine the impedance graphically and in a most comprehensible way even for very large values of the standing wave ratio. In connection with the measurement of the voltage distribution the standing-wave indicator is described.

Finally a number of other applications of the standing-wave indicator are dealt with, such as the measurement of characteristic impedance and attenuation constant of a transmission line and the measurement of net power flow along a transmission line.

(One system of units in electro-magnetic theory).

A short survey is given of the basic formulae of electromagnetism using rationalized Giorgi units (M.K.S. units). The didactic value of using these units is stressed.


For the contents of this paper the reader is referred to the article by J. L. Snoek and K. F. du Pré, Philips Techn. Rev. 8, 57, 1946 and to the book: J. L. Snoek, New developments in ferromagnetic materials, Amsterdam 1947 (see abstract No. 1729).


Above a certain transition temperature ($\theta$) crystals of barium titanate $BaTiO_3$ and related compounds, such as $SrTiO_3$, $Ba$, $Sr$ $TiO_3$ and $TiO_3$, show a cubic structure. At the temperature $\theta$ the permittivity has a sharp maximum. It decreases monotonically with increasing temperature. This decrease is explained from the Clausius-Mosotti formula. Taking into account the thermal expansion and ignoring the temperature dependence of the polarisability, it follows that for higher values of $\varepsilon$:

$$\varepsilon = \beta (T - C).$$

With the titanates the polarisability proves to be independent of the temperature. Then $\beta$ is the coefficient of thermal expansion.

It is believed that in the cubic region ($T < \theta$) there is no permanent dipole moment, whereas in the tetragonal region ($T < \theta$) the assumption of dipoles seems to be quite plausible.


In this thesis the relation between the power factor ($\tan \delta$) and the temperature coefficient of the dielectric constant of solid, amorphous dielectrics is dealt with theoretically as well as experimentally. This subject has already been treated in a paper by M. Gevers and K. F. Du Pré (Philips Techn. Rev. 9, 91, 1947). The methods of measurement are described and a number of special cases are dealt with. Finally some remarks are made on the properties of mixtures of dielectrics. (Also published
Polycrystalline nickel-iron (~50 weight % Ni) which has been severely cold rolled exhibits on recrystallisation at about 1000 °C a so-called cubic orientation. Aluminium does not show this texture upon recrystallisation. To trace any difference in slip mechanism between Ni-Fe and Al, the deformation and recrystallisation textures of polycrystalline Ni-Fe with cubic orientation were investigated and the findings were compared with observations of Burgers and Louwerse on single crystals of Al. On the whole the deformation textures were found to be the same. There are, however, marked differences due to the Ni-Fe specimen being not a mono-crystal. The recrystallisation textures are strongly different. The reason is to be found in the difference between the deformation textures. This can be explained by Burgers' theory. The second part contains a discussion of Barrett's criticism of this theory.


The effective permeability of compressed and sintered samples of TiO₂ has been measured and the results are discussed in terms of the theory developed by Polder and van Santen (abstract 1698). The experimental curves show that in loose powders the holes are more or less disc-shaped. The more the samples are sintered the more nearly spherical the holes become. As a whole the results confirm the theory mentioned.