Physical Properties and Cation Arrangement of Oxides with Spinel Structures II. Electronic Conductivity

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II. Electronic Conductivity

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The relations between the electronic conductivity of certain spinels and the arrangement of the cations in the crystal structure (see preceding paper) are studied. Several arguments favor the assumption that Fe_3O_4 contains both divalent and trivalent iron in the 16-fold position. The transition point in the neighborhood of liquid-air temperature is probably associated with an increased degree of order at low temperature in the distribution of the 8 electrons between the 16 Fe-lattice points per unit cell. The considerably increased conductivity below the transition points shows tetragonal anisotropy when the crystal is cooled in a magnetic field. The possible distributions of the electrons in the crystal at low temperature are discussed. In more complicated spinels, containing other metal atoms as well as iron in both the divalent and the trivalent state, the electronic interchange is more or less inhibited by the foreign metal atoms. The higher values of their resistance in comparison to that of Fe_3O_4 can be roughly described by an increased activation energy. The investigation of a number of substances with different arrangements of the cations shows that the activation energy (and therefore the electrical resistance) is lowest for those cases in which the electrons can travel, as in Fe_3O_4, along the Fe of the 16-fold position.

1. CATION ARRANGEMENT OF Fe_3O_4

THE simplest compound for which interesting relations appear to occur between electronic conductivity and the arrangement of the cations is Fe_3O_4.

In paper I of this series,[1] we classified Fe_3O_4 as an inversed Fe spinel $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, together with the Fe spinels of Mn^{2+}, Co, Ni, Cu, and Mg, as contrasted with the "normal" spinels $ZnFe_2O_4$ and $CdFe_2O_4$. This classification could be made plausible on the basis of a detailed consideration of the values of dimensions of the unit cell of a large number of spinels. Several years ago, however, this "inversed" arrangement had been already proposed by Verwey and de Boer[2] on the basis of the electrical properties of Fe_3O_4. The high electronic conductivity, $\sigma = 200$ ohm^{-1} cm^{-1}, in comparison with that of similar compounds (Mn_3O_4, γ-Fe_2O_3) which have a very low conductivity, was explained on the basis of the continuous interchange of the electrons between Fe^{2+} and Fe^{3+} at the 16-fold position. This picture was corroborated by the behavior of Fe_3O_4 at low temperatures, where below a transition point a sudden decrease of the conductivity was observed which was explained in terms of an order-disorder phenomenon of the Fe^{2+} and Fe^{3+} involved in the electronic conduction.[3]

a. The Value of the Parameter u

As an argument in favor of this inverse arrangement[2] the value of the parameter u had already been used in connection with the ionic radii of the Fe^{2+} and Fe^{3+} ions. This argument can now be further substantiated by the Madelung-potentials calculated in reference 1. This Madelung constant was given there as a function of u, and it is also possible to calculate the Born repulsion between the different iron ions and the surrounding O^{2-} ions as a function of this parameter. The total lattice potential (Coulomb + Born potential) can thus be calculated, for a given (i.e., experimental) value of the lattice constant a, and the value of u for which this total potential is a minimum can be determined.

For the repulsive potential we used the Born Mayer function

$$V_R = b \exp \{(r_+ + r_- - r)/\rho\}$$

with for Fe^{2+} $r_+ = 0.83$, for Fe^{3+} $r_+ = 0.67$, and for a

[1] E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. **15**, 174 (1947).

[2] E. J. W. Verwey and J. H. de Boer, Rec. trav. chim. **55**, 531 (1936).
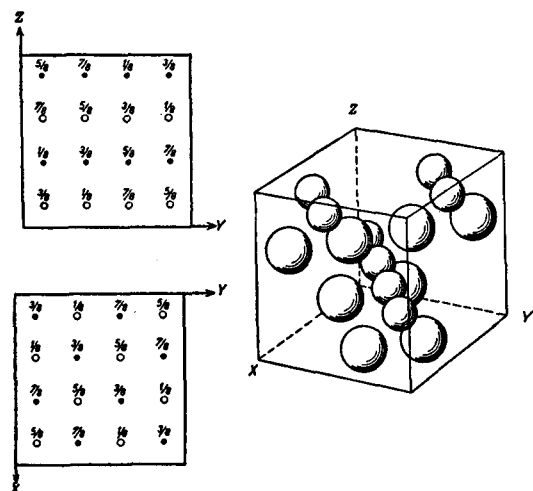
[3] E. J. W. Verwey and P. W. Haayman, Physica **9**, 979 (1941).

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FIG. 1. Unit cell showing possible arrangement at low temperature of Fe^{2+} (large spheres) and Fe^{3+} (small spheres) in 16-fold octahedrally-coordinated position. All 32 oxygens and eight Fe^{3+} in eightfold tetrahedrally-coordinated position are omitted for sake of clarity. Projection of the atoms in the 16-fold position onto the back zy-plane and bottom xy-plane are shown at the left. The numbers indicate the fraction of a above these planes, respectively. The small black dots represent Fe^{3+} and open circles Fe^{2+}.

mixture of Fe^{3+} and Fe^{2+} the average value $r_+ = 0.75$; for the oxygen ions $r_- = 1.40$; $\rho = 0.345$A, the usual constant. Substituting $u = \frac{3}{8} + \delta$, we obtain the total repulsive potential per molecule XY_2O_4, on the assumption that the oxygen-oxygen repulsion forms only a small contribution to the potential and can be neglected as a first approximation:

$$V_R = 4b \cdot \exp[\{2.07 - a\sqrt{3}(\tfrac{1}{8}+\delta)\}/0.345]$$
$$+ 12b \cdot \exp[\{2.15 - a(\tfrac{1}{4}-\delta)\}/0.345].$$

This function has a minimum value for $\delta = 0.002$ or $u = 0.377$. The attractive potential, however,

$$V_C = -Me^2/a$$

is also a function of u or δ, as can be seen from Table I in reference 1. After eliminating the constant b with the aid of the equilibrium condition $(dV/da) = 0$ for the experimental value of a, the total potential $V = V_C + V_R$ appears to have its minimum for $u = 0.379$. The experimental value found by Claassen[4] is $u = 0.379$, from the x-ray intensities determined with the aid of an ionization chamber for a large crystal of Fe_3O_4. For the normal spinel $Fe^{2+}(Fe^{3+}Fe^{2+})O_4$

we would have calculated a much larger value of u, in the neighborhood of $u = 0.390$ (here the mutual repulsion of the oxygens cannot be neglected, owing to the much larger deformation of the close packing of the oxygen ions corresponding to the larger value of u). The calculation shows that the larger values of u to be expected for normal 2–3 spinels (and actually found for all Al spinels, etc.) are mainly caused by the Coulomb potential, the absolute value of which increases considerably with increasing value of u.

b. Further Experiments on the Conductivity

Assuming for Fe_3O_4 the inversed spinel arrangement, the distribution of 8 Fe^{2+} and 8 Fe^{3+} about the 16 lattice points of the octahedral position can be described as a distribution of 8 electrons about 16 Fe^{3+} ions. Above the transition temperature this will approach a statistical distribution, because of the continual electronic interchange. Below this temperature, however, these conducting electrons will tend to arrange themselves according to some regular pattern. Without resorting to a larger unit cell this pattern of order can no longer be of cubic symmetry. The most probable pattern is one having a tetragonal cell and is shown in Fig. 1.

Hence the pattern of order can be described as being built up by continuous rows, consisting alternately of either Fe^{2+} or Fe^{3+} only, in the xy-plane. The Fe^{2+} rows are all parallel to each other, as are the Fe^{3+}, but in a direction perpendicular to the Fe^{2+} rows. If the Fe^{2+} ions in the plane $z = \frac{5}{8}$ occupy the lattice points $\frac{1}{8}, \frac{1}{8}$; $\frac{3}{8}, \frac{3}{8}$; $\frac{5}{8}, \frac{5}{8}$; $\frac{7}{8}, \frac{7}{8}$; the Fe^{2+} ions in the plane $z = \frac{1}{8}$ occupy the points $\frac{5}{8}, \frac{1}{8}$; $\frac{7}{8}, \frac{3}{8}$; $\frac{1}{8}, \frac{5}{8}$; $\frac{3}{8}, \frac{7}{8}$ etc.

If this description of the order-disorder transition at low temperature is correct, one should expect that the electronic conduction below the transition temperature would be different in different directions. This will be measurable only if the direction of the tetragonal axis can be fixed. Ching Hsien Li[5] has found that a single crystal of Fe_3O_4 becomes magnetically anisotropic at low temperature. Hence it seems possible to fix the tetragonal axis with the aid of a magnetic field. We did not have a single crystal of Fe_3O_4 of sufficient purity to show the transition at low

[4] A. Claassen, Proc. Phys. Soc. **38**, 482 (1925–26).

[5] Ching Hsien Li, Phys. Rev. **40**, 1012 (1932).

temperatures. In a previous paper[3] we have shown that the transition phenomenon is entirely suppressed by a small amount of oxygen in excess of stoichiometric proportions; small amounts of impurities dissolved in the lattice have the same detrimental effect as a deviation from the stoichiometric composition. We had to use, therefore, sintered bars of pure Fe_3O_4, consisting of agglomerates of small crystals oriented in all directions, where the expected effect will be reduced considerably. The following experiment, therefore, has only qualitative significance.

A sintered bar was cooled in a magnetic field, once in a direction parallel to the field, a second time in a direction perpendicular to the field. In the first case the electrical conductivity of the bar at liquid air temperature was 7.19×10^{-3} ± 0.02 ohm^{-1} cm^{-1}, in the second case 6.18×10^{-3} ± 0.02 ohm^{-1} cm^{-1}. After the bar had passed the transition temperature in the magnetic field the conductivity below this temperature was not altered perceptibly by the presence of the field, as could be established by changing its direction, switching it off, etc. The conductivity when the bar was cooled in the absence of a magnetic field was 6.45×10^{-3} ohm^{-1} cm^{-1}.

Hence there is a definite effect of the magnetic field orientation upon the electronic conductivity. The phenomenon can be explained by assuming that at the transition temperature the disorder-order transformation occurs preferentially in such a way that the tetragonal axis is that cubical axis of the high temperature crystal which lies nearest to the direction of the magnetic field. The electrical conductivity will then be highest in directions where Fe^{2+} and Fe^{3+} alternate, and lowest in directions where one meets either only Fe^{2+} or only Fe^{3+} ions. Hence it is to be expected that the conductivity will be highest parallel to the magnetic field; that is, more or less parallel to the directions in which the c-axis has been "frozen in." The picture of the disorder-order transition is in qualitative agreement with these experiments, which therefore corroborate the picture of Fe_3O_4 given here. They show at the same time that the ionic picture according to which the electrons are thought to be added entirely to one-half of the Fe^{3+} ions is much too simple. A low transition temperature is very rare

for a crystal lattice in which the atoms are held together by strong bonds, and has generally only been found for lattices in which *molecules* are held together by weak van der Waals-London bonds. In the present case the transition can occur at such a low temperature because it is an electronic transition between different atoms. The low transition temperature also proves that the energy of order is very small. The entropy of order is $R \ln 2$ per atom, and accordingly $T\Delta S$ is of the order of 0.01 ev (T is of the order of 100°K). Neglecting the polarization and the displacement of the oxygen ions, one would calculate an energy of the order of a few electron volts (each Fe^{2+} ion is surrounded by 4 Fe^{3+} and 2 Fe^{2+} ions in a first sphere of radius $r = \frac{1}{4}a\sqrt{2}$, by 4 Fe^{2+} and 8 Fe^{3+} ions in a second sphere of radius $r = \frac{1}{4}a\sqrt{6}$, by 6 Fe^{2+} ions at a distance $\frac{1}{2}a\sqrt{2}$, etc.). The actual energy will probably be several (say 5) times smaller due to the polarization of the surrounding medium. This, however, is obviously far too high, and suggests that the wave functions of the electrons extend over several atomic distances.

2. MORE COMPLICATED SPINELS

(a) Fe_2AlO_4

The x-ray investigation[1] has revealed that this substance can be described as consisting for the main part of $Fe(FeAl)O_4$, with Al in the octahedral holes. The intensity of the reflection with the lowest diffraction angle and the general rules derived in the preceding paper suggest that the Fe in the tetrahedral hole is the Fe^{3+} ion:

$$Fe^{3+}(Fe^{2+}Al)O_4$$

so that the substance belongs to the "inversed" spinels, with an averaged distribution of divalent and trivalent ions about the 16-fold positions. Hence the substance appears to be analogous to Fe_3O_4

$$Fe^{3+}(Fe^{2+}Fe^{3+})O_4$$
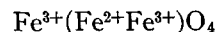
with the Fe^{3+} in the 16-fold position replaced by Al.

As already indicated by the x-ray intensities, the cation arrangement is not entirely that corresponding to the formula given above, and the best agreement with x-ray data was obtained by assuming that a small fraction of the Al has replaced Fe in the eightfold position. The sub-
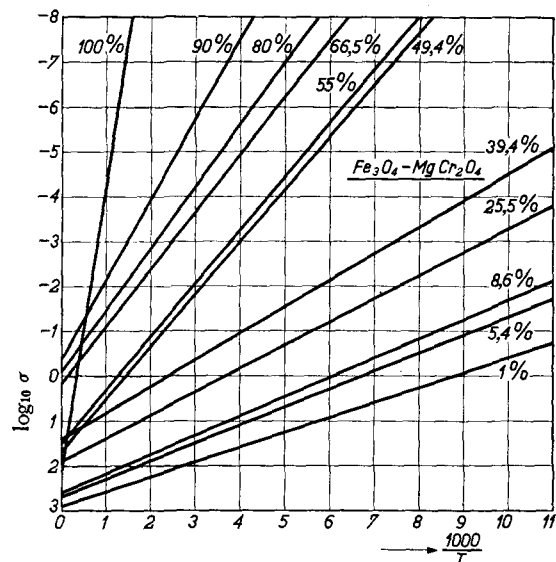
FIG. 2.

stance was prepared by heating an intimate mixture of iron and aluminum oxides in a suitable gas atmosphere, and it is therefore always possible that at the high temperature of preparation the energy difference between the two arrangements is insufficient to outweigh the gain of entropy accompanying a more uniform distribution of the Al about both positions.

These conclusions are corroborated by the electrical properties of the substance. If the substance were pure $Fe^{3+}(Fe^{2+}Al)O_4$ (or $Fe^{2+}(Fe^{3+}Al)O_4$) it would be a rather poor electronic conductor, as it does not contain Fe^{3+} and Fe^{2+} in equivalent lattice points. There might be a possibility of electronic transfer between Fe in the tetrahedral holes and Fe in the octahedral interstices, but this would only occur if the electronic levels in the two different positions were practically identical, which would be rather accidental.

The electrical conductivity of the substance appears to be about 10^3 times smaller than that of Fe_3O_4: viz. 0.2 ohm^{-1} cm^{-1}. This is, however, several powers of 10 greater than would be expected for the pure substance, even if we take into account that the sample showed a small deviation from stoichiometric proportions (for 1 Al ion it contained 1.005 Fe^{3+} and 0.995 Fe^{2+} ions). If the assumption that this residual conductivity is caused by a small fraction of Fe^{3+} in the 16-fold position is correct, one would expect the conductivity to be very sensitive to the heat treat-

ment. Actually we found that by annealing the sample in a small (evacuated and closed) quartz tube at a temperature of 850°C for $\frac{1}{2}$ hour, the conductivity decreased by a factor of 55, the new specific conductivity being 0.0037 ohm^{-1} cm^{-1}. Obviously, as a consequence of this heat treatment at a temperature well below the formation temperature (1300°C), more Al has gone over to the position of lower energy, and the formula $Fe^{3+}(Fe^{2+}Al)O_4$ of the pure material has been more closely realized.

This behavior is rather exceptional, as the conductive properties of other substances (to be described below) of similar type proved to be very insensitive to similar heat treatment, and such substances have even found technical application in cases for which a high thermal stability is required.

(b) Solid Solutions of Fe_3O_4 and $MgCr_2O_4$

$MgCr_2O_4$ is a very poor conductor and can even be called an insulator ($\sigma < 10^{-10}$ ohm^{-1} cm^{-1}). Solid solutions with Fe_3O_4 were prepared in the following way.

An intimate mixture of Fe_2O_3, MgO, and Cr_2O_3 in the proper proportions was pressed into bars of about 3 cm length and 0.3 to 0.4 cm diameter. These bars were preheated at 1200°C in a stream of pure CO_2, with the result that most of the Fe was reduced to the oxidation level of Fe_3O_4. Then the CO_2 was replaced by very pure N_2 and the temperature was raised to 1300°C. This temperature was maintained for one hour. After that the carrier with the bars was shifted to a cooler part of the furnace and the substance was allowed to cool in the same atmosphere. For preparations containing more than 50 percent $MgCr_2O_4$ the heating was conducted at about 1400°C, in order to obtain well-sintered bars. In this case the

TABLE I.

% $MgCr_2O_4$	ϵ in ev	σ_∞ in ohm^{-1} cm^{-1}
0.9	0.06$_5$	700
5.4	.07$_9$	550
8.6	.08$_7$	450
25.5	.10$_3$	100
39.4	.12$_9$	35
49.4	.21$_1$	35
54.6	.23$_0$	35
67.4	.30$_5$	8
80	.33$_4$	5
90	.35$_6$	0.05

atmosphere must be less reducing in order to prevent a deviation from stoichiometric proportions in the direction of FeO. Satisfactory results were obtained by heating at 1400°C in N_2 containing 1 percent of O_2. The content of ferrous ions was checked by dissolving a sample in chlorine-free hydrochloric acid under exclusion of atmospheric oxygen and determining the amount of Fe^{2+} in the solution by a titration with 0.01 normal ceric sulphate solution.

The electrical resistance of a series of bars with varying composition was measured over a wide range of temperatures. The results are given in Table I and summarized in Fig. 2.

These results show initially that there is a gradual transition from Fe_3O_4, with a high conductivity and a low temperature coefficient, to $MgCr_2O_4$, with a very low conductivity and a high temperature coefficient. The curves of $\log \sigma$ against $1/T$ are straight lines to a first approximation, with a slope continually increasing from Fe_3O_4 to $MgCr_2O_4$. The conductivity as a function of temperature can be described for each sample by the equation

$$\sigma = \sigma_\infty \exp(-\epsilon/kT),$$

and the gradual decrease of the conductivity at room temperatures with increasing content of $MgCr_2O_4$ is obviously mainly determined by the gradual increase of the "activation energy" ϵ, although the values of σ_∞ found by extrapolation, formally the conductivities at $T = \infty$, vary appreciably.

The theory for the electronic conductivity of the oxides of these "transition elements" is still not very satisfactory.[6] It has been suggested[2] that the high conductivity of Fe_3O_4 must be explained by the fact that, in an averaged distribution of Fe^{2+} and Fe^{3+} about equivalent lattice points (here those of the 16-fold spinel position), an interchange of electrons must be possible without requiring an appreciable amount of added energy. Hence the electrons would travel with a very low activation energy along the lattice points containing both Fe^{2+} and Fe^{3+}, and the effect of the different ions Mg^{2+} and Cr^{3+} in solid solutions of Fe_3O_4 with $MgCr_2O_4$ must, as a first result, be

[6] J. H. de Boer and E. J. W. Verwey, Proc. Phys. Soc. 49, 59 (1937). N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 167.
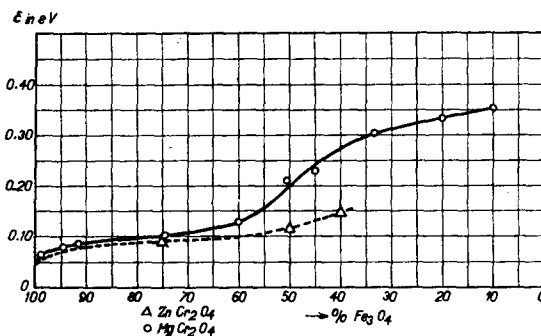

FIG. 3.

the blocking up of this irregular $Fe^{2+} - Fe^{3+}$ pattern. It therefore follows that with increasing $MgCr_2O_4$ content the electrons are forced to follow narrow and complicated channels to an increasing extent. These blocking barriers will be different from point to point in the crystal lattice of the solid solutions. Nevertheless, this dilution of Fe^{2+} and Fe^{3+} by the different ions of $MgCr_2O_4$ can be described up to a temperature of about 400°C with the aid of a single "activation energy." This behavior shows again that the conduction mechanism cannot be described completely with the aid of wave functions of the conduction electrons belonging to a single Fe^{2+} ion. On the other hand, the picture of the lattice wave functions (Wilson's theory of semi-conductors) fails entirely to explain the absence of conduction in these oxidic substances containing the transition elements Cr, Mn, Fe, Co, etc., and it is rather obvious that a better understanding of this case can be obtained only by introducing into the theory the interaction between a traveling electron and the positive hole left behind; i.e., by going again in the direction of localized wave functions.

Upon examining the curves of Fig. 2 more closely we observe a peculiar anomaly. It is interesting to consider this point in some detail, as it is directly connected with the cation arrangement in these solid solutions and may throw some more light on the conduction mechanism in these materials.

This anomaly is most easily demonstrated by plotting the activation energy of the different samples as a function of the composition (see Fig. 3).

Starting from the building principles derived in reference 1 for the cation distribution in
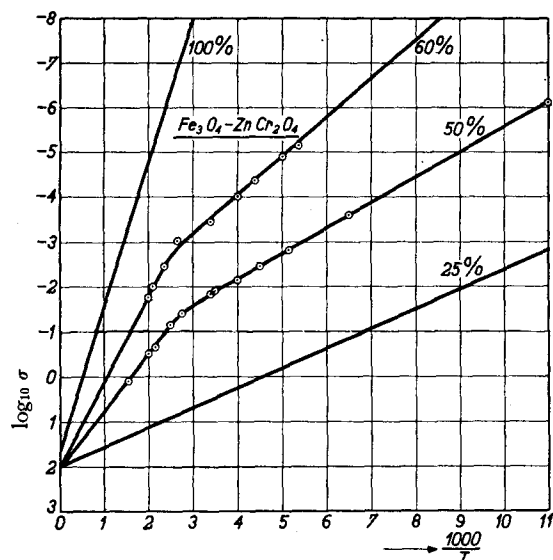
FIG. 4.

spinels, we would expect that the different cations in these solid solutions would have the distributions about the cation lattice points shown in Table II (we only give the compositions with 25, 50, and 75 molecular percent $MgCr_2O_4$).

Hence from 0 to 50 percent content of $MgCr_2O_4$ there are both Fe^{3+} and Fe^{2+} ions in the 16-fold positions, and the electronic conduction will occur along planes containing both of these ions. At 50 percent $MgCr_2O_4$, however, the preference of Fe^{3+} for the eightfold position results in a separation of the Fe^{3+} and the Fe^{2+} ions. Hence a rapid increase of the "activation energy" can be expected if we approach this composition. There are a number of possibilities for the mechanism of electronic conduction for compositions containing more than 50 percent of $MgCr_2O_4$. This depends on the distribution of the divalent ions in the region 50 to 100 percent $MgCr_2O_4$, for which two possibilities are given in Table II, but for which an intermediate distribution between these two extremes might also be possible. X-ray

evidence supports arrangement IIIa, but the differences in the calculated intensities corresponding to IIIa and IIIb are rather small, so that an intermediate distribution cannot be ruled out and is even highly probable in view of the small energy differences which can be expected to exist between the two extreme arrangements. Hence for compositions containing more than 50 percent of $MgCr_2O_4$ the conduction mechanism will be either an interchange of electrons between Fe^{3+} and a small amount of Fe^{2+} along the lattice points of the eightfold position, or an exchange of electrons between Fe^{3+} and Fe^{2+} from different positions. In both cases the "activation energy" will be increased; in the first case because of the blocking action of the Mg^{2+} ions and the large distance between the tetrahedral interstices ($\frac{1}{4}a\sqrt{3} = 0.43a$), in the second case because of the difference between the energy levels at the octahedral and the tetrahedral lattice positions, respectively, although the distance is slightly shorter ($\frac{1}{8}a11^{\frac{1}{2}} = 0.41a$, both distances to be compared with the shortest distance between two octahedral interstices, $\frac{1}{4}a\sqrt{2} = 0.35a$). The latter seems to be the less probable case. For example, in the case of $AlFe_2O_4$ (Section 2(a)) there were no indications in favor of such a mechanism, which would only be possible if the difference between the two energy levels happens to be small.

(c) Solid Solutions of Fe_3O_4 and $ZnCr_2O_4$

It is interesting to compare the behavior of these solid solutions of Fe_3O_4 and $MgCr_2O_4$ with those of Fe_3O_4 and $ZnCr_2O_4$. Here the different ions will be distributed over the different positions indicated in Table III. The Zn ions always occupy the eightfold position and are replaced by Fe^{3+} when the Fe_3O_4 content is increased. Simultaneously the Cr ions in the 16-fold position are replaced by $\frac{1}{2}Fe^{2+} + \frac{1}{2}Fe^{3+}$. Accordingly, there

TABLE II. Arrangement of cations in solid solutions of $Fe_3O_4 + MgCr_2O_4$.

Composition $Fe_3O_4:MgCr_2O_4$	Eightfold position (tetrahedral interstices)	16-fold position (octahedral interstices)
I 75:25	Fe^{3+}	$\frac{1}{2}Fe^{3+}$, $\frac{3}{4}Fe^{2+}$, $\frac{1}{4}Mg$, $\frac{1}{2}Cr$
II 50:50	Fe^{3+}	$\frac{1}{2}Fe^{2+}$, $\frac{1}{2}Mg$, Cr
III 25:75	(a) $\frac{1}{4}Fe^{3+}$, $\frac{3}{4}Mg$	$\frac{1}{4}Fe^{2+}$, $\frac{1}{2}Mg$, $\frac{3}{2}Cr$
	(b) $\frac{1}{4}Fe^{3+}$, $\frac{1}{4}Fe^{2+}$, $\frac{1}{2}Mg$	$\frac{1}{2}Mg$, $\frac{3}{2}Cr$

TABLE III. Arrangement of cations in solid solution of $Fe_3O_4 + ZnCr_2O_4$.

Composition $Fe_3O_4:ZnCr_2O_4$	Eightfold position (tetrahedral interstices)	16-fold position (octahedral interstices)
75:25	$\frac{3}{4}Fe^{3+}$, $\frac{1}{4}Zn$	$\frac{3}{4}Fe^{2+}$, $\frac{3}{4}Fe^{3+}$, $\frac{1}{2}Cr$
50:50	$\frac{1}{2}Fe^{3+}$, $\frac{1}{2}Zn$	$\frac{1}{2}Fe^{2+}$, $\frac{1}{2}Fe^{3+}$, Cr
25:75	$\frac{1}{4}Fe^{3+}$, $\frac{3}{4}Zn$	$\frac{1}{4}Fe^{2+}$, $\frac{1}{4}Fe^{3+}$, $\frac{3}{2}Cr$

are always equivalent amounts of Fe^{2+} and Fe^{3+} in the octahedral position, and there is no reason for a discontinuous increase of ϵ with increasing $ZnCr_2O_4$ content.

The corresponding $\log\sigma$ vs. $1/T$ curves are given in Fig. 4. At high temperatures the preparations containing large amounts of $ZnCr_2O_4$ show a break in the curves, suggesting that at these temperatures a second conduction mechanism covers the $Fe^{2+} - Fe^{3+}$ conduction prevailing for lower temperatures. The curves can be represented by

$$\sigma = \sigma_\infty \exp(-\epsilon/kT) + \sigma_\infty' \exp(-\epsilon'/kT).$$

As the specific conductivity of $ZnCr_2O_4$ is much greater than that of $MgCr_2O_4$ this phenomenon is most probably caused by the conductivity of $ZnCr_2O_4$ itself, so that at higher temperatures the conduction is taken over by Zn (or by Zn and Cr ions jointly) as a consequence of the higher temperature coefficient of this conduction mechanism.

In Fig. 3, therefore, where ϵ has again been plotted against the composition, the value of ϵ corresponding to the low temperature part of the curves has been used. The plot shows a continuous increase of ϵ with increasing $ZnCr_2O_4$ content.

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Integral Equations between Distribution Functions of Molecules

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Integral equations are derived that relate variations in the potentials of average force between molecules of a system at two different densities or activities. These permit the calculation of the change in thermodynamic properties, or of the change in the distribution of molecules in space, in a liquid or crystalline phase, if either the temperature is varied, or if the the mutual potentials between the molecules is assumed to change. The equations are in a somewhat complex, but still distinguishable, matrix form. A matrix operates on the variations in potential occurring at one activity and transforms them into those occurring at a second activity. The matrix elements are combinations of the distribution functions at the second activity, to which the transformation is made, multiplied by powers of the difference of the two activities. The matrix approaches the unit matrix in value as this activity difference approaches zero. The product of the two matrices, one which transforms from activity α to activity β, with that which transforms from activity β to α, is the unit matrix. This leads to an integral (matrix) equation between the distribution functions at any two activities.

The calculation of one element of this matrix product leads to a cell type equation for the computation of the activity, or free energy, of a system in terms of the potential between a single molecule and the molecules that immediately surround it in the system.

The transformation matrices have solutions, at certain values of the activity difference y, corresponding to variations in the potentials of average force, which are transformed into zero variations at the new activity. The activities at which such variations can occur are those of the phase transitions in the systems. The solutions at these special values of the activity are differences of combinations of the distribution functions in the two pure phases that can coexist at these activities.

INTRODUCTION

ONE may define "distribution functions" for a given number, n, of molecules as being proportional to the probability density of finding n molecules in a certain configurational position, averaged over all positions of the other molecules of the system. These functions are the exponent of minus the potential of average force between the molecules, divided by kT. The distribution functions of a given system at constant tem-