ELECTRONIC MAGNETIC RELAXATION IN MANGANESE FERRITES

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Abstract

Two electronic magnetic relaxation phenomena are reported for the manganese ferrite system, which are both explained by electron hopping processes between octahedral iron ions: the first one by hopping between Fe^{2+} and Fe^{3+} ions with a Mn^{2+} -ion as nearest neighbour and the second one by hopping between iron ions with only iron nearest neighbours.

Introduction

It has been well established that in high-permeability spinel ferrites, the dispersion of the dynamic magnetic permeability and the maxima in the loss factor are caused by electron diffusion between cations present in different valency states like e.g. the Fe^{2+} and Fe^{3+} -ions^{1,2)}. However, in the manganese ferrite system, $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$, two distinct electronic relaxation phenomena are observed around the composition $x = 0.8$, with activation energies of 0.015 and 0.06 eV, respectively³⁾. The assignment of these two relaxations to elementary processes is still controversial: inter- and intra-atomic electron transitions between the Fe-ions are claimed as one interpretation, whereas electron transitions between iron ions and/or manganese ions are another⁴⁾. In the present paper, the composition dependence of the electronic magnetic relaxations in the manganese ferrite system is reported and compared with the analogue Zn ferrite system, from which indications about the origin of the two relaxation processes in the Mn-system are obtained.

Experimental

Polycrystalline manganese and zinc ferrous ferrites toroids with inner and outer diameters of 30 and 35 mm, respectively, were prepared by ceramic techniques. Special precautions were taken to obtain single phase spinel materials⁵⁻⁷⁾. The complex initial permeability was measured by means of a LCR resonance method, using coils wired on the ferrite toroids, in the temperature range of 4-300 K and frequency range of 20-500 kc/sec. For all the measurements the maximum value of the magnetic induction used in the experiments was $5 \cdot 10^{-5}$ T, independent of the frequency.

Fig. 1 The complex permeability $\mu = \mu' - j\mu''$ for $\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ at 95 kc/s as a function of temperature.

Fig. 2a and b μ'' as function of temperature for the Mn and Zn ferrite system with the additional parameter x , the zinc or manganese concentration.

Results and Discussion

For all the manganese as well as for the Zn ferrite materials, clear exponential magnetic relaxation effects are found in the complex permeability ($\mu' - j\mu''$). A typical example is shown in fig. 1, where the temperature dependence of μ' and μ'' is plotted for $\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ at 95 kc/s. From the exponential shift of the maxima in μ'' with frequency, activation energies are determined as functions of the composition of the ferrite.

In fig. 2a and 2b, the imaginary part μ'' is plotted as a function of temperature with the manganese and zinc content X as a parameter. In the zinc ferrite system only one electronic relaxation phenomenon is observed, as can be seen from the single peak in the μ'' - T curve. In the manganese system, however, two relaxation phenomena A and B are observed

Fig. 3 The activation energy of the electronic relaxation in the zinc ferrite system compared with the activation energy of process A in the manganese ferrite system.

for the compositions between $0.6 \leq x \leq 0.9$, and only one for compositions with a lower manganese content $x \leq 0.5$. In fig. 3 the activation energy of the magnetic relaxation effect in the zinc ferrite system is compared with the energy determined from the manganese system; for the manganese composition between $x = 0.6$ and $x = 0.9$, the values for the low temperature effect A has been plotted. From the nearly identical values of the energies for the manganese and zinc concentration below $x = 0.6$ and the rather small and gradual changes in E_A with increasing Mn-concentration, the conclusion seems to be obvious, that the electronic relaxation phenomenon observed in the zinc ferrite system and the phenomenon A in the Mn-system are due to the same mechanism, i.e. a transfer of electrons between adjacent Fe^{2+} and Fe^{3+} ions on the octahedral sublattice of the spinel structure. This conclusion is further supported by the fact that the Zn^{2+} -ions are located on the tetrahedral sublattice of the spinel structure, which results in a concentration of $(1-x)\text{Fe}^{2+}$ ions on the octahedral sites; In the manganese ferrous ferrites, the Mn^{2+} -ions have also a tendency to be located on the tetrahedral sites⁸⁾, which results in a nearly identical ionic configuration for the octahedral sublattice in both systems: $(1-x)\text{Fe}^{2+}$ ions and $(1+x)\text{Fe}^{3+}$ ions.

Electrical conductivity measurements we performed on single crystals showed further that the composition dependence of activation energy for the conductivity behaves in a similar way as the magnetic activation energy, which is a strong evidence for the proposed Fe^{2+} - Fe^{3+} electron exchange mechanism.

An additional evidence for the same origin of the Fe^{2+} - Fe^{3+} relaxation in the zinc ferrite system and the mechanism A in the manganese system is the equal pre-exponential factor τ_0 describing the exponential relaxation in both systems: $\tau_0 = \tau \exp(-E/kT)$; with τ_0 varying between 10^{-12} - 10^{-9} s depending on X (Mn^{2+} or Zn^{2+} concentration).

Now, it seems apparently to attribute the mechanism B in the manganese system to the occurrence of an increasing number of octahedral Mn^{2+} , as it is known that for $x = 1.0$ up to 20% of the manganese ions can be located on the octahedral lattice, depending on the thermal treatment of the specimens⁸⁾. In order to study this in more detail, we performed permeability measurements on a specimen $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ after different thermal treatments to change the octahedral Mn-concentration. As the absolute value of μ'' can also depend on the value of μ' , due to the microstructure

of the specimens, the loss tangent $\delta = \mu''/\mu'$ is now plotted in fig. 4. The phenomenon A turns out to be independent of the thermal treatment, whereas the strength of relaxation B is strongly influenced by the annealing treatment i.e. by the octahedral Mn-concentration. The relaxation B can not be attributed to an electron-transfer between Mn^{2+} and Mn^{3+} or Fe^{3+} ions, because the energy needed for such a transition exceeds 0.3 eV⁹⁾, whereas for the process B we found values of E between 0.060 and 0.075 eV. However, the annealing experiments show clearly that the concentration of the octahedral manganese ions affects the relaxation B!

Fig. 4 Temperature dependence of the loss tangent μ''/μ' of $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ measured on specimens after different heat treatment.

1. As prepared and cooled from 1300°C to room temperature in 2 hours.
2. Annealed at 800°C in sealed silica tube, and cooled within 30 minutes to room temperature.
3. As 2 but quenched to room temperature.

The peak in the μ'' - T curve for the relaxation A in the Mn-system can be fitted by one single exponential relaxation, which means that there does not exist a distribution of relaxation times for this mechanism. The same sharp relaxation was observed for the Zn-system but a similar investigation of the relaxation in e.g. nickel ferrous ferrites showed substantial broadening of the μ'' - T peak indicating a distribution in relaxation times for the Ni-ferrous ferrite system¹⁰⁾. The different behaviour of the Zn and Mn ferrites on one side and of the nickel ferrite system on the other can be related to the inverse structure of the nickel ferrites. The Ni^{2+} ions are located on the octahedral sites, by which the electronic energy levels of the iron- nearest neighbours will be influenced by the deviating charge of the Ni^{2+} ion. In fact, one expects the activation energy for the electron transfer between the iron ions to depend on the number of Ni^{2+} nearest neighbours, and since the Ni^{2+} and iron ions will be statistically distributed on the octahedral sites, a distribution in relaxation times is expected. In the zinc ferrites only electronic and no static ionic disorder on the octahedral sites is possible, closely related to the Fe^{2+} and Fe^{3+} charge distribution and only one single relaxation time is expected for the electron hops between the adjacent iron ions. For the manganese ferrites we have more or less the same situation as for the zinc ferrites, with an exception for larger Mn concentrations between $x = 0.5$ and 1.0, where some Mn^{2+} -ions are entering the octahedral sublattice. The

most obvious explanation of the mechanism for relaxation B is an electron transfer between Fe^{2+} and Fe^{3+} -ions which are adjacent to an octahedral Mn^{2+} -ion. Due to the bivalent manganese ion and the relative large diameter of the Mn^{2+} -ion, there must be a distinct effect upon the energy levels of the neighbouring iron ions, which results in a quite different relaxation time for an electron hop between Fe^{2+} and Fe^{3+} -ions with or without a manganese nearest neighbour.

For the composition $x = 0.8$ about 5% of the octahedral sites are occupied by Mn^{2+} ions⁷⁾, which seems to be an optimum for the simultaneous appearance of relaxation A and B. Both relaxations can be interpreted on the basis of electron hopping between Fe^{2+} and Fe^{3+} ions only, if we take a certain ionic disorder on octahedral sites into account: process B is caused by electron hopping between iron ions with an octahedral Mn^{2+} ion as nearest neighbour and process A is caused by the electron hopping between iron ions without Mn^{2+} as nearest neighbour. So we can conclude that in the manganese ferrite system the presence of octahedral Mn^{2+} -ions introduces a static ionic disorder, which gives rise to the occurrence of two detached electronic magnetic relaxations.

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LOW TEMPERATURE ELECTRICAL PROPERTIES OF MAGNETITE AND Mn-FERRITES

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Electrical resistivity and thermoelectric power measurements have been made on single crystals of manganese ferrites, $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0, 0.5, 0.7, 0.8, 0.9$ and 0.95) in the temperature range 10 K to 300 K. Below the Verwey transition T_V of magnetite, the thermoelectric power is strongly influenced by the oxygen nonstoichiometry of the samples whereas the resistivity exhibits hardly any dependence on the changes of the oxygen content. Starting from the lowest temperatures, the electrical properties are explained in terms of the impurity band, variable range hopping, small polaron band and small polaron hopping conduction mechanisms where the long-range and the short-range orderings have to be taken into account.

Introduction

Extensive experimental and theoretical work have been done to understand the electronic structure and electrical transport mechanisms in magnetite (Fe_3O_4) and other spinel ferrites. Starting with early investigations of Verwey [1,2] who discovered a jump of two-orders of magnitude of the electrical resistivity ρ of magnetite at $T_V \approx 120$ K, a vast number of papers have been devoted to studying of this first-order structural, magnetic and electrical phase transition (see e.g. [2-8]).

In the same time, work on the electrical properties of the "substituted magnetites", i.e. iron-excess mixed ferrites like cobalt ferrites [9], manganese ferrites [10,11], nickel ferrites [12] etc. was going on, revealing that the classical semiconductor one-electron band picture breaks down. A new concept of more or less localized charge carriers (small polarons) was developed to account for the observed electrical, magnetic and optical properties of monoxides, sesquioxides and more complex magnetic oxide materials (for reviews see e.g. [13-15]). Taking into account a splitting of the conduction levels, it was possible to explain a complex behaviour of the thermoelectric power α near T_V in the case of magnetite [16,17].

However, the observed dependences of electrical properties of ferrites at low temperatures revealed early on that the simple small polaron picture must be modified in at least two ways:

a) impurities present in ferrites introduce band conduction or hopping of charge carriers which becomes important at low temperatures;

b) correlation effects must be introduced into the small polaron theories.

In such a way, the behaviour of the electrical conductivity and thermopower of the fluorine-substituted magnetite [18] and the low temperature properties of nickel ferrites [19] were described. Considering the

correlation effects of small polarons (leading to short range ordering) Ihle and Lorenz [20] were able to explain the conductivity maximum occurring in magnetite at about 300 K.

In this report, a more detailed investigation of the electrical resistivity and thermoelectric power of several samples of magnetite is made in order to clarify the behaviour of α below T_V . Measurements of electrical properties of iron-rich manganese ferrites give further informations on the influence of substitutional disorder on the behaviour of charge carriers.

Experimental part

Samples.

Single crystals of magnetite and manganese ferrites in the system $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ were prepared by the travelling - molten - zone technique as described elsewhere [21]. After growth the single crystal rods (approx. 5mm in diameter) were additionally heat-treated at $T_h = 1470$ K for 70 hours and slowly cooled to room temperature in controlled atmospheres, to secure the adjusted oxygen stoichiometry. From the rods, rectangular samples of $1 \times 5 \times 12 \text{ mm}^3$ were cut and finely polished. The remaining parts of the crystals were used for chemical analysis to determine final contents of cations and the active oxygen. Results of the analysis, partial oxygen pressures during heat-treatment and crystal axes are listed in Table 1. It was found that the gradients in chemical compositions along or across the samples were within the error limits of chemical analysis (i.e. 0.02 and 0.002 for x and γ resp.). Electrical contacts were made by rubbing in an eutectic In-Ga alloy at the opposite faces of the samples.

Electrical resistivity.

A four point dc potentiometric method was used to determine the electrical resistivity

Table 1
Final compositions and treatment conditions
of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+\gamma}$

Sample	x	γ	log pO ₂	T _h (K)	axis
A	0	0.046	-6.0	1370	<110>
B	0	0.008	-7.6	1420	<110>
C	0	0.007	-8.3	1420	<110>
D	0	0.006	-8.5	1420	<110>
E	0	0.005	-8.8	1420	<110>
F	0	0.009	-7.6	1400	<110>
G	0	0.004	-10.2	1470	<110>
0.5	0.52	0.009	-6	1470	<100>
0.7	0.70	0.009	-6	1470	<100>
0.8	0.79	0.005	-6	1470	<100>
0.9	0.90	0.002	-6	1470	<111>
0.95	0.95	0.002	-6	1470	<110>

of the low resistive samples at various current densities. Resistances (accuracy better than 1%) were determined at such current values where Ohm's law was fulfilled. At low temperatures when resistances reached $10^6 \Omega$ a voltage drop at probes was determined using a Keithley 640 electrometer with the input resistance exceeding $10^{15} \Omega$. At very high resistances ($>10^{11} \Omega$) a two point method exploiting a feed-back loop of the electrometer was used.

Sample temperature was varied by means of a liquid helium continuous-flow cryostat; temperature control (with accuracy of 0.1 K) was achieved with a DTC 2 (Oxford instruments) controller connected to a C.L.T.S. sensor.

Thermoelectric power.

To determine the thermoelectric power per 1 K (Seebeck coefficient α) the opposite ends of the sample were clamped in the arms of the aluminized sample holder (enabling a good thermal contact and securing a high electrical isolation of sample from the holder). The arms could be individually heated to establish a temperature gradients up to 5 K/cm along the sample in both directions. Temperatures of arms were measured by Au+0.03 %Fe vs. chromel thermocouples and the thermopowers generated by temperature gradients were determined by open input Keithley 640 electrometer. Slopes of the thermopower vs. temperature differences plots were used to calculate the values of α .

Results

Magnetites.

Temperature dependences of the electrical resistivities of magnetite samples in $\log \rho$ vs. $1/T$ representation are shown in Figs. 1,2.

Fig. 1 Temperature dependences of the resistivity of magnetites in the 80 K to 300 K range (see Table 1 for sample details)

It is seen that with the exception of the highly non-stoichiometric sample A all other specimens have identical temperature dependences of resistivity down to 10 K. Although the concept of activation energy has different meanings in various theories of transport mechanisms it is worthwhile (for the sake of comparison and estimation) to define a conductivity activation energy as

$$(1) \quad \epsilon(\text{eV}) = 1.895 \cdot 10^{-4} d(\log \rho) / d(1/T)$$

Values of ϵ as determined for the magnetite samples just above and just below the Verwey transition and at 10 K are listed in Table 2.

Table 2
Activation energies for magnetites
(see Table 1 for sample details)

Sample	$\epsilon(T > T_V)$	$\epsilon(T < T_V)$	$\epsilon(T = 10 \text{ K})$
A	0.05	0.12	0.006
B to G	0.05	0.15	0.008

Fig. 2. Temperature dependences of the resistivities of magnetites at 10 K to 100 K (see Table 1 for sample details).

The temperature dependences of the thermoelectric power for representative samples of magnetite are depicted in Fig. 3. The other samples display intermediate behaviour and, to avoid possible confusion, were not included in Fig. 3. A salient feature is the strong dependence of α below T_V on the heat treatment conditions of samples, as opposed to the small changes of α above T_V with α remaining practically constant up to room temperature. The most remarkable is the behaviour of sample G where a transition from n-type to p-type conductivity occurs at 100 K followed by a maximum at 80 K and another transition to n-type at about 50 K. Below 40 K all samples behave in a similar manner with $\alpha \rightarrow 0$ for $T \rightarrow 0$.

Fig. 3. Temperature dependences of the Seebeck coefficient α for magnetite samples.

Mn ferrites.

Temperature dependences of the electrical resistivities of manganese ferrites are shown in Figs. 4 and 5. At higher temperatures (Fig. 4), resistivities increase with rising manganese content while the activation energies ϵ , decrease attaining the minimum value for $x = 0.9$ - see table 3. Below 100 K (Fig. 5) the sequence of resistivities is altered, resulting in a reversed succession of ρ with x . The only exception is $x = 0.95$ sample for which ρ and ϵ are larger than the values of the other samples down to 15 K.

Fig. 4. Temperature dependences of the electrical resistivities of Mn ferrites at 80 K to 300 K range. The symbols indicate the various contents of manganese.

Sample	ϵ (T=100 K)	ϵ (T=10 K)
0.5	0.044	0.009
0.7	0.034	0.008
0.8	0.030	0.007
0.9	0.025	0.005
0.95	0.036	0.008

Fig. 5. Temperature dependences of the electrical resistivities of Mn-ferrites in 10 K to 100 K region. The symbols indicate the various contents of manganese.

In Fig. 6 temperature dependences of the Seebeck coefficients of Mn-ferrites are represented. Starting at room temperature a slight increase of α in decreasing temperatures is first observed. In the 150 K to 50 K region α reaches a maximum followed by a regular decrease (down to zero) when $T \rightarrow 0$.

Fig. 6. Temperature dependences of the Seebeck coefficient of Mn-ferrites. The symbols indicate the various contents of manganese.

Discussion

A number of conduction mechanisms were suggested to account for the complex behaviour of the temperature dependence of the electrical resistivity of magnetite. In agreement with other experiments [22,23] our low temperatures measurements confirm the importance of the impurity conduction mechanism. The impurities in the form of cation vacancies are introduced in magnetite as a result of the oxygen nonstoichiometry (see Table 1) acting as donor centres. In manganese ferrites, the impurity levels are also formed by the electrons trapped at octahedral Mn^{3+} ion sites or in the neighbouring iron ions (for discussion of the trapping centers see [10,11]). The theory of correlated hopping transport leading to impurity band conduction [24] yields for the temperature dependence of resistivity the following formula

$$(2) \quad \rho = \rho_0 T^{-n}$$

Relation (2) seems to be well fulfilled in our measurements as may be seen on Fig. 7 which shows the linear dependence of $\log \rho$ vs. $\log T$ at $T < 40$ K.

Fig. 7. Demonstration of the $\rho = \rho_0 T^{-n}$ plots for magnetites (full signs) and Mn ferrites (open signs). The symbols indicate the various sample compositions.

Such a relationship has also been found recently in nickel ferrous ferrites [19]. Correlated hopping is also supported by measurements of the thermopower where at low temperatures the relation after [25]

$$(3) \quad \alpha \approx T^{1/2}$$

seems to be obeyed by magnetite as well as by Mn-ferrite samples.

Fig. 8. Demonstration of the Mott's law for magnetites and Mn-ferrites. Symbols indicate the various sample compositions.

At higher temperatures ($T > 40$ K) the variable range hopping yielding the Mott's law

$$(4) \quad \rho = A \exp(B/T^{1/4})$$

becomes a more appropriate description in the case of manganese ferrites as shown on Fig. 8. In magnetite, however, relation (4) seems to be satisfactorily obeyed only at low temperatures ($T < 20$ K) and at temperatures just below T_v (cf. also [22]), the intermediate region being the most difficult to interpret. Let us recall the complicated behaviour of α for magnetite samples and the occurrence of maxima in Mn-ferrites. The latter are similar to maxima encountered in fluorine-substituted magnetites [18] and nickel ferrites [19] and may be seen as an evidence for the formation of the Coulomb gap in these materials (see discussion e.g. in [5]).

The behaviour of the electrical conductivity of magnetite above T_v has been successfully explained by the simultaneous contribution of small polaron hopping and small polaron band conduction taking into account short-range ordering effects [20]. The behaviour of manganese ferrites above 100 K may instead be interpreted in the frame of the ordinary nearest neighbour hopping of small polarons as was demonstrated earlier [26].

Conclusions

The conduction mechanism in magnetite and iron rich manganese ferrites below room temperature has a rather complex character. At low temperatures ($T < 40$ K), a correlated many electron hopping mechanism of localized charge carriers predominate with high resistivities, low activation energies and thermopower varying as $T^{1/2}$. At higher temperatures ($40 \text{ K} < T < 120 \text{ K}$) a variable range hopping mechanism becomes important obeying Mott's law and leading to maxima in the temperature dependences of the thermopower of manganese ferrites. In magnetite, the thermopower in this particular region is very sensitive to the specific dopants, to the degree of oxygen stoichiometry and to the conditions of heat treatment. At the Verwey transition of magnetite a jump in electrical properties is caused by the disappearance of the long-range ordering of charge carriers. A certain degree of a short-range ordering above T_V is responsible for the occurrence of the conductivity maximum at about 300 K. The electrical properties of Mn-ferrites above 100 K are explained by nearest-neighbour small polaron hopping.

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