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A Neutron-Diffraction Study of Manganese Ferrites

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A neutronographic analysis of the system $Mn_xFe_{3-x}O_4$ ($0.43 \leq x \leq 1.58$) has been carried out using single crystals prepared by Verneuil's method. We produced our neutronograms at the room temperature and above the Curie-point.

Here we discuss the question of the dependence of the inversion-degree and oxygen-parameter on the chemical composition of Mn-ferrites.

The obtained data have been examined simultaneously with the data of magnetic, electric and other measurements.

The problems of cation distribution in the system of manganese ferrites $Mn_x Fe_{3-x} O_4$ ($x > 0$) have been approached by a large number of authors. The conclusions made are mostly based upon the measurements of various magnetic[1)-6)] and electric[7)] characteristics together with the analyses of thermodynamic[8)] and other properties. The existence of a number of parameters which are difficult to be estimated and simultaneous presence of manganese and iron in different valency states (Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+} and perhaps Mn^{4+}) are reasons of large discrepancies in the interpretation of experimental data.

In the case of Mn-ferrites the establishment of the cation distribution from X-ray data becomes complicated by the nearly equal scattering powers of Fe and Mn and in solving this question the neutron-diffraction data are extremely useful. The amplitudes of the nuclear scattering of iron and manganese differ in their absolute value in the ratio more than 2.5 : 1. They have opposite signs and besides do not depend on the valency state of these cations. Thus making use only of the powder neutron-diffraction data, Hastings and Corliss[9)] have shown that, in the case of the Mn-ferrite with the stoichiometrical composition ($x=1$), not less than 80% of tetrahedral positions are occupied by Mn-ions. Other compositions belonging to this system have not been investigated by means of neutron diffraction.

Using neutron diffraction technics we studied the system $Mn_x Fe_{3-x} O_4$ ($0.43 \leq x \leq 1.58$) on single crystals which had been grown* by Verneuil's method[10)]. The specimens to be analysed were prepared by igniting a mixture of iron-ammonium alum and manganous-sulfate at temperature 1060-1100°C. We ought to notice that single crystals with an excess of iron ($x < 1$) grow less perfect than single crystals with an excess of manganese ($x > 1$). On the basis of the X-ray analyses all specimens were members of one continuous series of solid solutions and consisted only of one spinel phase. On the single specimens of the obtained series a study of magnetic, electric and supperhigh frequency properties has been carried out[11)-13)].

The neutron diffraction intensities ($\lambda = 1.047$ Å) have been measured using specimens of standard shapes and dimensions (spheres ϕ 6 mm) both at the room temperature and temperature above Curie point. With each specimen we have made 67 measurements for reflexions of planes pertaining to two zones [110] and [100] (among these ~10 reflexions had zero intensities). The intensities of the neutron scattering by Fe-Mn-spinel can be represented as a function of two parameters z and u. The inversion-degree z shows that portion of Mn-ions which occupy the tetrahedral positions and u indicates the displacement of oxygen-ions from their ideal positions in the closest cubic packing ($u = 0.250$ if the origin has been placed at the centre of symmetry).

A preliminary numerical evaluation of the degree of inversion and oxygen-parameter has been made using the intensities of the weak reflexions belonging to the group:

$$h+k=4n \qquad k+l=4n+2 \qquad l+h=4n+2$$

for which the structure factor of the nuclear scattering has the form (space group $O_h^7 = Fd3m$):

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* Our sincere thanks are due to Mrs. A. A. Popova, a most skilled expert in these methods.

$$F=-8b_{\mathrm{A}}\cdot\cos(\pi/4)l_{\mathrm{A}}\cdot\sin(\pi/4)h\cdot\sin(\pi/4)k$$
$$-32b_{\mathrm{O}}\cdot\cos 2\pi lu\cdot\sin 2\pi hu\cdot\sin 2\pi ku$$

here: b_{A} is the amplitude of scattering by ions in tetrahedral positions

b_{O} is the amplitude of scattering by oxygen ions

Proceeding from the above formula of the structure factor it is easy to discern the reflexions for which the intensities are due only to the scattering from the oxygen atoms and those for which they represent the simple function of the inversion degree. According to the space group requirements the reflexions with two zero indices disappear and their non-vanishing intensities result from the higher harmonic of a half wavelength which remains unextinguished. The contribution of this higher harmonic ($\lambda/2$) has been estimated as 0.43%.

For studied spherical specimens, following Hamilton[14,15], we have evaluated the magnitude of the coefficient of the secondary extinction and starting from 32 weakest reflexions we have obtained a more accurate value of the oxygen parameter together with the degree of inversion. The angular disorientation of blocks of our mosaic evaluated by this method for different specimens ranges from 80″ to 90″. The magnitude of the isotropic temperature factor has been estimated by the ordinary method[16] and also from the curve of decreasing intensities of reflexions with large $\sin\theta/\lambda$ against the temperature varying from the room temperature to 760°K. Its value was found to be $2B=0.95\pm0.20$ Å^{-2}.

Here is the table of our results:

Chemical composition x	0.43	0.53	0.84	1.03	1.06	1.10	1.28	1.50	1.58
Fraction of tetrahedral sites occupied by Mn z ($\Delta^*=\pm0.04$)	0.00	0.00	0.78	0.80	0.81	0.83	0.84	0.89	0.92
Oxygen parameter u ($\Delta^*=\pm0.002$)	0.256	0.258	0.258	0.260	0.260	0.261	0.261	0.262	0.263

Δ^* is the average deviation of the experimental results for the selected specimens.

These data show that there is within the range $0.53\leq x\leq0.84$ a jump on the curve of the degree of inversion of our system. It is reasonable to relate this jump with the minimum on the curve of the constant of anisotropy K_I which has been observed by Penoyer and Shafer[17] and Funatogawa *et al.*[4] in the same composition region.

For compositions $x>1$ within the accuracy of our experiment the obtained data on the degree of inversion are in accordance with those conforming to the model of Broz *et al.*[6] which was based on the measurements of some magnetic properties and electric conductivities.

The chemical analysis of this system permits no more than to estimate the average value of the valency state without the possibility of establishing the valencies of separate ions. The assessment of different valency states to Fe and Mn ions could be performed if we knew from the analysis the magnetic contribution into the intensities of reflexions corresponding to the small values of $\sin\theta/\lambda$. But the insufficient accuracy of the separate measurements of magnetic contributions together with difficulty of exact estimation of the coefficient of extinction for these reflexions make it impossible to insist upon any far going inference.

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DISCUSSION

H. A. ALPERIN: I would like to present some data which bears directly on the matters discussed in the previous paper. About one and half years ago, Dr. S. Pickart and I performed neutron diffraction measurements of the iron-rich manganese ferrite of composition $Mn_{0.6}Fe_{2.4}O_4$ (Bul. Am. Phys. Soc. II, 5 (1960) 458) and we recently examined the material of composition $Mn_{0.4}Fe_{2.6}O_4$. Both samples were in polycrystalline powder form. Our results are summarized in the table below:

Chemical composition x	0.40	0.60
Fraction of tetrahedral sites occupied by Mn^{2+}	0.35 ± 0.02	0.54 ± 0.02
Oxygen Parameter u	0.3833 ± 0.0005	0.3827 ± 0.0005
A site moment	$4.0\ \pm0.4\mu_B$	$4.8\pm0.4\mu_B$
B site moment	$4.5\ \pm0.5\mu_B$	$4.0\pm0.4\mu_B$

The important point to be noted is that our data would seem to imply a linear relation between the fraction of Mn^{2+} on A site and x, between the values $x=0$ and $x=1$, which is the sort of reasonable behavior one expects. This is however in direct contradiction with the data presented in the previous paper.

S. IIDA (to H. A. ALPERIN): What kinds of heat treatment was made for the specimens?

H. A. ALPERIN: There is some evidence that there is a very slight impurity in our samples which might be Mn_3O_4. What you suggest is of course possible; namely that differences in stoichiometry might account for the different results obtained by us and authors of the previous paper.

S. IIDA: Since $Mn_xFe_{3-x}O_4$ are the ferrites which are easily oxidized or reduced, I hope you would apply our technique using sealed quartz container, and examine carefully the distribution of Mn^{2+} by changing the temperature of annealing and quenching, from 1400°C to 600°C. If you could find any change of the distribution, it would give a very important information for these ceramics.