DISACCOMMODATION OF PERMEABILITY IN MANGANESE-ZINC-TITANIUM FERRITES

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IN MANGANESE-ZINC-TITANIUM FERRITES

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Résumé. — Le spectre de traînage des ferrites MnZuTi ne présente, en général, qu'un seul pic à — 30 °C environ, dans la zone — 50° à 120 °C. L'amplitude du pic est proportionnelle au nombre d'ions ferreux localisés, c'est-à-dire aux paires $Fe^{II} Ti^{IV}$. Le déplacement vers le bas du pic situé d'habitude à 10 °C est dû à une diminution de l'énergie d'activation de 0,85 à 0,7 eV; cet effet est attribué aux forces électrostatiques s'exerçant entre l'ion quadrivalent et ses voisins. L'absence de pic à haute température, stade ^{II}, est compatible avec la localisation des ions ferreux. On a trouvé que $Fe_{2.82}Ti_{0.18}O_4$ montrait aussi un pic de traînage secondaire à — 30 °C.

Abstract. — The disaccommodation spectra of MnZnTi ferrites generally show only a single peak, at about — 30 °C, in the range — 50 to 120 °C. The amplitude of the peak is proportional to the number of localized ferrous ions, i. e. $Fe^{II}Ti^{IV}$ pairs. The shift in the peak down from the usual 10 °C is due to a lowering of the activation energy from 0.85 to 0.7 eV, and this decrease is attributed to the effect of electrostatic forces between the quadrivalent ion and its neighbours. The absence of the high temperature peak, process II, is consistent with the localization of the ferrous ions. It was found that $Fe_{2.82}Ti_{0.18}O_4$ also showed an additional disaccommodation peak at — 30 °C.

1. Introduction.

Stijntjes et al. [1], [2] have recently described how ferrites having very good technical properties may be prepared by substituting titanium (Ti^{4+}) into typical manganese zinc ferrite compositions. The present work examines the nature of the magnetic after effect associated with these same materials.

2. Disaccommodation in titanium substituted ferrites.
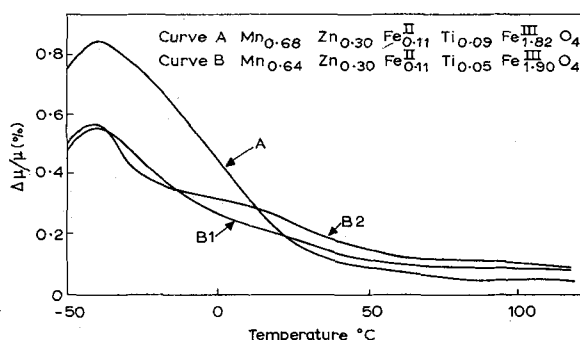
— Figure 1 shows the spectra of two titanium

FIG. 1. — Disaccommodation spectrum of Ti substituted MnZn ferrite.

substituted ferrites. As was found by Marais and Merceron [4], whose measurements covered the range — 80° to + 50 °C, the addition of titanium shifts the position of peak III (see e. g. Braginski [3]) by some 40 °C : the shifted peak we label III'. The present work shows that peak II is absent, so the long term stability of the material should be very good.

The ferrites described by Stijntjes et al. may be regarded as being of three types :

a) Nominally equal Ti^{4+} and Fe^{2+} content. *b)* Excess of Ti^{4+} with respect to Fe^{2+}. *c)* Excess of Fe^{+2} with respect to Ti^{4+}.

Figure 1 shows the spectra of two compositions of type *c*. The two compositions A and B 1 were fired

under the same conditions, and it may be supposed that the vacancy concentration is the same in each. The ratio of the height of the peaks is proportional to the Ti^{4+} concentration. As surmised by Smit et al. [5] it may be supposed that each Ti^{4+} ion has an Fe^{2+} ion as a neighbour. The observed amplitude of the peaks may then be taken as being proportional to the number of localized ferrous ions (and also to the vacancy concentration). The excess ferrous ion then contributes to the normal process III. This is demonstrated by sample B 2 which was fired slightly differently from B 1 and contains a larger Fe^{2+} concentration (and so a smaller excess oxygen content, γ) as indicated by a lowered resistivity and a better defined peak III. Now the amplitude of III' is proportional to $0.05 \times \gamma$, and the amplitude of III to

$$(0.11 - 0.05 - 2\gamma) \times \gamma .$$

Thus for typical values of γ of around 0.02 per formula unit, the amplitude of III is much more sensitive to γ than is III', as is indicated in the figure 1.

The absence of II implies that the formation of Fe^{2+}-Fe^{2+} pairs [3] is very unlikely, which is of course a consequence of the existence of the strongly bound Fe^{2+}-Ti^{4+} pairs. Measurements on samples of type *a* and *b* were also in agreement with this interpretation. One sample of type *c* with a high vacancy concentration, showed a just detectable peak II. For samples of a lower vacancy concentration (as in Fig. 1), this process was presumably so slow that the residual peak II lay above T_c, and so could not be observed.

To assist in the identification of the origin of III' the activation energy of the disaccommodation process was determined, the composition being

$$Mn_{.655}Zn_{.285}Fe_{.11}Ti_{.05}Fe_{1.9}O_4 .$$
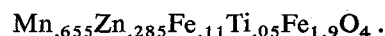
The value found was 0.7 eV (standard deviation 0.06 eV) ; τ was 9×10^{-13} s (from 1 to 60 $\times 10^{-13}$ s). The usual value for III is about 0.85 ± 0.1 eV. It would seem that the quadrivalent ion reduces the

activation energy associated with III, with a consequent downward shift on the temperature scale of the disaccommodation peak.

3. The origin of the lowering of the activation energy.

— It is well known that process III originates in the diffusion of cation vacancies in the presence of ferrous iron. Gerber [6] has suggested a mechanism (although in a different context) which accounts for the magnitude of the activation energy. This mechanism is based on a « hard sphere » model, which is of course rather crude, but perhaps adequate for our purpose. It was proposed that the cation (e. g. Fe^{2+}) in the course of jumping to a vacant site has to displace momentarily two oxygen ions as shown in figure 2a.
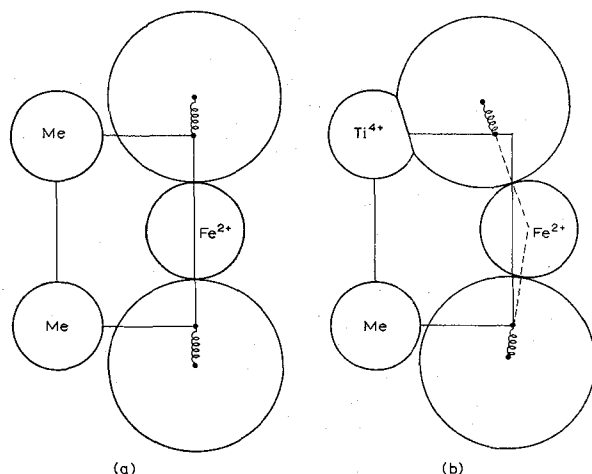

FIG. 2. — B sublattice and anions in the (110) plane, drawn to scale. (a) After Gerber [6] (b) As modified by Ti^{4+} ion.

The motion of the cation is of course normal to the plane of the figure. The magnitude of the displacement is readily calculated to be about 0.56 Å along < 110 >. The activation energy is proportional to the square of the displacement of the anions, so that if the movement of each anion was reduced in some way to 0.50 Å, it would account for the observed reduction in activation energy.

It is now suggested that the large electrostatic charge of the Ti^{4+} ion has two effects, as indicated in figure 2b.

a) The six nearest neighbour anions are slightly displaced towards it. b) The migrating cation is similarly slightly repelled, so that it follows a curved path which deviates slightly from the < 110 > direction :

figure 2b shows the cation (e. g. Fe^{2+}) at the middle point of its jump.

Assume for simplicity that the permanent displacement of the one anion and the maximum deviation of the cation from its direct path are equal. It may then be shown that a value for each of 0.25 Å is sufficient to reduce the temporary displacement of each anion to the required 0.50 Å.

It follows that a smaller quadrivalent ion would produce a larger change in activation energy, and vice-versa.

Marais and Merceron [4] suggested that the shift in position of peak III is associated with a change in sign of K_1. To verify that this was not the case, a polycrystalline sample of $Fe_{2.82}Ti_{0.18}O_4$ was prepared. It is known from the work of Syono and Ishikawa [7] that K_1 for this composition is negative. The disaccommodation spectrum for our sample is shown in figure 3. It may be seen that there is a well
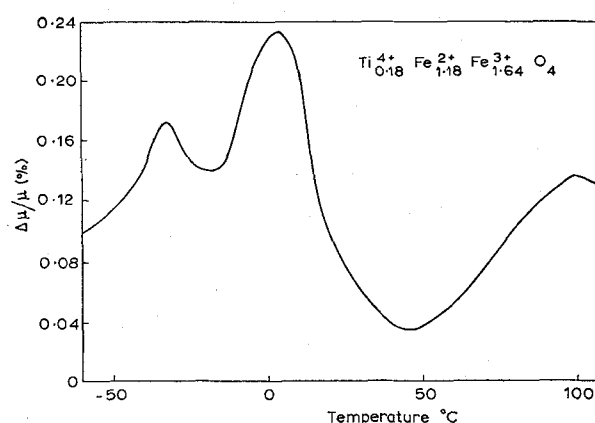

FIG. 3. — Disaccommodation spectrum of Ti substituted magnetite.

defined peak III' at − 33 °C, in addition to the usual peak III at 3 °C.

The progressive shift of the disaccommodation peak observed by Marais and Merceron [4] may perhaps be attributed to the changing ratio of the amplitudes of effects III and III', since their compositions contained a large excess of Fe^{2+} with respect to Ti^{4+} ion.

4. Acknowledgements.

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