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Study of Relaxation Spectrum of $Mn_xFe_{3-x}O_{4+\gamma}$ Ferrites

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The diffusion relaxation spectrum of $Mn_xFe_{3-x}O_{4+\gamma}$ ferrites, $x<1$, derived from disaccommodation measurements and previously reported, is now studied in greater detail and in a more quantitative way. This spectrum is composed of several relaxation bands; some of them have been found also in other iron rich ferrites the existence of others being conditioned by the presence of Mn ions in the lattice. The influence of the chemical composition specially that of the oxygen excess γ, on the relaxation spectrum is studied and the possible mechanisms of the relaxation processes composing the spectrum are discussed.

The diffusion relaxation spectrum of $Mn_xFe_{3-x}O_{4+\gamma}$, $x<1$, previously reported in Ref. 1) was studied in greater detail. This spectrum derived from the measurements of initial permeability disaccommodation at temperatures -200 to $+200$°C could be resolved into several bands some of which have been found also in other iron rich ferrites[2]. A further relaxation band at temperatures above $+200$°C was more recently reported by Braginski and Merceron[3]. The main purpose of the present work was to study the influence of chemical composition, especially the oxygen excess γ, on the relaxation spectrum and the mutual relations between particular processes composing the spectrum.

The measurements were carried out on two series of samples having $x=0.85$ and 0.52 respectively and prepared under various oxidation conditions in order to vary their oxygen content γ. The absence of any second phase (*e.g.* αFe_2O_3) was checked microscopically and by *X*-rays; only samples consisting of single phase were taken into consideration. Preliminary results were also obtained with compositions $x=0.95$, 0.78 and 0.19 having $\gamma\approx 0$. The typical relaxation spectra for the chosen time interval ($t_1=1$ sec, $t_2=100$ sec) are given in Fig. 1 where the relative change of reciprocal susceptibility $(1/\chi(t_2)-1/\chi(t_1))/1/\chi(t_1)$ is plotted against temperature; the respective peaks I to IV are denoted in agreement with Ref. 1) and 3). A further peak situated above 300°C was observed in samples with $x=0.52$ which most probably is different from IV″ reported in Ref. 3); for materials with $x=0.85$ this temperature range falls above their Curie point, which may be the reason for its absence. Because the relaxation mechanism corresponding to process I is supposed to be understood on the basis of valency exchange $Fe^{2+}\rightleftarrows Fe^{3+}$ similarly as electrical conductivity it will be dropped out of our further consideration.

Our experimental results can be summarized as follows:

(1) The magnitude A^{III} of the relaxation peak III depends strongly on γ (Fig. 2); this dependence can be approximated in the normalized scale by the product of vacancy and Fe^{2+} concentrations $C(\square)\cdot C(Fe^{2+})=(3/4)\gamma\cdot(1-x-2\gamma)$ (the relation holds under the assumption that the presence of a certain fraction of Mn-ions in the *B* positions does not increase the effective number of ferrous ions). The shift of the experimental points may be caused by a higher concentration of cation vacancies due to the imperfections of the crystallites than is the concentration resulting from chemical analysis.

(2) A similar dependence takes place for the peak II. As is shown in Fig. 3 the ratio $A^{\mathrm{II}}/A^{\mathrm{III}}$ increases monotonously with increasing x and seems to be nearly proportional to the concentration of Mn in *B* positions[4]. This agrees with the absence of the process II in other iron rich ferrites not containing manganese and exhibiting a strong disaccommodation III[2),5)].

(3) The peak IV″ is placed above 200°C for very low vacancy concentration and shifts with increasing $C(\square)$ to lower temperatures. The increase in vacancy concentration is further accompanied by a decrease of $A^{\mathrm{IV}''}$ in contrast to A^{III} which grows at the same time.

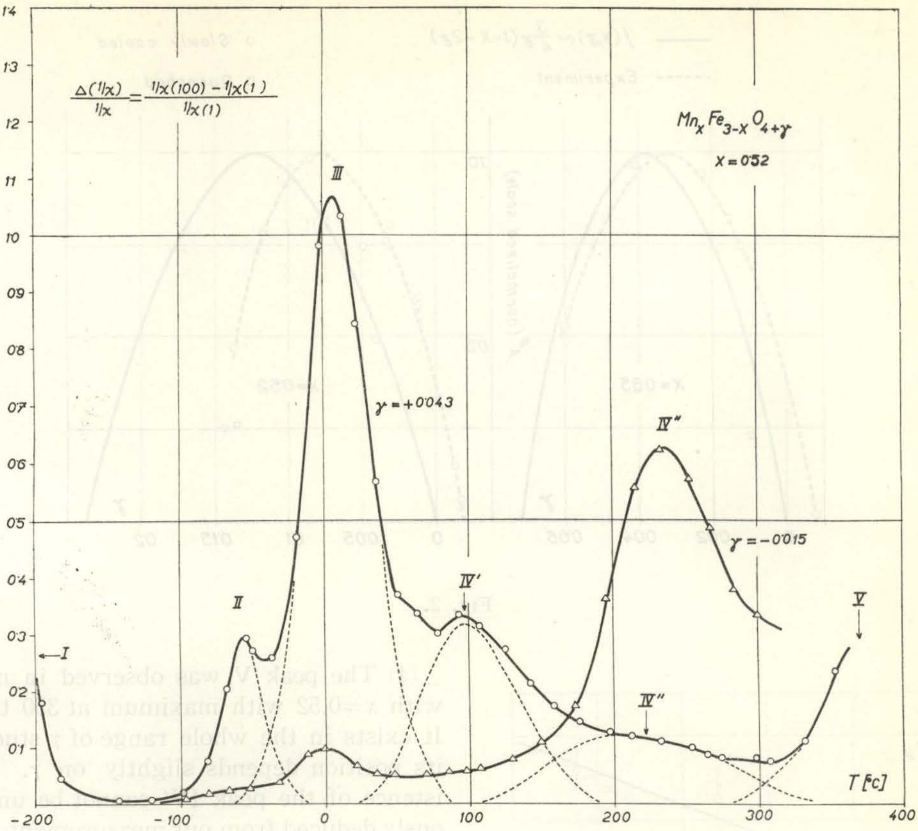
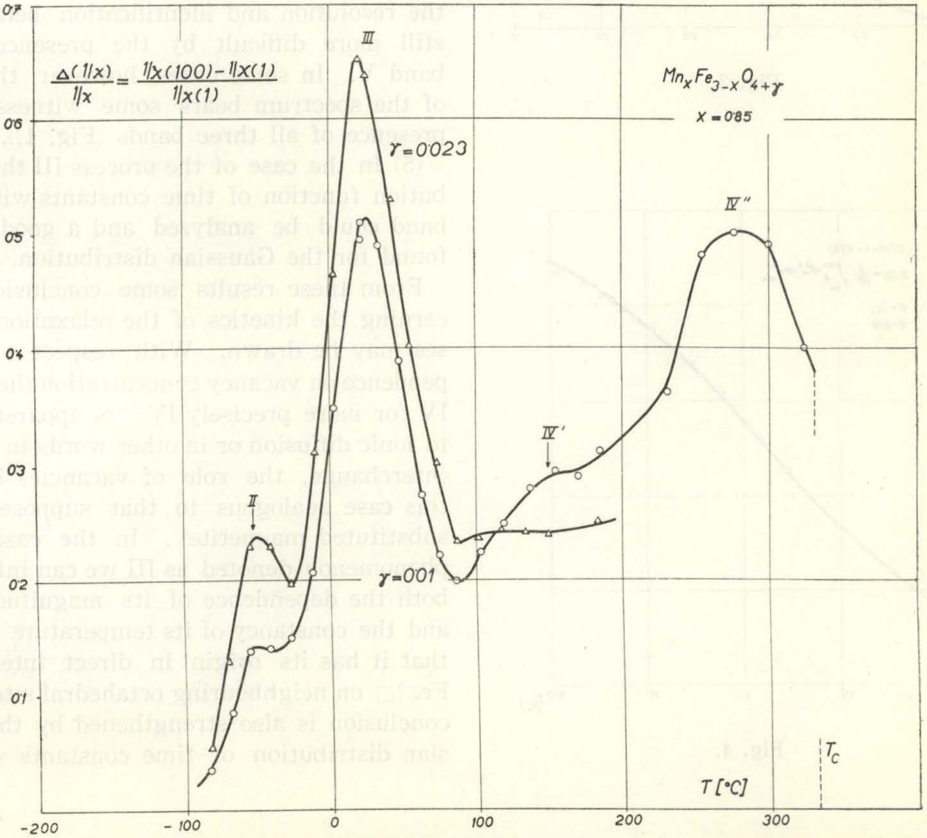

$\frac{\Delta(1/\chi)}{1/\chi} = \frac{1/\chi(100) - 1/\chi(1)}{1/\chi(1)}$
$Mn_x Fe_{3-x} O_{4+\gamma}$
$x = 0{\cdot}52$
$\gamma = +0{\cdot}043$
$\gamma = -0{\cdot}015$
I
II
III
IV'
IV''
IV''
V
T [°C]
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
-200
-100
0
100
200
300
400

Fig. 1. (a)


$\frac{\Delta(1/\chi)}{1/\chi} = \frac{1/\chi(100) - 1/\chi(1)}{1/\chi(1)}$
$Mn_x Fe_{3-x} O_{4+\gamma}$
$x = 0{\cdot}85$
$\gamma = 0{\cdot}023$
$\gamma = 0{\cdot}01$
I
III
IV'
IV''
T_c
T [°C]
0·7
0·6
0·5
0·4
0·3
0·2
0·1
-200
-100
0
100
200
300

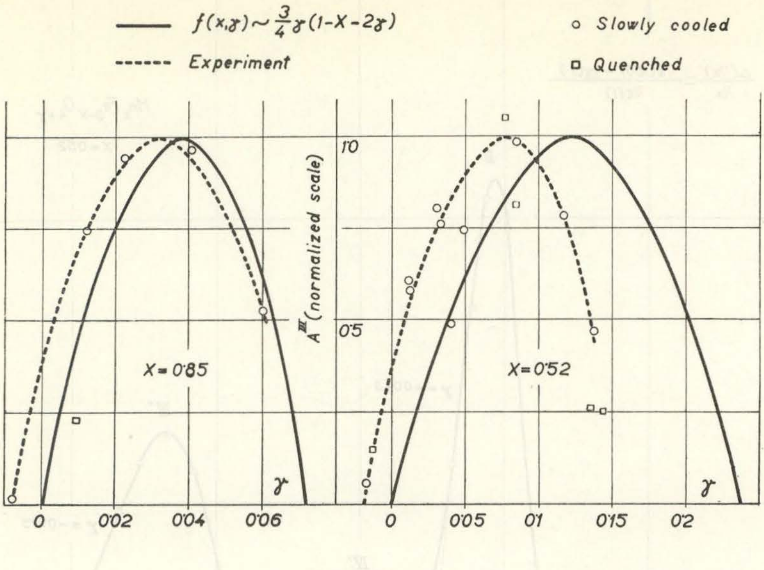


Fig. 2.

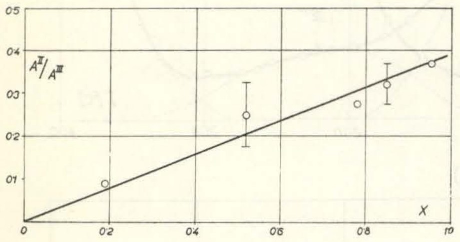


Fig. 3.

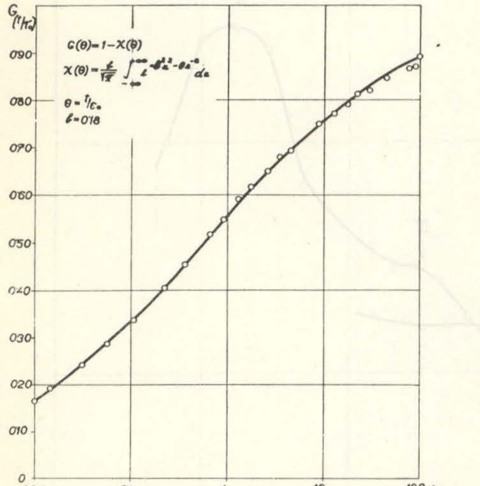


Fig. 4.

(4) The peak V was observed in materials with $x=0.52$ with maximum at 350 to 400°C. It exists in the whole range of γ studied and its position depends slightly on γ. The existence of the peak IV′ cannot be unambiguously deduced from our measurements because of the probable coalescence of IV′ and IV″ the resolution and identification being made still more difficult by the presence of the band V. In some cases, however, the shape of the spectrum bears some witness on the presence of all three bands (Fig. 1.).

(5) In the case of the process III the distribution function of time constants within the band could be analyzed and a good fit was found for the Gaussian distribution. (Fig. 4.)

From these results some conclusions concerning the kinetics of the relaxation processes may be drawn. With respect to its dependence on vacancy concentration the process IV (or more precisely IV″) is apparently due to ionic diffusion or in other words to Mn$\rightleftarrows$Fe interchange, the role of vacancies being in this case analogous to that supposed in Co substituted magnetite[6]. In the case of the phenomenon denoted as III we can infer from both the dependence of its magnitude on γ, and the constancy of its temperature position that it has its origin in direct interchange Fe$\rightleftarrows$□ on neighbouring octahedral sites. This conclusion is also strengthened by the Gaussian distribution of time constants we have found. The striking feature of II which has similar characteristics as III is its direct dependence on Mn content. The value of activation energy of the order of 0.5 to 0.7 eV does not exclude the possibility of an electronic process via Mn in this case.*) As to the mechanism responsible for V we can only guess from its features that it may be due to the interchange of ions between *A* and *B* positions or within the *A* sublattice.

For the decision about the type of ordering involved and its physical origin the results of induced anisotropy measurements on single crystals are as a rule more suitable. In spite of this we believe that the following concluding remark may be done. If we ascribe the induced anisotropy to the crystalline fields effects[8)], it follows from our measurements that the active ion is most probably Fe^{2+}, perhaps with one exception which may be the process IV′.

The type of the induced anisotropy found in some iron rich ferrites by other authors[9)] cannot be explained, however, on the basis of any one-ion model using the crystalline field of three-fold symmetry. Hence a pair ordering, or more physically the crystalline fields of lower symmetry, should be taken into consideration. In this sence both Mn ions and vacancies could be active similarly as proposed by Iida[10)], the former ones being most probably responsible for process IV″ and the latter for III and II. In addition, if this is true III is energetically more preferable than IV″. And as the process II has similar dependence on vacancy and ferrous ions concentration as III has, it is possible that both represent the same type of local order realised in two different ways. To support these conclusions we are planning to make a study of induced anisotropy; the preliminary results obtained on several samples cut from materials studied in the present work show a satisfactory agreement between the relative magnitude of disaccommodation and induced anisotropy.

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DISCUSSION

O. ECKERT: I think, from chemical and crystallographical consideration, it seems to be impossible to squeeze an big oxygen ion into a spinel lattice. Vacancies you are talking about, in reality, are mixed-charge of manganese, or that of iron, not oxygen vacancy.

It would be wise, from my stand point, to alter and take more care of divalent and trivalent cations: Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+} and to leave out γ value of oxygen content, although we cannot chemically analyze at the same time Fe^{2+}, Fe^{3+} and Mn^{3+}.

S. KRUPIČKA: As I understood, you mean that we must make some attempt to measure the contents of various ions of different valences. That is quite impossible without knowing exact reaction in dissolving specimens. In such a process valence may change. This measurement is based on modified Gorter's method for finding the whole oxygen content of sample.

Oxygen contents may seem as a semiquantitative parameter of cation vacancy

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* A similar behaviour was found[7)] in NiZn-ferrite with Co, the latter ion also being able to change its valency.

concentration.

E. W. GORTER: I should like to ask Dr. Krupicka to explain the paragraph, "the type of induced anisotropy found in some iron-rich ferrites cannot be explained, however, on the basis of any one-ion model using the crystalline field of 3-fold symmetry," in connection with Dr. Smit's paper at the beginning of this session.

S. KRUPIČKA: The type of induced anisotropy reported in the papers cited is such that it has no G term but only F term. So that, the anisotropy cannot be explained in the basis of one ion model.

S. IIDA: Unfortunately in the case of iron-cobalt ferrites our model of directional order with vacancy is not applicable. The essential point is that so long as the vacancy can move, cations are due to move and this gives rise to rearrangement of cation configurations, resulting in an induced anisotropy which is $1/\gamma$ times as large as our original model.

In this case, since the main relevant ions are all in S state (M^{2+}, Fe^{3+} or $Fe^{3+}+e^-$), theory can predict for the configurational unit anisotropy which is about 10^{-2} times smaller than the case of Co^{2+}. Therefore the well-known statistical calculation gives $(10^{-2})^2=10^{-4}$ times smaller value for the equilibrium uniaxial anisotropy energy compared to the Co^{2+} case. The value thus expected is $10^6\times10^{-4}=10^2$ erg/cc and is in a good agreement with experiments.

I should point out further that, if our original model could be applicable, the contribution normally expected from it should be only γ-times of that expected from the above model, so that it is unreasonable to ascribe the largest peak III to this mechanism.