14 R
62.

PHYSICAL AND CRYSTALLOGRAPHICAL PROPERTIES OF SOME SPINELS

F. C. ROMEIJN

PHYSICAL AND CRYSTALLOGRAPHICAL PROPERTIES OF SOME SPINELS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN OP GEZAG VAN DE RECTOR MAGNIFICUS DR J. J. L. DUYVENDAK, HOOGLERAAR IN DE FACULTEIT DER LETTEREN EN WIJSBEGEERTE. TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP WOENSDAG 17 JUNI 1953 TE 15 UUR

DOOR

FRANS CORNELIS ROMEIJN

GEBOREN TE ROTTERDAM IN 1920

PROMOTOR:
PROF. DR. A. E. VAN ARKEL

Aan mijn Ouders
Aan mijn Vrouw

PHYSICAL AND CRYSTALLOGRAPHICAL PROPERTIES OF SOME SPINELS

by F. C. ROMEIJN

Summary

From X-ray measurements on simple and complicated spinels regularities in the ionic distribution and lattice constants have been investigated. These regularities have been explained partly by general methods as the calculation of the Madelung potential and geometrical considerations, partly by taking into account the individual properties of the ions that are correlated with the distribution of electrons within the ion. We found the calculated correlation between the ionic distribution and the oxygen parameter *u* to be confirmed by the facts. The ultimate choice of the distribution, however, is governed by the individual properties of the ions, partly by their dimensions partly by the distribution of electrons. Some physical properties of the compounds investigated have been correlated with the ionic distribution.

Résumé

Des mesures par les rayons X sur les spinelles simples et compliquées, l'on a déduit quelques règles sur la distribution ionique et les constantes du réseau élémentaire. On peut comprendre ces règles d'une part par des considérations générales comme le calcul du potentiel Madelung et la géométrie et d'autre part par une considération des propriétés individuelles des ions qui sont liées à la distribution des électrons dans ceux-ci. Le calcul de la corrélation calculée entre la distribution ionique et la paramètre *u* des ions d'oxygène fut confirmée par les expériences. Le choix de la distribution est guidé en fin de compte par les propriétés individuelles des ions comme leurs dimensions et leurs distributions électroniques. Quelques propriétés physiques des substances examinées ont été liées avec leurs distributions ioniques.

Zusammenfassung

Auf Grund von Röntgenmessungen an einfachen und komplizierten Spinellen konnten Regelmäßigkeiten in der Ionenverteilung und bei den Gitterkonstanten festgestellt werden. Zur Erklärung dieser Erscheinung wurden teils allgemeine Methoden, wie die Berechnung des Madelung-Potentials, sowie geometrische Überlegungen benutzt, teils wurden die individuellen Eigenschaften der Ionen, die durch die Elektronenverteilung innerhalb des Ions bedingt sind, in Betracht gezogen. Der berechnete Zusammenhang zwischen Ionenverteilung und Sauerstoffparameter *u* wurde durch die Tatsachen bestätigt.
Die endgültige Wahl der Verteilung wird gleichwohl durch die individuellen Eigenschaften der Ionen wie Dimension und Elektronenverteilung bestimmt. Einige physikalische Eigenschaften der untersuchten Substanzen sind aus ihrer Ionenverteilung gedeutet worden.

CHAPTER I

GENERAL CONSIDERATIONS

The mineral spinel of formula $MgAl_2O_4$ has given its name to a large class of compounds having the same crystal structure, such as the aluminates $MeAl_2O_4$, the chromites $MeCr_2O_4$, the ferrites $MeFe_2O_4$, the germanates Me_2GeO_4, the titanates Me_2TiO_4 etc., Me being a divalent metal such as Mg, Zn, Cd, Mn, Fe, Co, Ni, Cu. Most of these compounds crystallize in a cubic structure of spacegroup Fd3m, $O_h{}^7$ (notation according to International Tables) in which the following positions are occupied:
8*a*: $000, \frac{1}{4}\frac{1}{4}\frac{1}{4}$. (+f.c.c);
16*d*: $\frac{5}{8}\,\frac{5}{8}\,\frac{5}{8},\ \frac{5}{8}\,\frac{7}{8}\,\frac{7}{8},\ \frac{7}{8}\,\frac{5}{8}\,\frac{7}{8},\ \frac{7}{8}\,\frac{7}{8}\,\frac{5}{8}$. (+f.c.c.);
32*e*: $u\ u\ u,\ u\ \bar{u}\ \bar{u},\ \bar{u}\ u\ \bar{u},\ \bar{u}\ \bar{u}\ u,$
$\frac{1}{4}-u\ \frac{1}{4}-u\ \frac{1}{4}-u,\ \frac{1}{4}-u\ \frac{1}{4}+u\ \frac{1}{4}+u,\ \frac{1}{4}+u\ \frac{1}{4}-u\ \frac{1}{4}+u,\ \frac{1}{4}+u\ \frac{1}{4}+u\ \frac{1}{4}-u$. (+f.c.c).
The oxygen ions occupy the 32-fold position, the cations are distributed among the 8-fold and the 16-fold positions. For $u = 0{\cdot}375$ the oxygen ions form a cubic close packing, in which the metal ions occupy partly the tetrahedral interstices 8*a*, and partly the octahedral interstices 16*d*. For $u > 0{\cdot}375$ the tetrahedral interstices become larger, but keep the same symmetry, the octahedral interstices shrink and lower their symmetry.

For a spinel XY_2O_4 or $X_8Y_{16}O_{32}$ per unit cell, the most obvious distribution of the metal ions from a crystallographic point of view is the one in which the X ions occupy the 8*a* (tetrahedral) positions, and the Y ions the 16*d* (octahedral) positions. Barth and Posnjak¹) have drawn attention to the fact, that there are at least two other possibilities, viz. X+Y distributed randomly among 8*a* and 16*d*, and Y at 8*a*, X + Y randomly at 16*d*.

The first structure will be called the normal one, the second structure the random one, and the third structure the inverse one. If it is necessary to write down explicity the ionic distribution, we shall write the cation at the tetrahedral positions first, followed between brackets by the ions at the octahedral positions, e.g.
$Mg[Al_2]O_4$, $Fe[NiFe]O_4$, $Ge[Co_2]O_4$, $Co[CoTi]O_4$. For abbreviation the first and the second one will be called 2-3 spinels, the third and fourth ones 2-4 spinels.

When the scattering powers for X-rays of the cations are sufficiently different, it is possible to decide between the normal, the inverse and the completely random structures. In this way Barth and Posnjak¹), and Verwey²) concluded that all aluminates and chromites are normal, all ferrites except Zn and Cd ferrite are inverse, and all 2-4 spinels such as the titanates and the stannates are inverse.

When the difference in scattering power is too small it is impossible to draw conclusions from the X-ray intensities. Verwey, however, observed that when a spinel has the inverse structure, its cell constant *a* is about 0·06 Å. smaller than it would have been in the normal structure.

Substance	lattice constant
$Mg[Al_2]\,O_4$	8·086 Å
$Zn\,[Al_2]\,O_4$	8·086
$Mg[Cr_2]\,O_4$	8·32
$Zn\,[Cr_2]\,O_4$	8·31
$Fe\,[MgFe]\,O_4$	8·38
$Zn\,[Fe_2]\,O_4$	8·44

This assumption made it possible to decide for the inverse structure for the ferrites of Mn, Fe^{2+}, Co and Ni, and for the normal structure for $MgAl_2O_4$. The neutron diffraction experiments of Shull a.o. confirmed these results [8]) [9]).

The question arises: what determines the ionic distribution? The ideal solution would be the one, in which the various energy terms could be written as a function of the ionic distribution and minimalized.

However, the only energy term that can be calculated accurately enough is the Madelung potential. The Born repulsion cannot be taken into account because of a lack of data, and what other energy terms arise when complicated ions with a partially filled d shell occur is unknown. We shall restrict ourselves to a combination of the Madelung potential and, instead of the Born repulsion, geometrical considerations. Verwey, De Boer and Van Santen [4]) [5]) calculated the Madelung constant for normal and inverse spinels with divalent, trivalent and tetravalent ions as a function of the oxygen parameter *u*; see fig. 1. The inverse spinels have been calculated with an average charge at the octahedral interstices of $2^1/_2$ for the 2-3 spinels and of 3 for the 2-4 spinels. This is equivalent to the assumption of a perfectly random distribution.

From fig. 1 we see that for a fixed value of the lattice constant a normal structure is stable for $u > 0{\cdot}379$ in case of 2-3 spinels, and for $u < 0{\cdot}385$ for 2-4 spinels. Otherwise inverse spinels are stable. The most favourable situation is a small *u* (0·375) for normal 2-4 spinels and a large *u* (0·385) for normal 2-3 spinels and inverse 2-4 spinels, whereas the Madelung constant of inverse 2-3 spinels is hardly dependent upon *u*.

The accuracy of the determination of *u* is rather small, the best known values being

$Mg\ [Al_2]\ O_4$ $u = 0{\cdot}387 \pm 0{\cdot}001$ 9),
$Zn\ [Fe_2]\ O_4$ $u = 0{\cdot}385 \pm 0{\cdot}002$ 10),
$Fe^{3+}[Fe^{2+}Fe^{3+}]\ O_4$ $u = 0{\cdot}379 \pm 0{\cdot}001$ (?) 11),
$Ge\ [Co_2]\ O_4$ $u = 0{\cdot}375 \pm 0{\cdot}003$ (this paper, chapter III).

The first and second values have been obtained from neutron diffraction experiments, the third and fourth ones from X-ray data.

We can simplify this result by correlating u and the charge at the tetrahedral interstices, viz.

charge	u
4	0·375
3	0·38
2	0·387

This supports the calculations of Verwey et al. but, unfortunately, we cannot predict the ionic distribution. Obviously u and ionic distribution are correlated, but it is difficult to see what decides between the different possibilities.

Now we shall take into account the dimensions of the ions. We have calculated for a constant value of the lattice constant a the available

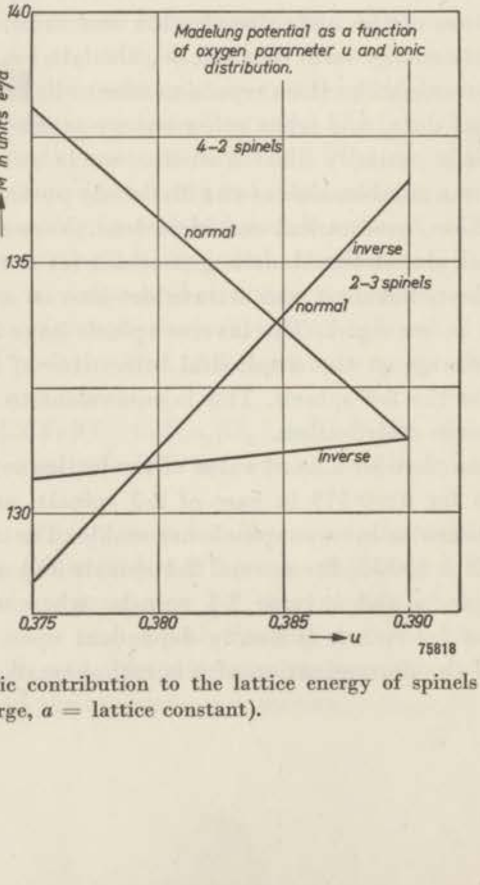

Fig. 1. Electrostatic contribution to the lattice energy of spinels (in units e^2/a, where e = electronic charge, a = lattice constant).

space at the octahedral and tetrahedral interstices for three different values of the oxygen parameter u for different spinels (aluminates, chromites, germanates, ferrites, titanates). According to the above relation between u and the charge, we must combine the different possibilities for u and ionic distribution. For example: the germanates (2-4 spinel) can be normal with $u = 0{\cdot}375$ or inverse with $u = 0{\cdot}387$. Other combinations are ruled out from electrostatic considerations. We must compare now the admissible radii at both interstices (table I) with the radii of the ions (table II).

TABLE I

Radii (in Å) of the inscribed spheres, calculated for an oxygen radius of 1·32 Å.

u	$a = 8{\cdot}10$ Å aluminates		$a = 8{\cdot}30$ Å chromites germanates		$a = 8{\cdot}40$ Å ferrites titanates	
	tet	oct	tet	oct	tet	oct
0·375	0·43	0·70	0·47	0·76	0·50	0·78
0·381	0·51	0·65	0·55	0·70	0·58	0·73
$0{\cdot}387_5$	0·59	0·59	0·64	0·64	0·67	0·67

Of the three u values in table I, $u = 0{\cdot}375$ corresponds to the ideal close packing, $u = 0{\cdot}387_5$ is a maximum value, for at this value both interstices are equally large and at $a = 8{\cdot}30$ Å there is anion-anion contact, and $u = 0{\cdot}381$ is about the critical value for the inversion of 2-3 spinels.

TABLE II

Ionic radii in Å

Ge^{4+}	0·44	Mg^{2+}	0·78
Ti^{4+}	0·64	Zn^{2+}	0·78
Al^{3+}	0·57	Ni^{2+}	0·78
Cr^{3+}	0·63	Co^{2+}	0·82
Fe^{3+}	0·67	Fe^{2+}	0·84

From a geometrical point of view only in the case of the germanates a good fit can be obtained for the normal distribution but it is impossible to see why $Mg[Cr_2]O_4$ favours a normal distribution with $u = 0{\cdot}387$ and $Fe[MgFe)O_4$ the inverse one with $u = 0{\cdot}381$.

$Mg\,Al_2\,O_4$ has two possibilities:

$Mg[Al_2]\,O_4$ with $u = 0{\cdot}387$ or $Al[MgAl]\,O_4$ with $u = 0{\cdot}381$.

For $a = 8{\cdot}10$ Å we derive from table I the following admissible radii: 0·59 Å for the Al^{3+} ion in the normal case, and 0·65 Å and 0·51 Å in the inverse case. In the normal structure actually found the Al^{3+} ions fit rather closely, whereas the fit for the Mg^{2+} ions is worse.

For Mg_2TiO_4 we have:

$Ti[Mg_2]O_4$ with $u = 0{\cdot}375$ or $Mg[MgTi]O_4$ with $u = 0{\cdot}387$; a lattice constant of 8·40 Å gives: 0·50 Å for the Ti^{4+} ion with the normal distribution or 0·67 Å with the inverse distribution. Here the best fit for Ti^{4+} corresponds with the inverse structure actually observed.

In both cases the ionic distribution is determined by the ion of the highest valency. This is understandable, because the higher the valency of the ion, the less its compressibility *).

Al^{3+} and Ti^{4+} are the only ions that have noble-gas shells, so they are the least complicated. For the binary spinels with more complicated ions such as Cr^{3+}, Fe^{3+}, Zn^{2+} etc. we can only use the empirical distribution scheme of Verwey and Heilmann[2]):

Zn^{2+}, Cd^{2+}, Ga^{3+}, In^{3+}, Fe^{3+}, Mn^{2+}, Fe^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} Cr^{3+}, Ti^{4+}.

At the left hand side are the ions which favour the tetrahedral interstices, at the right hand side the ions which favour the octahedral ones.

There are two complications we have not taken into account viz.

(a) As mentioned before, for 2-3 spinels the lattice shrinks about 0·7% at the inversion. This shrinkage indicates a stabilization of the inverse structure but we cannot estimate how much it affects the lattice energy, because it it impossible to make an estimation of the repulsion forces.

(b) For the calculation of the Madelung constant we have assumed that the divalent and the tri (or tetra) valent ions are distributed randomly in the inverse spinels. This is probably not allowed, however, for, if the divalent and tri (or tetra) valent ions order in one way or another, a large amount of energy is gained. An obvious pattern is the one already predicted by Verwey and Haaijman[6]) for Fe_3O_4, viz. rows of the same ions in the [110] directions, according to the following distribution:

divalent ions at

$\frac{1}{8}\ \frac{5}{8}\ \frac{1}{8},\ \frac{5}{8}\ \frac{1}{8}\ \frac{1}{8},\ \frac{3}{8}\ \frac{7}{8}\ \frac{1}{8},\ \frac{7}{8}\ \frac{3}{8}\ \frac{1}{8},\ \frac{1}{8}\ \frac{1}{8}\ \frac{5}{8},\ \frac{5}{8}\ \frac{5}{8}\ \frac{5}{8},\ \frac{3}{8}\ \frac{3}{8}\ \frac{5}{8},\ \frac{7}{8}\ \frac{7}{8}\ \frac{5}{8};$

tri (or tetra) valent ions at

$\frac{3}{8}\ \frac{5}{8}\ \frac{3}{8},\ \frac{5}{8}\ \frac{3}{8}\ \frac{3}{8},\ \frac{1}{8}\ \frac{7}{8}\ \frac{3}{8},\ \frac{7}{8}\ \frac{1}{8}\ \frac{3}{8},\ \frac{3}{8}\ \frac{1}{8}\ \frac{7}{8},\ \frac{1}{8}\ \frac{3}{8}\ \frac{7}{8},\ \frac{7}{8}\ \frac{5}{8}\ \frac{7}{8},\ \frac{5}{8}\ \frac{7}{8}\ \frac{7}{8}.$

---

*) According to a private communication of Prof. Dr A. E. van Arkel the heats of formation of SiF_4, PF_5 and SF_6 are far too great when they are calculated with the normal Born repulsion formula. The Born repulsion is greater than calculated, which is equivalent to a compressibility rapidly increasing with decreasing interionic distance.

According to De Boer, Verwey and Van Santen [5]) the electrostatic contribution to the energy of order is about 1·7 eV for inverse 2-3 spinels and about 6·8 eV for inverse 2-4 spinels.

The symmetry of the lattice is reduced by this ordering process from cubic to orthorhombic. In this symmetry class there are, of course far more parameters than in the original cubic one, so we cannot describe the influence of order upon the *u* values in the cubic spinel and perhaps the electrostatic calculation of the energy of order is too rough an approximation. Generally speaking, however, the order will increase the stability of the inverse structure.

The only spinel in which this order has been observed is Fe_3O_4. (In $Fe[Fe_{3/2}Li_{1/2}]O_4$ another type of order has been found, which can occur if the octahedral positions are occupied by different ions in the ratio 3 : 1, and in $Fe_{1/2}Li_{1/2}[Cr_2]O_4$ [18]) order among the ions at the tetrahedral interstices occurs). For Fe_3O_4 the first indication of a deviation from the cubic symmetry has been found by Li [12]) who observed a decrease in the magnetic symmetry of Fe_3O_4 at 115 °K.

Ellefson and Taylor [13]) measured a large peak in the specific heat between 100° and 130 °K (excess value of $\int C_p \mathrm{d}T$ about 120 cal/mole). Verwey, Haaijman and Romeijn [3]) found the conductivity at 90 °K to be dependent upon the direction of the magnetic field applied during the cooling of the specimen from above to below the transition point at 115 °K and concluded to uniaxial symmetry in accordance with the pattern of Verwey and Haaïjman [6]). They overlooked the fact, however, that in this structure there is no fourfold axis of symmetry, and they predicted a tetragonal structure, whereas the proposed one is orthorhombic (pseudo-tetragonal).

X-ray measurements of Tombs and Rooksby [14]) [15]) revealed the fact, that below 115 °K some lines split, from which they concluded (wrongly) to rhombohedral symmetry.

The measurements of Bickford [16]) who measured with the aid of strain gauges the deformation of a single crystal of Fe_3O_4 at the transition point in different directions of an external magnetic field established firmly the orthorhombic symmetry.

Finally, at Von Hippel's laboratory[16]) Fe_3O_4 below 115 °K was found to belong to the orthorhombic space group Imma — D_{2h}^{28} with dimensions $a = 5{\cdot}912$ Å, $b = 5{\cdot}945$ Å, $c = 8{\cdot}388$ Å (a en b are about $\frac{1}{2} a' \sqrt{2}$, in which a' is the lattice constant in the cubic modification; c is about a').

These experiments confirm the hypothesis of Verwey and Haaijman, who assumed the discontinuity in the resistivity of Fe_3O_4 at 115 °K to be caused by an order-disorder transformation among the electrons in the octahedral interstices.

The difficulties in this picture are, however,
(a) the calculated electrostatic energy of order (1.7 eV) does not correspond to a transition temperature as low as 115 °K,
(b) why is Fe_3O_4 the only orthorhombic spinel?
We could account for these discrepancies, by assuming that there is always a fair degree of short-range order, the observed transition point indicating the transition from long-range to short-range order only. Van Santen 7) has calculated that in ionic crystals the energy difference between long-range and short-range order is fairly small, corresponding to low transition temperatures. The ionic mobility at low temperatures would be far too small to realize long-range order, and only by a migration of electrons as in Fe_3O_4, long-range order can be brought about. If this were true, there would always be a fairly large amount of short-range order in inverse spinels.

There are a number of experimental arguments for this statement, viz.
(a) Molten potassium chloride shows an ionic conductivity of about 150 Ωcm^{-1}, indicating a large number of ions in the melt. There is of course no long-range order, but a fairly strong short-range order must persist, for, if the K^+ and Cl^- ions were distributed randomly in the melt, the heat of melting would be about as large as the total lattice-energy, whereas it is only several per cents of the latter. The existence of short-range order in the melt has been proved by the investigations of Lark-Horowitz and Miller 17).
(b) There are crystals that have the outward appearance of normal crystals, but give an X-ray pattern not of a crystalline medium but of an amorphous substance. Vegard 19) coined the word "metamikt" for these crystals. This effect is shown by thorite $ThSiO_4$ which outwardly is isomorphous with zircone $ZrSiO_4$ but, unlike this, gives no definite X-ray pattern19). In some zircone crystals the same phenomenon is found too; these crystals are invariably strongly radioactive 20). I propose the tentative explanation that, due to the high-energy particles emitted by the radioactive atoms (Th in $ThSiO_4$, Th or U in $ZrSiO_4$) a considerable fraction of the atoms is displaced from the ideal positions. In this way the long-range order is destroyed, and no definite X-ray pattern can be obtained.

The energy difference between these crystals and a normal crystal, however, will be small, for otherwise the crystals would be very unstable.

These facts corroborate the calculations of Van Santen 7), and we shall assume the inverse spinels to have a large degree of short-range order. As the total lattice energy of spinels is about 230 eV the conclusions drawn from the Madelung potential are not changed appreciably by the phenomenon of order.

The problems in the spinels can be summarized as follows: if from three metal ions of appropriate size (0·45-0·95 Å) with a total valency of eight a spinel is formed, there are four variables:

(1) the lattice constant *a*,
(2) the oxygen parameter *u*,
(3) the distribution of the cations among the octahedral and tetrahedral interstices,
(4) the amount of order among the ions in the octahedral (and tetrahedral) interstices.

A calculation of the Madelung constant shows a correlation between (2) and (3), but we cannot predict what choice will be made.

Geometrical considerations can only be applied for ions with noble-gas structure, but the other ions give difficulties.

In the experimental part of this paper we shall discuss some physical properties of spinels (chapter II) and extend our knowledge of spinel systems by X-ray measurements (chapter III).

CHAPTER II

OPTICAL AND ELECTRICAL PROPERTIES OF SOME SPINELS

1. Optical properties of Co and Ni containing spinels

It has been known very long, that the colour that is given to compounds by ions of the transition elements varies with the coordination number of the ion and with the nature of the chemical bond.

Examples of the dependence of the colour on the nature of the bond are numerous; the differences in colour between complex compounds of Cr, Co and Ni and the hydrated ions can be attributed largely to this difference in type of binding.

In glasses where the bonds are at least partly ionic the differences in colour are obvious too. According to Weil [21]) and Stevels [22]) the purple colour of some nickel containing glasses is caused by a Ni^{2+} ion, when it acts as a network-forming ion (tetrahedrally surrounded), whereas the greenish-yellow colour of other Ni containing glasses is caused by a Ni^{2+} ion in octahedral surroundings (network-modifying ion).

The same differences are known in cobalt containing glasses; in the blue glasses cobalt acts as a network-forming ion, in the pink ones as a network-modifying ion.

For crystalline compounds similar differences are known: Co_2SiO_4 (Co in octahedral positions) is pink, solid solutions of CoO in MgO are pink, $CoAl_2O_4$ (Co in tetrahedral positions) is dark blue (Thénard's blue [23])).

We are comparing here compounds of different crystal structure, which may complicate the effect. For Co containing spinels, however, we can vary the surroundings of the Co^{2+} ion within the same crystal structure.

In the pink $Ge[Co_2]O_4$ we have Co^{2+} in octahedral interstices, in the blue $Co[Al_2]O_4$ in tetrahedral interstices, in the green $Co[CoTi]O_4$ in both. In order to obtain more detailed information we investigated several solid solutions.

In solid solutions of $Co[Al_2]O_4$-$Zn[Al_2]O_4$ we can reduce the Co content without a change in surroundings, in the system $Co[CoTi]O_4$-$Mg[MgTi]O_4$ most probably too. In the system $Co[CoTi]O_4$-$Zn[ZnTi]O_4$, however, the reduction in Co content is accompanied by a change in surroundings, for in compounds containing over 50% Zn_2TiO_4 the Co^{2+} ions occupy the octahedral interstices only. These different distributions of the Co^{2+} ions influence the colours of the compounds. In the systems $Co[Al_2]O_4$-$Zn[Al_2]O_4$ and $Co[CoTi]O_4$ - $Mg[MgTi]O_4$ the result of the decrease in Co content is only a diminution of the intensity of the colours (dark blue becomes light blue, dark green becomes light green). In the system $Co[CoTi]O_4$ - $Zn[ZnTiO_4]$, however, around 50% Zn_2TiO_4 the colour changes suddenly from green at high Co contents to greyish pink at lower Co contents.

For Ni we do not have such an extensive system, for the spinel with Ni^{2+} in tetrahedral interstices only is the dark brown $Ni[Cr_2]O_4$; the colours are complicated by the Cr^{3+} ion, which in $Mg[Cr_2]O_4$ and $Zn[Cr_2]O_4$ causes a green colour.

In $Ge[Ni_2]O_4$ the yellowish green colour is due to Ni^{2+} ions in octahedral interstices, in $Ni_{1/4}Al_{3/4}[Ni_{3/4}Al_{5/4}]O_4$ the blue colour is caused by Ni^{2+} ions in both interstices (cf. chapter III).

From the polycrystalline compounds we prepared it is impossible to obtain an absorption spectrum, so we measured the reflectivity of a specimen at small intervals (100 Å) from 4000 to 7500 Å, relative to the reflectivity of $MgCO_3$.

Assuming no light is transmitted through the specimen we can obtain the absorption from

$$\text{absorption} = 1 - \text{reflection}$$

We cannot calculate the absorption coefficient in this way, because we do not know the effective thickness of the specimen for the reflection process.

In figs 2-7 are plotted the reflectivities of the following compounds: $Co[Al_2]O_4$ (2), $Co_{1/8}Zn_{7/8}[Al_2]O_4$ (3), $Ge[Co_2]O_4$ (4), $Co[CoTi]O_4$ (5), $Mg_{3/2}Co_{1/2}TiO_4$ (6) and $Zn[Zn_{1/2}Co_{1/2}Ti]O_4$ (7).

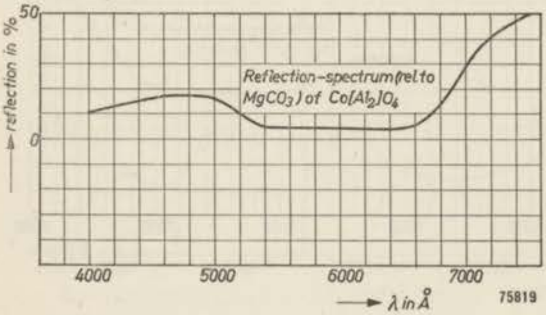

Fig. 2

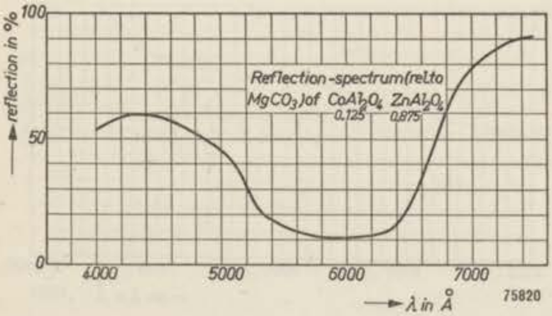

Fig. 3

Figs 2 and 3. Reflection spectra of various Co containing spinels.

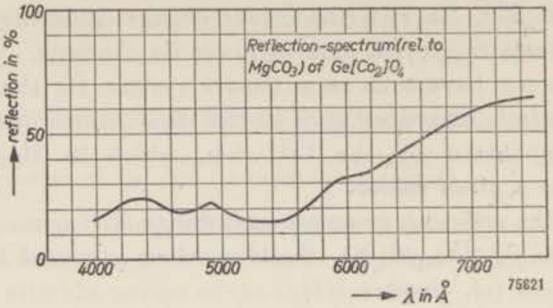

Fig. 4

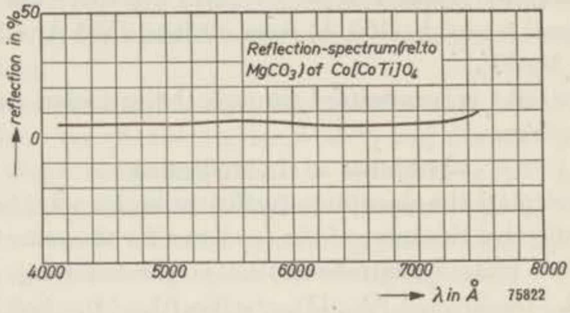

Fig. 5

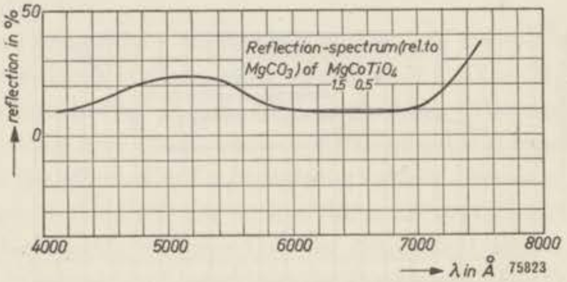

Fig. 6

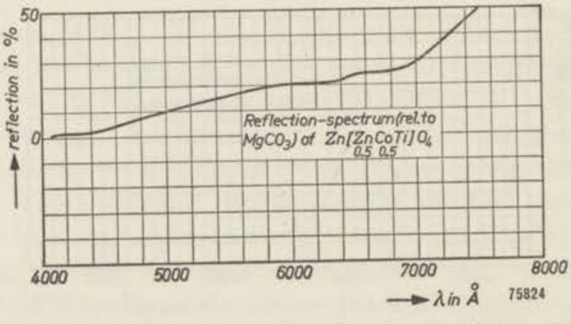

Fig. 7

Figs 2-7. Reflection spectra of various Co containing spinels.

$Co[Al_2]O_4$ is very dark, the details are easier to see in the diluted compound of fig. 3. The blue colour corresponds to a peak in the reflectivity between 4000 Å and 5200 Å, the peak from 6600 Å on towards higher wavelengths contributes hardly to the visible part of the spectrum.

In $Ge[Co_2]O_4$ high reflectivities occur in the region from 5800 Å on towards higher wavelengths, in accordance with the red colour.

The spectrum of the dark green $Co[CoTi]O_4$ has hardly any peaks in the visible region; the diluted compound of fig. 6 has a feeble peak between 4600 Å and 5600 Å.

$Zn[Zn_{1/2}Co_{1/2}Ti]O_4$ has a reflection spectrum resembling that of $Ge[Co_2]O_4$, but with a less pronounced structure.

The difference between $Ge[Co_2]O_4$ and $Zn[Zn_{1/2}Co_{1/2}Ti]O_4$ may be caused by two different factors:

(a) in the latter compound some of the Co^{2+} ions occupy the tetrahedral interstices,

(b) the differences in oxygen parameter u (about 0·375 in the germanates and 0·387 in the titanates) influence the absorption spectrum of the Co^{2+} ion at the octahedral interstices.

As (a) would give strong absorption in the yellow part of the spectrum, which is absent in fig. 6 we believe (b) to be true.

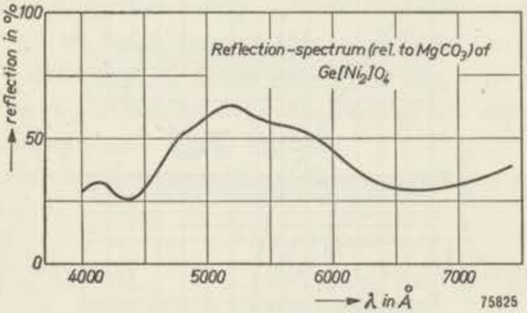

Fig. 8

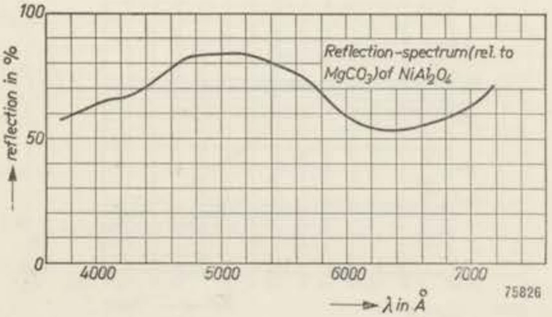

Fig. 9

Fig. 8 and 9. Reflection spectra of various Ni containing spinels.

When we compare diluted $Co[Al_2]O_4$ (3) with diluted $Co[CoTi]O_4$ (6), the most important difference is the shift in the maximum value of the reflection from 4400 Å in the former to 5200 Å in the latter. Although a quantitative description is impossible, we can understand this shift by assuming the absorption of diluted $Co[CoTi]O_4$ to be a superposition of the absorption of diluted $Co[Al_2]O_4$ and $Zn[Zn_{1/2}Co_{1/2}Ti]O_4$ (7).

For the sake of completeness the reflection spectra of nickel germanate and nickel aluminate are given in figs. 8 and 9.

Although no quantitative conclusions can be drawn, the influence of the ionic distributions upon the optical properties of these spinels is clearly demonstrated in the reflection spectra.

2. Electrical conductivity of some spinels

(a) *Electrical properties of* Fe_3O_4 *and related compounds*

The most interesting spinel for its electrical properties is Fe_3O_4. Fe_3O_4 is an electronic semiconductor with a resistivity of 5.10^{-3} Ωcm at room temperature. Its resistivity below room temperature follows the general exponential law for semiconductors $\varrho = C \exp \varepsilon/kT$. Between 300 °K and 120 °K $\varepsilon = 0{\cdot}05$ eV, between 120 °K and 115 °K the resistivity increases about 100-fold, and below 115 °K $\varepsilon = 0{\cdot}10$ eV (fig. 10).

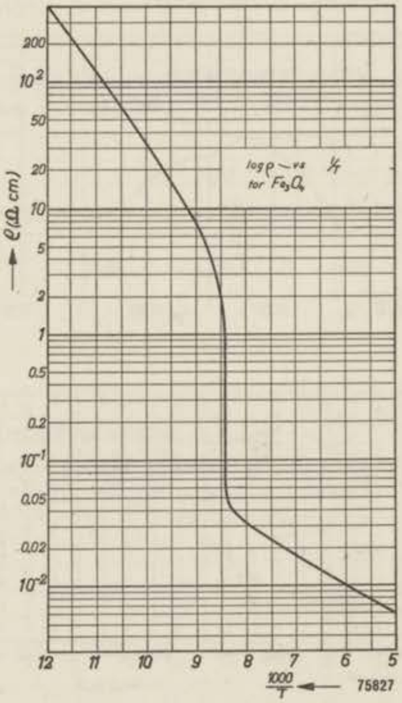

Fig. 10. Resistivity ϱ of Fe_3O_4 as a function of the reciprocal value of temperature.

The rather large conductivity is attributed to the simultaneous occurrence of Fe^{2+} and Fe^{3+} ions at the same crystallographical positions, viz. the octahedral interstices, which permits a fairly easy exchange of electrons between the different ions.

The discontinuity in the resistivity at 120 °K is caused by a rearrangement among the Fe^{2+} and Fe^{3+} ions at the octahedral interstices, accompanied by a small change in crystal structure (cf. p. 10). The electrical properties of Fe_3O_4 are changed profoundly when small deviations from stoichiometric ratio accur; the discontinuity at 120 °K disappears and above the transition point the "activation energy" ε increases.

We investigated rather extensively the electrical properties of the solid solutions in the systems Fe_3O_4-$MgCr_2O_4$ and Fe_3O_4-$ZnCr_2O_4$. For the details of these experiments see Verwey, Haaijman and Romeijn [3]). At that time only D.C. measurements were made, which we expected to be reliable.

Some time afterwards, however, the experiments of the late Mr Koops [24]) showed the resistivity of these oxidic semiconductors to be dependent upon the frequency. The effect can be rather large, the resistivity at 100 kc/s being about 20% of the D.C. resistivity for large resistivities (10^6 Ω cm) and about 50% of the D.C. resistivity for smaller values (10^3 Ω cm) of the resistivity.

Although the absolute value of the resistivities mentioned in our paper is not reliable, the activation energy ε is not much affected by the above considerations, for at room temperature a factor 5 in the resistivity corresponds to a difference of about 0·04 eV in the activation energy.

In fig. 11 we have plotted the activation-energy vs. composition in the systems Fe_3O_4-$ZnCr_2O_4$ and Fe_3O_4-$MgCr_2O_4$.

According to the distribution scheme, the compositions can be approximated as follows.

$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$	$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$
$Zn^{2+}_{1/2}Fe^{3+}_{1/2}[Fe^{2+}_{1/2}Fe^{3+}_{1/2}Cr^{3+}]O_4$	$Fe^{3+}[Mg^{2+}_{1/2}Fe^{2+}_{1/2}Cr^{3+}]O_4$
$Zn^{2+}[Cr^{3+}_2]O_4$	$Mg^{2+}[Cr^{3+}_2]O_4$

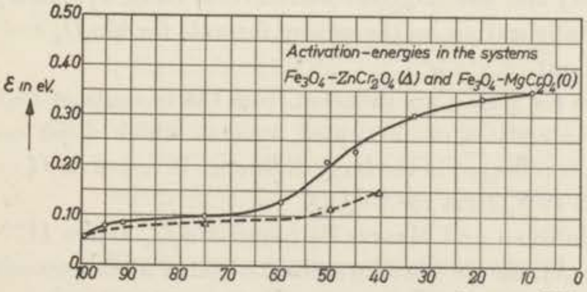

Fig. 11. "Activation energy" ε for solid solutions of Fe_3O_4 and non-conducting spinels.

In the system Fe_3O_4-$ZnCr_2O_4$ there are always $Fe^{2+} + Fe^{3+}$ ions at the octahedral interstices; in the other systems, however, only from 0-50% $MgCr_2O_4$. $Fe^{2+} + Fe^{3+}$ ions can be found simultaneously at the octahedral interstices, from 50% $MgCr_2O_4$ upwards the Fe^{2+} and Fe^{3+} ions occupy different positions.

This difference in ionic distribution is reflected in the activation energies. When the conductivity process can be thought of by an exchange of electrons between iron ions at the same type of interstices, the activation energy is rather small; the conductivity caused by electron exchange between iron ions at different crystallographical positions is accompanied by a larger activation energy.

The first process occurs in the system Fe_3O_4-$ZnCr_2O_4$ and in the iron-rich part of the system Fe_3O_4-$MgCr_2O_4$, whereas the second mechanism is found in the chromite-rich part of the latter system.

(b) *Electrical conductivity of* Mn_3O_4 *and* $ZnMn_2O_4$.

The crystal structure of Mn_3O_4 can be described as a tetragonally deformed spinel with an axial ratio of about 1·14 ($a = 8{\cdot}14$ Å, $c = 9{\cdot}42$ Å). The dimensions of $ZnMn_2O_4$ [25]) are nearly the same ($a = 8{\cdot}08_3$ Å, $c = 9{\cdot}22_6$ Å); it forms complete solid solutions with Mn_3O_4. A comparison of the intensities of the X-ray diagram shows clearly that Zn occupies the tetrahedral interstices, so for this compound there are only two formulae possible, viz. $Zn^{2+}[Mn_2^{3+}]O_4$ and $Zn[Mn^{2+}Mn^{4+}]O_4$. From analogy with this compound the possible formulae for Mn_3O_4 are

$$Mn^{2+}[Mn_2^{3+}]O_4 \text{ (I)} \quad \text{and} \quad Mn^{2+}[Mn^{2+}Mn^{4+}]O_4 \text{ (II)}.$$

The first formula is the most obvious one, because from the ionization potentials the energy difference between $Mn^{2+} + Mn^{4+}$ and $2Mn^{3+}$ is 18 eV in favour of the latter arrangement.

However, if the Mn^{2+} and Mn^{4+} ions order, some 9 eV of energy is gained; furthermore, the crystalline field is most favourable for Mn^{4+} (d^3 configuration) and the large distortion from cubic symmetry perhaps stabilizes this configuration, so the second formula for Mn_3O_4 and $ZnMn_2O_4$ cannot be ruled out.

Both formulae for Mn_3O_4 are different from the formula of Fe_3O_4 (where the octahedral interstices are occupied by ions which differ one unit in valency), which is reflected in the large difference in resistivity ($\varrho = 10^7 \Omega$ cm for Mn_3O_4 and $5{\cdot}10^{-3}$ Ω cm for Fe_3O_4).

Mc Murdie, Sullivan and Maurer [26]) found Mn_3O_4 above 1170 °C to be cubic ($a = 8{\cdot}64$ Å). As we were interested whether at this transition point the conductivity would change (compare Fe_3O_4 at 120 °K) we measured the D.C. resistivity of Mn_3O_4 below and above this transition point (fig. 12).

The resistivity of Mn_3O_4 can be described up to about 1075 °C by the exponential formula $\varrho = C \exp \varepsilon/kT$ ($\varepsilon = 1{\cdot}3$ eV). From 1075 °C to 1150 °C the resistivity drops rather rapidly to about 20% of its former value, then again follows an exponential law with $\varepsilon = 0{\cdot}75$ eV.

On cooling the same phenomena are observed in the reverse direction, with a marked thermal hysteresis, however.

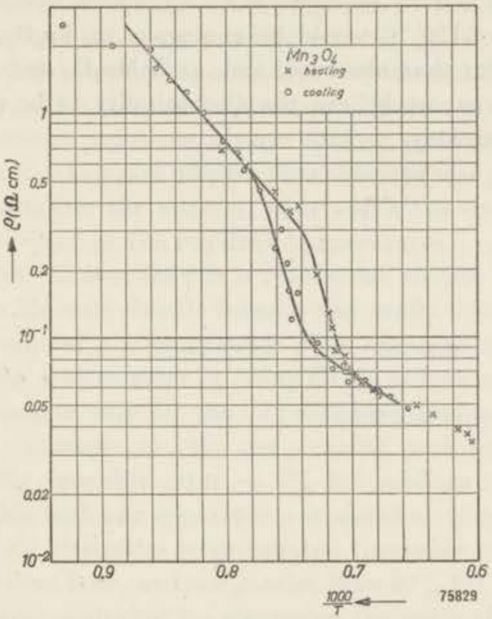

Fig. 12. Resistivity ϱ of Mn_3O_4 as a function of the reciprocal value of temperature.

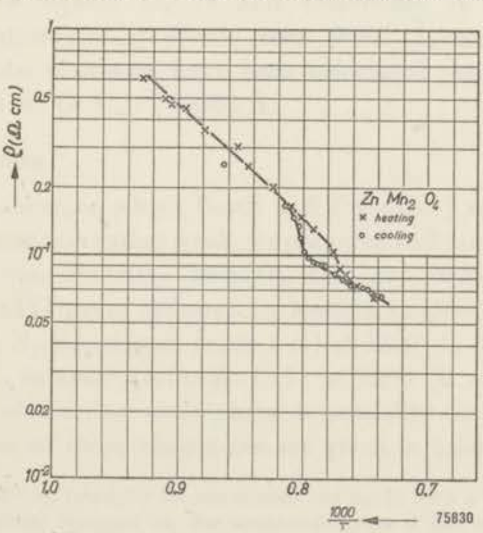

Fig. 13. Resistivity ϱ of Zn Mn_2O_4 as a function of the reciprocal value of temperature.

$ZnMn_2O_4$ exhibits the same phenomena at a somewhat different temperature (fig. 13). The sudden decrease begins at 950 °C and ends at 1025 °C, the change in activation energy being from 1·0 to 0·6 eV. Here again hysteresis occurs.

For Mn_3O_4 the end of the transformation coincides with the transition temperature found by Mc Murdie; we assume $ZnMn_2O_4$ to become cubic too above 1025 °C.

If Mn_3O_4 above 1150 °C would be analogous to Fe_3O_4, its resistivity would be far smaller than observed, and, as $ZnMn_2O_4$ and Mn_3O_4 exhibit the same phenomena, we believe the discontinuity to be caused only by the change in symmetry.

CHAPTER III

PREPARATION AND X-RAY INVESTIGATION OF SOME SPINELS

1. General details of preparation and investigation

A large number of spinels were prepared in the following way: An aqueous solution of the corresponding nitrates (if necessary mixed with an insoluble oxide) were evaporated to dryness under a 500 Watt incandescent lamp. This is far easier than on a flame or in an electric furnace, for the concentrated solutions always sputter when heated from below.

The mixture of oxides and nitrates thus obtained was preheated at 500 °C in order to decompose the nitrates, after which the resulting powder was compressed and fired at the required temperatures.

Firing at 1000° C was done in a Ni-chrome electric furnace, at higher temperatures a Mo-wire electric furnace was used.

X-ray diagrams of the compounds thus obtained were usually made with the Norelco spectrometer *), using Co K_α radiation. Films were made with CrK_α radiation only for the Cr containing compounds. As a rule, it was sufficiently accurate to take the recorded peak height as a measure for the intensity (possible error $\pm$ 5% for medium lines). The utmost accuracy possible with our apparatus was aimed at with nickel aluminate, in which case all intensities were counted (probable error about 1% for strong and medium lines, and not greater than 10% for the weakest lines). The spacings were evaluated by measuring the angle of the reflections for which $h^2+k^2+l^2$ equals 72, 75 and sometimes 76 with the Norelco high-angle spectrometer (probable error 0·001 Å, unless stated otherwise). The lattice constants have been calculated using as wavelengths Co K_α: 1·77890 Å, Cr K_α : 2·28962 Å.

2. The aluminates

Since the evidence on which Barth and Posnjak [1]) assumed the aluminates to be normal was rather weak, we prepared and investigated a number of aluminates viz. $MnAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$, $NiAl_2O_4$ and $ZnAl_2O_4$. $CoAl_2O_4$ and $ZnAl_2O_4$were prepared by heating at 1200 °C in air, $MnAl_2O_4$ by heating in a N_2-H_2 mixture (ratio 2 :1) at 1200° C, $FeAl_2O_4$ by heating in a N_2-H_2-CO_2 mixture (ratio 2 : 1 : 2) at 1200 °C and slowly cooling. The hydrogen containing atmosphere is necessary to prevent oxidation.

The intensities of these aluminates are given in table III.

---

*) In the spectrometer, intensity measurements are made with a Geiger-Müller counter of the X-radiation, focussed on the counterslit from a flat powder specimen. The Geiger-Müller counter is rotated with twice the angular speed of the specimen.

TABLE III

Relative intensities ($I_{311} = 100$) of

hkl	$MnAl_2O_4$	$FeAl_2O_4$	$CoAl_2O_4$	$NiAl_2O_4$	$ZnAl_2O_4$
111	5	4	3	25	3
220	50	56	75	23	85
311	100	100	100	100	100
222	2	3	2	2	2
400	30	22	25	50	10
331	5	3	8	2	15
422	15	16	25	10	30

From these intensities we conclude that the aluminates of Mn, Fe, Co, and Zn are normal, but that nickel aluminate is clearly an exception. I_{220} is far too weak for a normal spinel, but if the structure were inverse, I_{111}, I_{222} and I_{331} would be far stronger than observed. The structure is an intermediate one; therefore the intensities were very carefully measured (table IV).

TABLE IV

Relative intensities ($I_{311} = 500$) of $NiAl_2O_4$

hkl	*I*
111	118 ± 1
220	107 ± 1
311	500 ± 5
222	5 ± 0·5
400	213 ± 2
331	6 ± 0·5
422	38 ± 1
333 511	163 ± 2
440	277 ± 3

We calculated with the method of least squares, minimalizing the function $\Sigma \frac{|F_0 - F_c|}{|F_0|}$ in which F_0 and F_c are the observed and the calculated structure factors, the distribution of ions and the oxygen parameter u. We used the atomic scattering factors of the International Tables, corrected if necessary with the aid of Hönl's formulae [27]) for the influence of the absorption edge.

The inversion is expressed in the inversion parameter δ, δ being the fraction of the ions under consideration (i.e. the Ni^{2+} ions) at octahedral interstices; a normal spinel has $\delta = 0$, an inverse spinel $\delta = 1$. We found nickel aluminate to have $\delta = 0{\cdot}76 \pm 0{\cdot}02$, with an oxygen parameter $u = 0{\cdot}381 \pm 0{\cdot}002$.

The approximated formula of nickel aluminate is $Ni_{1/4}Al_{3/4}[Al_{5/4}Ni_{3/4}]O_4$. This is a rather unexpected result, for it is between the inverse ($\delta = 1$) and the random ($= 0{\cdot}67$) distribution. It indicates a rather strong preference of Ni^{2+} for the octahedral positions, strong enough to compensate for a large part the general tendency of the aluminates to be normal.

The intensities of the diffraction pattern were not influenced by the heat-treatment of the specimen, for heating at 1300 °C and quenching made no difference. In order to confirm our results, we prepared solid solutions in the systems $ZnAl_2O_4$ - $NiAl_2O_4$ and $ZnAl_2O_4$ - $CoAl_2O_4$. The intensities of the diffraction patterns show the difference between the two systems (tables V and VI).

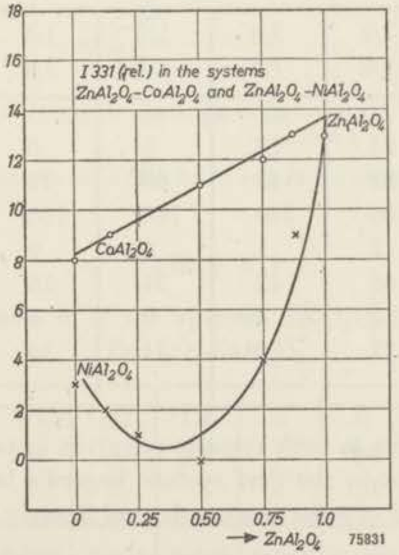

Fig. 14. Relative intensities of 331 reflections for Zn-Co and Zn-Ni aluminate solid solutions.

The results of our calculation are corroborated by the fact, that the intensities of 111, 222 and 331 go through zero in the system $ZnAl_2O_4$-$NiAl_2O_4$, whereas they are nearly constant in the system $ZnAl_2O_4$ - $CoAl_2O_4$ (fig. 14).

As the intensity of the 220 reflection is only determined by the ions at the tetrahedral interstices, this reflection is a simple indicator for the change in ionic distribution (fig. 15).

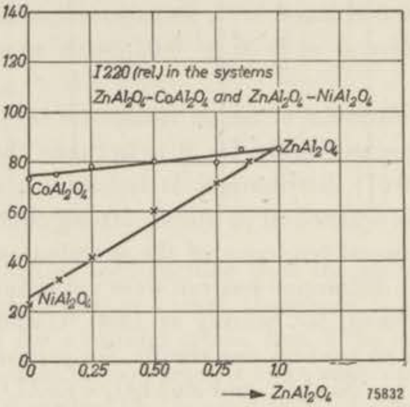

Fig. 15. Relative intensities of 220 reflections for Zn-Co and Zn-Ni aluminate solid solutions

TABLE V

Relative intensities ($I_{311} = 100$) in the system $NiAl_2O_4$ - $ZnAl_2O_4$

$NiAl_2O_4$ $ZnAl_2O_4$	1 0	7/8 1/8	3/4 1/4	1/2 1/2	1/4 3/4	1/8 7/8	0 1
hkl							
111	25	23	13	6	0	2	4
220	23	33	42	60	71	80	85
311	100	100	100	100	100	100	100
222	3	2	1	0	0	1	2
400	50	46	43	24	18	11	11
331	3	2	1	0	4	9	13
422	9	11	12	21	23	24	31

The lattice constants in both systems are given in table VII and fig. 16.

Fig. 16 shows, that in the first system Vegard's law*) is not obeyed, whereas in the second one the spacing depend linearly on the composition.

---

*) According to Vegard's law, the lattice constants of solid solutions are linear functions of their compositions.

TABLE VI

Relative intensities ($I_{311} = 100$) in the system $CoAl_2O_4$ - $ZnAl_2O_4$

$CoAl_2O_4$ $ZnAl_2O_4$	1 0	7/8 1/8	3/4 1/4	1/2 1/2	1/4 3/4	1/8 7/8	0 1
hkl							
111	3	3	3	3	3	4	4
220	73	75	79	80	80	85	85
311	100	100	100	100	100	100	100
222	2	2	2	2	2	2	2
400	25	22	19	16	13	14	11
331	8	9	10	11	12	13	13
422	25	24	28	30	31	31	31

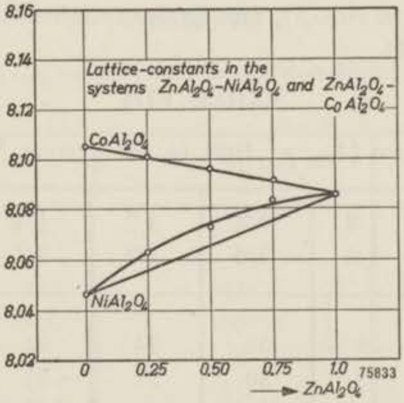

Fig. 16. Lattice constants (in Å) for Zn-Ni and Zn-Co aluminate solid solutions.

TABLE VII

Lattice constants *a* of the systems $ZnAl_2O_4$-$NiAl_2O_4$ [28]) and $ZnAl_2O_4$-$CoAl_2O_4$

$NiAl_2O_4$ $ZnAl_2O_4$ $CoAl_2O_4$	1 0 0	3/4 1/4 0	1/2 1/2 0	1/4 3/4 0	0 1 0	0 3/4 1/4	0 1/2 1/2	0 1/4 3/4	0 0 1
a (in Å)	8·046	8·063	8·073	8·083	8·086	8·091	8·096	8·101	8·105

The lattice constants of $MgAl_2O_4$ and $ZnAl_2O_4$ are 8·09 Å, of MgO and NiO 4·18 Å, so we can assume the ionic radii of Mg^{2+}, Ni^{2+} and Zn^{2+} to be nearly equal, and thus we should expect $Ni[Al_2]O_4$ (the "normal", non-existent structure) to have a lattice constant of 8·08 Å, a value which could be extrapolated from the slope on the Zn-rich side of the diagram. If on the Ni-rich side of the system the Ni^{2+} ions would occupy the tetrahedral interstices, this high value of the lattice constant could be expected. A comparison, however, of the intensities in the systems $ZnAl_2O_4$-$NiAl_2O_4$ and $ZnAl_2O_4$-$CoAl_2O_4$ (figs 14 and 15) shows that this is not true: the Ni^{2+} ions occupy preferentially the octahedral interstices.

On the Ni-rich side of the diagram the lattice-contraction is fairly large; this may be caused by the occurence of the order, mentioned in chapter I.

To investigate if Ni^{2+} retains its preference for the octahedral interstices in other spinel systems, we prepared and measured solid solutions in the systems $MgAl_2O_4$-$NiAl_2O_4$.

The intensities remain fairly constant throughout the whole range from which the conclusion can be drawn that the Ni^{2+} ions are distributed in the same way as in $NiAl_2O_4$ among the tetrahedral and octahedral interstices (table VIII).

TABLE VIII

Relative intensities ($I_{311} = 100$) in the system $NiAl_2O_4$-$MgAl_2O_4$

$NiAl_2O_4$ $MgAl_2O_4$	1 0	7/8 1/8	3/4 1/4	1/2 1/2	1/4 3/4	1/8 7/8	0 1
hkl							
111	30	34	36	34	31	30	32
220	28	32	30	32	31	36	44
311	100	100	100	100	100	100	100
222	3	2	2	2	2	2	2
400	60	66	61	63	63	62	65
331	3	3	3	2	1	1	2
422	12	11	10	10	10	12	12

Conclusion

Of the aluminates $MgAl_2O_4$, $MnAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$, and $ZnAl_2O_4$ are normal, whereas $NiAl_2O_4$ is partly inverse with an approximate formula $Ni_{1/4}Al_{3/4}\,[Ni_{3/4}Al_{5/4}]O_4$.

In systems of nickel aluminate with normal aluminates ($MgAl_2O_4$ and $ZnAl_2O_4$) the distribution of Ni^{2+} ions among tetrahedral and octahedral interstices is the same as in pure $NiAl_2O_4$. The low value of the lattice constant of $NiAl_2O_4$, compared with those of $MgAl_2O_4$ and $ZnAl_2O_4$, must be attributed to this difference in ionic distribution (cf. the difference in lattice constants between $Fe[MgFe]O_4$ and $Zn[Fe]O_4$ mentioned on p. 6).

3. The germanates

Fairly little is known about germanates of the formula Me_2GeO_4. Zn_2GeO_4 29) is reported to have phenacite structure, Mg_2GeO_4 29) 30) to be dimorphous with both spinel and olivine structure, Ni_2GeO_4 29) to have spinel structure.

We prepared Co_2GeO_4, Ni_2GeO_4 and $CoNiGeO_4$ by firing at 1000 °C the powder obtained from GeO_2 and the solutions of Co and Ni nitrate. Co_2GeO_4 is pink, Ni_2GeO_4 yellowish green and $CoNiGeO_4$ fawn-coloured; all compounds had the spinel structure.

The intensities and lattice constants of the three compounds are given in table IX and fig. 17.

TABLE IX

Relative intensities ($I_{311} = 100$) and lattice constants of Co_2GeO_4, Ni_2GeO_4 and $CoNiGeO_4$.

Co_2GeO_4		$CoNiGeO_4$	Ni_2GeO_4
hkl			
111	0	0	2
220	44	41	42
311	100	100	100
222	8	8	8
400	18	16	19
331	0	0	2
422	20	20	20
333 511	35	40	42
440	48	49	49
a (in Å)	$8{\cdot}317_5 \pm 0{\cdot}000_5$	$8{\cdot}268 \pm 0{\cdot}001$	$8{\cdot}221_0 \pm 0{\cdot}000_5$

Although the differences in scattering power between Co (Ni) and Ge are rather small, these intensities point definitely to a normal structure, $Ge[Co_2]O_4$. The structure factor for the 111 reflection is $4\sqrt{2}(A_{\text{tet}}) - 8(A_{\text{oct}}) - f(u - 3/8)$, and $4\sqrt{2}(A_{\text{tet}}) - 8(A_{\text{oct}}) + f'(u - 3/8)$ for 331,

A_{tet} and A_{oct} denoting the average scattering factor of the atoms at tetrahedral and octahedral interstices respectively, $f(u-\frac{3}{8})$ and $f'(u-\frac{3}{8})$ being functions of the deviation of the oxygen parameter from the ideal value. When we make the reasonable assumption, that the dependency of the scattering factor of the diffraction angle is the same for Co and Ge, the absence of both reflections 111 and 311 in $GeCo_2O_4$ can only be explained if both structure factors are equal. As their only difference is the difference in sign between the oxygen contributions in both factors, those contributions must be zero. This is only possible for $u = 0{\cdot}375$.

From the fact that in $Ge[Ni_2]O_4$ both reflections are just observable, we can estimate the probable error in u. A simple calculation shows this to be 0·003, so for the normal 2-4 spinels $Ge[Co_2]O_4$ and $Ge[Ni_2]O_4$ $u = 0{\cdot}375 \pm 0{\cdot}003$. The solid solutions in this system obey Vegard's law (fig. 17).

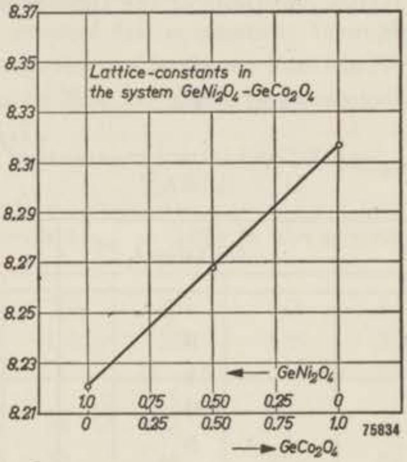

Fig. 17. Lattice constants (in Å) for Ni-Co germanate solid solutions.

According to Jander and Stamm [30]) Mg_2GeO_4 has the olivine structure above 1060 °C and the spinel structure below this temperature. This is not impossible, but it would be a deviation from the rule that at high temperatures the more symmetrical structure is favoured (e.g. α, β and γ Mn, tetragonal and cubic Mn_3O_4, tetragonal and cubic $BaTiO_3$ etc.). We tried to prepare the spinel modification in different ways: $Mg(NO_3)_2$ and GeO_2 were evaporated to dryness and heated at 850 °C for several days, the same mixture was heated to 1200 °C and quenched, or tempered at 850 °C for several days, and also a mixture of MgO and GeO_2 was heated at the temperatures, mentioned above. In all cases the X-ray diagram was very complicated, most probably corresponding to the olivine structure. To make sure of the non-existence of the spinel modification we tried to prepare solid solutions in the systems $Ge[Co_2]O_4$-$Ge[Mg_2]O_4$ and $Ge[Ni_2]O_4$-$Ge[Mg_2]O_4$. With less than 50% cobalt or nickel germanate the magnesium germanate lines were clearly visible, but due to the large number and faintness of these lines this method is unsuitable for finding the solubility. The lattice constant of $Ge[Co_2]O_4$ saturated with magnesium germanate was 8·305 Å, to be compared with 8·317 Å for pure $Ge[Co_2]O_4$; assuming equal radii for Mg^{2+} and Ni^{2+}, we can from the $Ge[Ni_2]O_4$-$Ge[Co_2]O_4$ diagram fix the solubility limit at 10-15%.

From these experiments we conclude that most probably Jander and Stamm are wrong on the dimorphism of magnesium germanate.

It was impossible to prepare solid solutions in the systems magnesium aluminate-germanate and magnesium titanate-germanate. The non-occurrence of Mg germanate in the spinel structure is the more remarkable, as the germanates are the only spinels for which the primitive description is true: a cubic close packing of oxygen ions, in which the smaller (tetrahedral) interstices are occupied by the smaller ions (Ge) and the larger (octahedral) interstices by the larger ions (Co and Ni).

From geometrical considerations it is impossible to see why magnesium germanate does not crystallize in the spinel structure, for the radius of Mg^{2+} is either equal to or somewhat larger than the radius of Ni^{2+} and definitely smaller than the radius of Co^{2+}.

4. The titanates

The titanates are reported by Barth and Posnjak[1]) to be inverse; due to the small difference in scattering power of Ti and Mn, Fe, Co it is difficult to verify this statement, but for magnesium and zinc titanate the inverse structure is firmly established.

Although nickel titanate is unknown, it is possible to substitute about 50% of the Zn in Zn_2TiO_4 by Ni [31]).

As Zn occupies preferentially the tetrahedral interstices, this compound will have the formula $Zn[NiTi]O_4$ according to the strong preference of Ni^{2+} for the octahedral interstices.

We investigated the lattice constants in the systems $Co[CoTi]O_4$-$Mg[MgTi]O_4$ and $Co[CoTi]O_4$-$Zn[ZnTiO_4]$ (table X, figs 18 and 19). The intensities of the X-ray diagrams were nearly the same over the whole range of compositions; the only conclusion which can be drawn from this fact is a more or less random substitution of Mg by Co in the former system.

There is a typical difference in colour in these preparations. The solid solutions of the system Mg_2TiO_4-Co_2TiO_4 are green; only $Co_{1\frac{1}{2}}Zn_{\frac{1}{2}}TiO_4$ is green too, the other Zn containing compounds being light greyish - pink. This is due to the preference for the tetrahedral interstices of Zn, the result

TABLE X

Lattice constants in the system Mg_2TiO_4-Co_2TiO_4-Zn_2TiO_4

Mg_2TiO_4	1	3/4	1/2	1/4	0	0	0	0	0
Co_2TiO_4	0	1/4	1/2	3/4	1	3/4	1/2	1/4	0
Zn_2TiO_4	0	0	0	0	0	1/4	1/2	3/4	1
a (in Å)	$8{\cdot}44_5$*)	8·443	8·445	8·447	8·445	8·445	8·448	8·456	8·465

*) The lines of this compound were rather blurred, so the probable error is somewhat larger (0·005 Å) than for the other compounds.

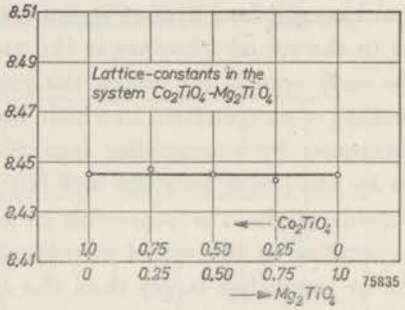

Fig. 18. Lattice constants (in Å) for Mg-Co titanate solid solutions.

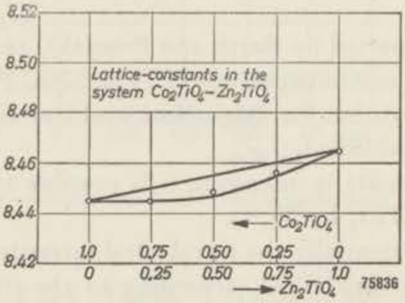

Fig. 19. Lattice constants (in Å) for Co-Zn titanate solid solutions.

of which is the absence of Co on tetrahedral interstices in these compounds (cf. chapter II, section 2).

This difference in substitution is reflected in the lattice constants too: the first atom of Zn hardly affects the lattice constants, the second one enters into the lattice with a larger radius. The explanation of this phenomenon is found in the preference of Zn for the tetrahedral interstices, as the substitution goes as follows:

$$Co[CoTi]O_4 \rightarrow Zn[CoTi]O_4 \rightarrow Zn[ZnTi]O_4 .$$

This preference is most probably caused by some covalent contribution to the binding energy; this covalent bond is only possibly in tetrahedral surroundings (sp^3 orbitals), and causes a decrease in Zn-O distance. When Zn occupies an octahedral interstice this covalent bond is not possible, and the radius of the Zn is somewhat larger.

In the Co_2TiO_4 - Mg_2TiO_4 this phenomenon is absent because Co and Mg behave as if they have the same type of binding and substitute more or less at random.

5. The ferrites

The difference in scattering power between most of the divalent ions and Fe^{3+} is too small to draw conclusions on the ionic distribution from the X-ray diagrams. A general classification has been made by Verwey with the aid of the lattice constants (cf. chapter I) but the most exact information can be obtained from the values of the magnetic saturation at low temperatures. This will be treated by Mr E. W. Gorter (to be published in Philips Research Reports). We shall give graphically the results, obtained by Vegard 28) on the only non-magnetic system, viz. $Cd[Fe_2]O_4$ - $Zn[Fe_2]O_4$ (fig. 20).

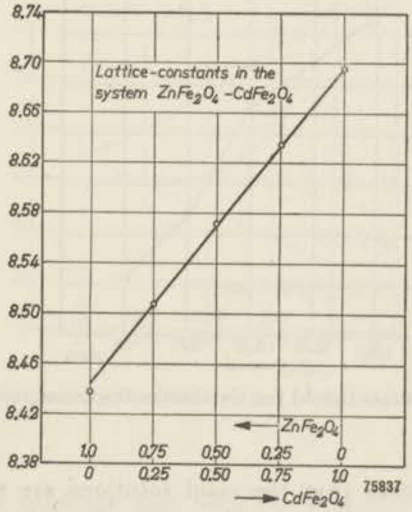

Fig. 20. Lattice constants (in Å) for Zn-Cd ferrite solid solutions.

More complicated spinel systems

In order to obtain more information on spinels, we investigated a number of systems, in which normal and inverse spinels with ions of different valencies were combined, viz.

normal	2-3	with	normal	2-4	spinels.	Section	6.
inverse	2-4	,,	,,	2-4	,,	,,	7.
,,	2-3	,,	,,	2-4	,,	,,	8.
,,	2-4	,,	,,	2-3	,,	,,	9.
,,	2-3	,,	,,	2-3	,,	,,	10.

The number of possible combinations is not too great, because the maximum allowable difference in lattice constant is about 2-3%.

6. The system $CoAl_2O_4$-$GeCo_2O_4$

Cobalt aluminate and cobalt germanate form solid solutions only with difficulty. At 1000 °C the two phases were the nearly pure components, at 1200 °C the mutual solubility was somewhat greater (some 25%) and only at 1400 °C it was possible to obtain a homogeneous product.

The intensities of the diffraction lines and the spacings in this system are given in table XI and figs 21 and 22.

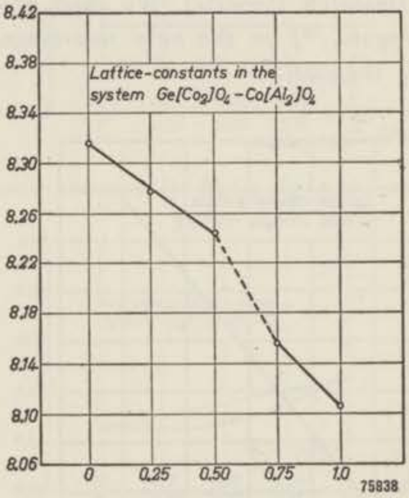

Fig. 21. Lattice constants (in Å) for Co aluminate-germanate solid solutions.

The intensities indicate that the solid solutions are not regular intermediates between the orginal substances. The fully drawn line in fig. 22 indicates the expected intensities for regular *) solutions, the dashed one the expected values for regular solid solutions between $Ge[Co_2]O_4$ and the hypothetical $Al[CoAl]O_4$.

---

*) In "regular" solid solutions the ions are distributed in the same way as in the pure components.

TABLE XI

Relative intensities and spacings in the system $Co[Al_2]O_4$ - $Ge[Co_2]O_4$

$Co[Al_2]O_4$ $Ge[Co_2]O_4$	0 1	1/4 3/4	1/2 1/2	3/4 1/4	1 0
hkl					
111	0	13	8	3	3
220	44	39	41	50	75
311	100	100	100	100	100
222	8	6	7	4	2
400	18	20	18	30	25
331	0	3	2	2	8
422	20	11	13	16	25
a (in Å)	8·317	8·277	8·244	8·156	8·105

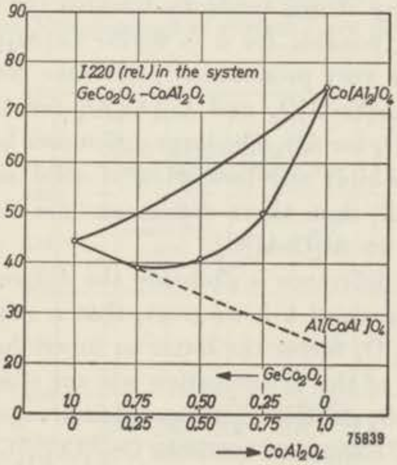

Fig. 22. Relative intensities of 220 reflections for Co aluminate-germanate solid solutions.

From fig. 22 we conclude that with the first 25% of cobalt aluminate the Al ions occupy preferentially the tetrahedral positions; with larger amounts of aluminate, the Al ions occupy both positions. As the difference in scattering power between Co and Ge is rather small, we cannot find whether on the Al-rich side of the system Ge occupies the tetrahedral positions or not.

These important changes in ionic distribution affect the lattice constants appreciably; as shown in fig. 21 Vegard's law is not obeyed.

The difficulty in the formation of solid solutions can be explained as follows: although the difference in lattice constants is rather small, there is a large difference in "internal" properties of $Co[Al_2]O_4$ and $Ge[Co_2)O_4$, as shown in table XII (the properties of the hypothetical $Al[CoAl]O_4$ are recorded too).

TABLE XII

	a	u	radius of ion at $8a$	average radius of ion at $16d$
$Co[Al_2]O_4$	8·105 Å	0·387	0·82 Å	0·57 Å
$Ge[Co_2]O_4$	8·317 Å	0·375	0·45 Å	0·82 Å
$Al[CoAl]O_4$		0·380	0·57 Å	0·70 Å

We suggest the following explanation for the "forced" inversion of $Co[Al_2]O_4$: Ge has a very strong tendency towards the tetrahedral interstices, but this is only possible for $u = 0{\cdot}375$. $Co[Al_2]O_4$ is normal but neither Co nor Al has a very pronounced preference for either interstice (compare $Ge[Co_2]O_4$, $Co[CoTi]O_4$ and $Co[Al_2]O_4$ for Co, and $Co[Al_2]O_4$ and $Al_{3/4}Ni_{1/4}$ $[Al_{5/4}Ni_{3/4}]O_4$ for Al). The large differences between $Ge[Co_2]O_4$ and $Co[Al_2]O_4$ would inhibit any formation of solid solution, (compare the differences in radii) but these differences are diminished by the inversion of $Co[Al_2]O_4$ to $Al[CoAl]O_4$.

The most important difference is probably the difference in u; the tendency for Ge to force a small u is so great, that a substitution by 25% of $Ge[Co_2]O_4$ in $Co[Al_2]O_4$ forces the latter to invert halfway.

The original purpose of this investigation was the study of the ordering phenomenon: if $Co[Al_2]O_4$ and $Ge[Co_2]O_4$ would form regular solid solutions, the formula of the 50-50 compound would be $Ge_{1/2}Co_{1/2}[CoAl]O_4$. Compared with the original substances this compound would show order on the octahedral as well as on the tetrahedral interstices. This would stabilize the normal distribution very much (about 5 eV), but nothing is found to indicate this effect. The difference in ionic radii is probably too large for this phenomenon to occur. This is an experimental proof that the dependence of the lattice energy upon the oxygen parameter u may be more important than the influence of order.

We tried to prepare solid solutions in the system nickel aluminate-germanate, without any succes. Even after firing at 1500 °C and quenching we observed two spinel phases in all preparations. Firing at high temperatures is rather difficult because GeO, that can be formed if the porcelain furnace tube becomes permeable for the hydrogen containing gas used for the protection of the Mo heating wire, is rather volatile. Once we observed not only both spinel phases, but the NiO phase too. Blowing a slow current of oxygen (2 l/min) through the porcelain tube prevents the formation of GeO.

We should expect the formation of solid solutions in this system to be easier than in the corresponding Co system, because the difference in lattice constants is smaller, and because nickel aluminate is partly inverse, but the reverse is true. We cannot explain this phenomenon.

7. The system $Co[CoTi]O_4$-$Ge[Co_2]O_4$

In this system again incomplete solid solutions are formed. $Co[CoTi]O_4$ dissolves at least 50% of $Ge[Co_2]O_4$, but the latter does not dissolve an appreciable amount of $Co[CoTi]O_4$, for the compositions containing 12·5% and 25% of cobalt titanate were distinctly two-phase systems, even after firing at 1400 °C.

Due to the small differences in scattering power we did not attempt to analyse the intensities of the X-ray diagrams. The same holds for the systems 8, 9 and 10. The spacings of system 7 are given in table XIII, fig. 23.

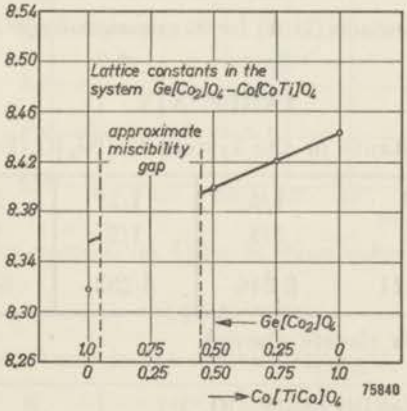

Fig. 23. Lattice constants (in Å) for Co germanate-titanate solid solutions.

TABLE XIII

Lattice constants in the system $Ge[Co_2]O_4$-$Co[CoTi]O_4$

$Ge[Co_2]O_4$ $Co[CoTi]O_4$	1 0	1/2 1/2	1/4 3/4	0 1
a (in Å)	8·317	8·397	8·421	8·445

8. The system $Ge[Ni_2]O_4$-$Fe[NiFe]O_4$

This is the only germanate-other spinel system, in which no indications for segregation were found; after firing at 1200 °C the samples were homogeneous. Here again a discussion of the intensities is impossible, but we can predict the behaviour of the system: Ge favours the tetrahedral interstices, Ni the octahedral ones, and the *u* values are as close as possible in the original substances, so we expect a quite regular distribution. For spacings see table XIV, fig. 24.

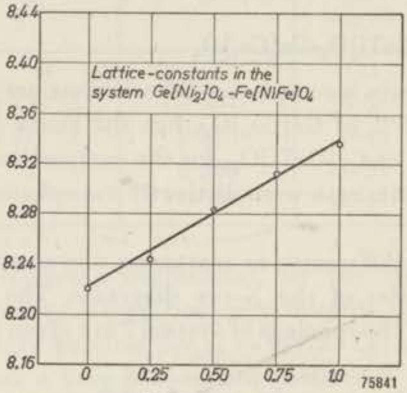

Fig. 24. Lattice constants (in Å) for Ni germanate-ferrite solid solutions.

TABLE XIV

Lattice constants in the system $Ge[Ni_2]O_4$-$Fe[NiFe]O_4$

$Fe[NiFe]O_4$ $Ge[Ni_2]O_4$	0 1	1/4 3/4	1/2 1/2	3/4 1/4	1 0
a (in Å)	8·221	8·246	8·283	8·312	8·337

Vegard's law is rather closely obeyed.

9. The system $Zn[ZnTi]O_4$-$Zn[Fe_2]O_4$

Solid solutions were prepared without difficulties. The spacings are given in table XV, fig. 25.

TABLE XV

Lattice constants in the system $Zn[ZnTi]O_4$-$Zn[Fe_2]O_4$

$Zn[ZnTi]O_4$ $Zn[Fe_2]O_4$	0 1	1/4 3/4	1/2 1/2	3/4 1/4	1 0
a (in Å)	8·440	8·448	8·456	8·462	8·465

A small, positive deviation from Vegard's law is observed.

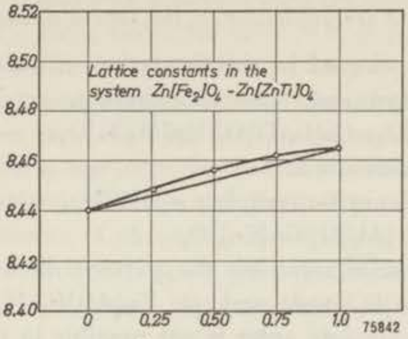

Fig. 25. Lattice constants (in Å) for Zn titanate-ferrite solid solutions.

10. The system Ni[Cr$_2$]O$_4$-Fe[NiFe]O$_4$

The preparation offered no difficulties. Only the spacings are given in table XVI and fig. 26.

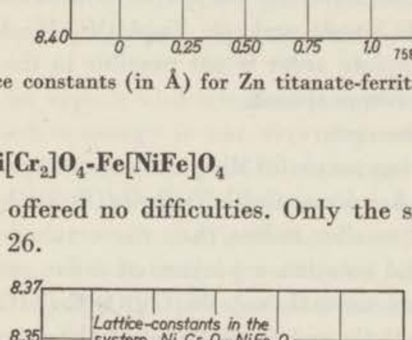

Fig. 26. Lattice constants (in Å) for Ni chromite-ferrite solid solutions.

TABLE XVI

Lattice constants in the system Ni[Cr$_2$]O$_4$-Fe[NiFe]O$_4$

Ni[Cr$_2$]O$_4$ Fe[NiFe]O$_4$	0 1	1/4 3/4	1/2 1/2	3/4 1/4	1 0
*a**) (in Å)	8·337	8·320	8·305	8·310	8·328

*) possible error ±0·003 Å.

Due to the tendency of both Cr and Ni for the octahedral interstices, the distribution will most probably be as follows

$Ni[Cr_2]O_4$-$Ni_{1/2}Fe_{1/2}[Cr_{3/2}Ni_{1/2}]O_4$-$Fe[NiCr]O_4$-$Fe\ [NiCr_{1/2}Fe_{1/2}]O_4$-$Fe\ [NiFe]O_4$.

The large, negative deviation from Vegard's law is due to this anomalous distribution.

11. Discussion of the results

(a) *Regularities and irregularities in the lattice constants*

Vegard's law is obeyed in the formation of solid solutions of spinels with the same type of ionic distribution, e.g. $Co[Al_2]O_4$-$Zn[Al_2]O_4$, $Ge[Co_2[O_4$-$Ge[Ni_2]O_4$, $Co[CoTi]O_4$-$Mg[MgTi]O_4$.

Positive deviations occur

(1) When the tendency for complete solid solution is small, e.g. $Co[CoTi]O_4$-$Ge[Co_2]O_4$ and $Co[Al_2]O_4$-$Ge[Co_2]O_4$.

(2) When in the solid solutions the pattern of order is destroyed, e.g. $Zn[Fe_2]O_4$-$Zn[ZnTi]O_4$ and perhaps $Zn[Al_2]O_4$-$Ni_{1/4}Al_{3/4}[Al_{5/4}Ni_{3/4}]O_4$. In nickel aluminate complete order is not possible in the ratio 1 : 1, for this is only possible in inverse spinels.

Negative deviations occur

(1) When the same ion occurs at different crystallographic positions with a different chemical bond e.g. $Co[CoTi]O_4$-$Zn[ZnTi]O_4$. The tetrahedrally bound Zn ion has a smaller radius than the octahedrally bound one.

(2) When in the solid solution a pattern of order persists, although one of the components is normal, e.g. $Ni[Cr_2]O_4$-$Fe[NiCr]O_4$-$Fe[NiFe]O_4$.

These deviations are the only indications of the existence of short-range order, because a decrease in order can be expected to increase the mutual repulsion between the metal ions and vice versa.

(b) *Regularities in the ionic distribution*

Assuming the Verwey-Heilmann scheme, we can predict the ionic distribution if no antagonistic effects occur and the difference in the oxygen parameters is not too large, e.g. $Ge[Ni_2]O_4$-$Fe[NiFe]O_4$. When the difference in parameter is large, and there is only one ion with a pronounced preference, this ion determines the average valency at the tetrahedral (or octahedral) interstices; then the ionic distribution will be chosen which gives the best fit with this parameter, e.g. $Ge[Co_2]O_4$-$Co[Al_2]O_4$.

We shall try to understand the Verwey-Heilmann scheme which we write as follows

(a) Ions with preference for tetrahedral interstices:

$$Zn^{2+},\ Cd^{2+},\ Ga^{3+},\ In^{3+},\ Ge^{4+}.$$

(b) Ions with preference for octahedral interstices:

$$Ni^{2+},\ Cr^{3+},\ Ti^{4+},\ Sn^{4+}.$$

(c) Indifferent ions:

$$Mg^{2+},\ Al^{3+},\ Fe^{2+},\ Co^{2+},\ Mn^{2+},\ Fe^{3+},\ Cu^{2+}.$$

The ions in this scheme are fairly different, viz. ions with a noble-gas shell: Mg^{2+}, Al^{3+}, Ti^{4+}; ions with a partially filled d shell: Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}; ions with a filled d shell (or 18-electron configuration): Zn^{2+}, Cd^{2+}, Ga^{3+}, In^{3+}, Ge^{4+}, Sn^{4+}.

The latter are known for their tendency to form a covalent bond with sp^3 orbitals. The oxidic compounds are fairly ionic, but the covalent contribution can be rather large (if not, ZnO would crystallize in the NaCl structure). If the radius is too large, instead of a tetrahedral structure an octrahedral one is chosen. (CdO has the NaCl structure, unlike ZnO).

According to the scheme of chapter I, the divalent ions at tetrahedral interstices determine u at 0·387; as at this u value both interstices are equally large, Zn and Cd favour the tetrahedral interstices above the octahedral ones.

The ideal u value for spinels with trivalent ions at tetrahedral interstices is 0·381, but the lattice energy is not very dependent upon u; for the gallates with $Ga^{3+} = 0·61$ Å and $a = 8·30$ Å, a reasonable fit is obtained with $u = 0·381$ (cf. table I), but for the indates ($a = 8·80$ Å, $In^{3+} = 0·78$Å) the available space at the tetrahedral interstices is rather small (0·65 Å).

For tetravalent ions at tetrahedral interstices u must be 0·375, so here only small ions can occupy the tetrahedral interstices; Ge occupies the tetrahedral interstices, Sn the octahedral ones, in spite of the electronic structure of the Sn^{4+} ion.

Of the ions with a noble-gas shell only Ti^{4+} shows a preference for the octahedral positions, which is caused, just as with Sn, by a combination of a high charge and a rather large radius. If Ti^{4+} would occupy the tetrahedral interstices with $u = 0·375$, the lattice-constant of the titanates would be 9·0 Å instead of 8·4 Å, a difference of 7%. Al^{3+} fits best in the octahedral interstices, but the difference with the tetrahedral ones is not very marked. Mg^{2+} would fit in the octahedral interstices, but, due to its small charge, it does not determine the structure.

The ions with a partially filled d-shell are the most difficult ones to analyse [32]).

Cr^{3+} has d^3 configuration, Mn^{2+} and Fe^{3+} d^5, Fe^{2+} d^6, Co^{2+} d^7 and Ni^{2+} d^8 configuration.

As the d^5 configuration has a spherically symmetrical charge distribution, Mn^{2+} and Fe^{3+} may be treated as noble-gas shell ions; for the other ones we must take into consideration the influence of the electrical field of the surrounding oxygen ions (the so-called crystalline field) upon the spatial distribution of the electrons.

For the sake of simplicity we shall omit the mutual interaction of the d electrons of the transition-group ion; then a d electron belonging to a free ion can be in five different states that all have the same energy but can be distinguished by the different spatial arrangement of their electron clouds, i.e. a d electron can occupy five different but energetically equivalent orbits.

In a crystal, however, these five different states do not have the same energy any more, because for some states the corresponding orbits come close to the surrounding (negative) oxygen ions, whereas for other states the orbits have a tendency to avoid the negative neighbours. A more exact analysis shows that due to this crystalline field the five-fold degenerate level splits into two sub-levels, one two-fold, the other one three-fold degenerate. The shape of the electron cloud in the two-fold degenerate level is such as to avoid the points of a regular tetrahedron, so the repulsion between this electron cloud and the surrounding oxygen ions is lowest in tetrahedral surroundings. In the three-fold degenerate level it is the other way round, so here the repulsion is lowest in octahedral surroundings.

As the d^3 and d^8 ions (Cr^{3+} and Ni^{2+}) have three electrons to accommodate in the first or second half of the shell, these ions will favour the octahedral interstices, whereas the d^6, d^7 and d^9 ions can adapt their electron clouds both to octahedral and tetrahedral surroundings. We will call this the radius effects, because the apparent radius of Cr^{3+} and Ni^{2+} is small in octahedral surroundings.

The crystalline field influences the average energy level of the electrons too. This influence is only small for d^6 ions (Fe^{2+}); for d^7 ions (Co^{2+}) the average level is lowest for a tetrahedral field, for d^3 and d^8 ions (Cr^{3+} and Ni^{2+}) the most favourable field is an octahedral one, for d^9 ions (Cu^{2+}) the influence is small again.

In table XVII both effects are represented schematically.

TABLE XVII

Influence of the crystalline field on the apparent radius and average energy effect of the ions of the transition elements.

configuration		ions		radius effect		energy effect	
				tet	oct	tet	oct
d^0	d^5	Mn^{2+},	Fe^{3+}	0	0	0	0
d^1	d^6	V^{4+}	Fe^{2+}	not important		weak	
d^2	d^7	V^{3+}	Co^{2+}	not important		+	—
d^3	d^8	Mn^{4+},Cr^{3+}	Ni^{2+}	—	+	—	+
d^4	d^9	Mn^{3+}	Cu^{2+}	not important		weak	

(+ denoting an energetically favourable configuration, — an unfavourable configuration).

The preference for the octahedral interstices of Cr^{3+}, and Ni^{2+} can be attributed to the simultaneous influence of the radius effect and the energy-level effect.

The other ions will behave more or less as the noble-gas-like ions of the same radius and valency.

We feel to have explained a large part of the crystallographic properties of the oxidic spinels. The lack of unity in the arguments used is caused by the large number of ions which form spinels, for of the 42 metals that form stable oxides 21 are known to take part in the formation of oxidic spinels.

Only the non-existence of Mg germanate in the spinel modification is a serious flaw. Perhaps this is due to an (magnetic?) interaction between the Co^{2+} and Ni^{2+} ions in Co and Ni germanate which we did not take into account, the lack of which in Mg germanate stabilizes the olivine modification.

Acknowledgement

I am very much indebted to Dr E. J. W. Verwey for his interest in my work, for his valuable suggestions and for his consent to publish these results. Thanks are due too to Miss N. van Houselt, whose accurate assistance in the preparation and measurements of most of the compounds described here has been very valuable.

The discussion of the transition elements has been stimulated by the work of Dr J. H. van Santen, whose critical sense has been helpful.

Eindhoven, April 1953

NABESCHOUWING

De spinellen zijn door verschillende onderzoekers uitvoerig onderzocht; dit vindt gedeeltelijk zijn oorzaak in het belang van deze stoffen voor de electrotechniek, omdat vele stoffen die deze kristalstructuur hebben, zich onderscheiden door opmerkelijke electrische en magnetische eigenschappen.

In dit proefschrift zijn voornamelijk de kristallografische aspecten van deze verbindingen behandeld. De spinellen lenen zich uitstekend voor een nadere bestudering van de kristalchemie, omdat ze betrekkelijk gemakkelijk te onderzoeken zijn door hun kubische structuur en toch voldoende vrijheidsgraden bezitten om ionen van uiteenlopende eigenschappen in hun rooster op te nemen.

Reeds lang was bekend, dat de uit kristallografisch oogpunt meest waarschijnlijke verdeling der ionen niet altijd met de werkelijkheid overeenkomt.

Uit een electrostatische berekening volgt zowel een correlatie tussen de ionenverdeling en de zuurstofparameter u als de mogelijkheid voor ordening der ionen in de octaederholten.

Beide verschijnselen zijn door de hier beschreven experimenten zeer waarschijnlijk gemaakt.

Indien we rekening houden met de grootte der ionen, kunnen we de distributie der ionen met edelgasstructuur voorspellen. Voor meer gecompliceerde ionen is het echter noodzakelijk, rekening te houden met andere eigenschappen, zoals de neiging tot vorming van covalente bindingen (Zn^{2+} en Cd^{2+}), of de invloed van het kristalveld op de grootte der ionen en hun energieniveau's (Ni^{2+} en Cr^{3+}). Wanneer we deze effecten niet verwaarlozen, kunnen we ook van deze ionen de verdeling voorspellen.

De verdeling der ionen heeft grote invloed op de electrische, optische en magnetische eigenschappen van deze stoffen; door de bestudering van de physische eigenschappen van deze spinellen kunnen we een bijdrage leveren tot een beter inzicht in de physica van de vaste stof.

REFERENCES

1) T. F. W. Barth, E. Posnjak, Z. Kristall. **82**, 325, 1932.
2) E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. **15**, 174, 1947.
3) E. J. W. Verwey, P. W. Haaijman and F. C. Romeijn, J. Chem. Phys. **15**, 181, 1947.
4) F. de Boer, J. H. van Santen and E. J. W. Verwey, J. Chem. Phys. **16**, 1091, 1948.
5) F. de Boer, J. H. van Santen and E. J. W. Verwey, J. Chem. Phys. **18**, 1932, 1950.
6) E. J. W. Verwey and P. W. Haaijman, Physica, 's-Grav, **9**, 979, 1941.
7) J. H. van Santen, Philips Res. Rep. **5**, 282, 1950.
8) G. G. Shull, E. O. Wollan and W. C. Koehler, Phys. Rev. **84**, 912, 1951.
9) G. E. Bacon, Acta Cryst. **5**, 684, 1952.
10) J. M. Hastings, L. M. Corliss. Washington Conference on Magnetism, 1952.
11) A. Claassen, Proc. Phys. Soc. **38**, 482, 1925-26.
12) Ching Hsien Li, Phys. Rev. **40**, 1012, 1932.
13) B. S. Ellefson, N. W. Taylor, J. Chem. Phys. **2**, 58, 1934.
14) N. C. Tombs, H. P. Rooksby, Nature **165**, 442, 1950.
15) N. C. Tombs, H. P. Rooksby, Acta Cryst. **4**, 474, 574, 1951.
16) Private Communication from Massachusetts Institute of Technology.
17) K. Lark-Horowitz, E. P. Miller, Phys. Rev. **49**, 418, 1936.
18) To be published in Physica, 's-Grav.
19) L. Vegard, Phil. Mag. **32**, 65, 1916.
20) A. Bauer, Neues Jahrbuch für Min. Geol. Paläont. **75**, 159, 1939.
21) W. A. Weil, "Coloured glasses", Society of Glass Technology, Sheffield, 1951.
22) J. M. Stevels, Verres et refractaires **5**, 197, 1951.
23) R. Hill, O. R. Howell, Phil. Mag. **48**, 833, 1924.
24) C. G. Koops, Phys. Rev. **83**, 121, 1951.
25) Brian Mason, Amer. Miner. **32**, 326, 1947.
26) H. F. McMardic, B. M. Sullivan, F. A. Maurer, J. of Res. Bur. St. **45**, 35, 1950.
27) H. Hönl. Z. Phys. Lpz., **84**, 1, 1933.
28) L. Vegard, A. Borlaag, Avh. Norske Videnskapsakademi Oslo, I. Nat. Naturw. Kl. no. **5**, 1-19.
29) V. M. Goldschmitt, Nachr. Ges. Wiss. Göttingen, Mat.-Phys. Klasse 184-190, 1931.
30) W. Jander, W. Stamm, Z. Anorg. Chem. **207**, 289, 1932.
31) H. Birnbaum, R. K. Scott, J. Amer. Chem. Soc. **72**, 1398, 1950.
32) J. H. van Santen, J. S. van Wieringen, Rec. trav. Chim. **71**, 420, 1952.

STELLINGEN

I

De metaaltheorie van Pauling is niet in overeenstemming met de magnetische verzadigingsmomenten voor Ni- en Mn-legeringen.

L. Pauling. J. Am. Chem. Soc. **69** (1947) 542.	W. Gerlach. Z.f. Metallk. **29** (1937) 124. O. Heusler, Ann. Phys. **19** (1934) 155.

II

De gebruikelijke voorwaarden voor volledige mengbaarheid in vaste toestand, n.l. isomorphie, chemische analogie en gering verschil in roosterconstante zijn nodig, doch niet voldoende.

III

Bij het onderwijs in de preparatieve anorganische chemie worde meer aandacht besteed aan de thermodynamica van het bereidingsproces.

IV

De indeling door Nowotny en Sibert van de verbinding CuMgSb bij de fluorietstructuur is niet alleen formeel onjuist, zij geeft ook een verkeerd beeld van de chemische binding in deze stof.

H. Nowotny, W. Sibert. Z.f. Metallk. **33**, (1941) 391.

V

De physische grondslag van een belangrijke artistieke uiting van de Chinese cultuur is de kristalchemie.

VI

De opvattingen van Zener over het magnetisme in α-ijzer worden weerlegd door de experimenten van Shull.

C. Zener, Phys. Rev. **85** (1952) 324.
C. G. Shull, Rev. of Mod. Phys. Vol. **25**, no. 1, 1953

VII

In de preparatieve organische chemie biedt het gebruik van $Ni(CO)_4$ vaak voordeel boven het gebruik van CO onder druk.

Reppe: Neue Entwicklungen auf dem Gebiete der Chemie der Acetylens und Kohlenoxyds, blz. 100.

VIII

Het geringe verschil in roosterconstante tussen $NiCr_2O_4$ en $NiFe_2O_4$ moet worden toegeschreven aan de combinatie van d^3 en d^8 electronen toestanden in de eerstgenoemde stof.

Dit proefschrift: hoofdstuk III.

XI

Het is in sommige gevallen mogelijk, ook zonder Röntgenanalyse een aanwijzing te krijgen over het coördinatiegetal van tweewaardige ionen in ionogene verbindingen.

R. Hill, O. W. Howell, Phil. Mag. **48** (1924) 833.

X

De conclusies door Hauffe getrokken uit zijn onderzoekingen over het geleidend vermogen van ZnO met verschillende bijmengsels zijn niet gerechtvaardigd.

K. Hauffe, A. L. Vierk. Z. Phys. Ch. **196** (1950) 161.

XI

De verklaring, die Petri en Staverman geven voor de invloed van formaldehyde bij verschillende PH op de dialyse potentiaal van proteine membranen is aan bedenkingen onderhevig.

E. M. Petri, A. J. Staverman. Discussions of the Faraday Society **13** (1953) 157.

XII

Ten onrechte meent Müser, dat de beschouwingen van Hintenberger over de relatie tussen de stoechiometrie en de electrische eigenschappen van PbS onjuist zijn.

H. Müser. Z.f. Naturf. 5a (1950) **18**. H. Hintenberger. Z. Phys. **119** (1942) 13.

2/8/