

Effect of magnetic order on the conductivity in Ni-Zn ferrites

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The electrical resistivity and thermo-emf were measured for a series of samples of the system $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, \text{ and } 0.6$). Transition from the ferrimagnetic to the paramagnetic region, is accompanied by an increase of the activation energy for conductivity by an amount ΔE ranging from about 0.1 e.v. to 0.13 e.v. Relatively great values of ΔE are obtained on highly stoichiometric samples prepared by the precipitation method and explained as being due to the fairly strong (B-B) exchange interaction in Ni-Zn ferrites. A corresponding change in the thermo-emf (about $\pm 8\%$) is obtained only for a sample $x = 0.6$ prepared by the usual ceramic technique. The behaviour of α and ΔE is discussed in the light of current theories.

1. INTRODUCTION

Transition from ordered ferrimagnetic state to the paramagnetic state is accompanied by various changes in physical, magnetic and electrical properties of ferrites. The activation energy for electrical conductivity was found to be smaller in the ferrimagnetic region than in the paramagnetic region (Sychkov 1959, Ghani & Miryasov 1972, Roslecu 1969). For ferrites containing non-magnetic ions such as Zn or Cd contradictory results were found in the literature. In some works (Sychkov 1959, Ghani & Miryasov 1972) a pronounced change of activation energy for conductivity E_a was observed at the transition temperature. While in other works (Roslecu 1969) no change of E_a was reported at this temperature.

An attempt was previously made to explain this discrepancy for Cu-Cd ferrites (Ghani & Miryasov 1972). The aim of the present work is to study on the same sample the behaviour of the conductivity and the thermo-emf for Ni-Zn ferrites during transition to the paramagnetic state. Majority of previous data were reported only for one of these two transport parameters separately.

2. EXPERIMENTAL

A series of samples of the system $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with compositions ($x = 0.2, 0.4 \text{ and } 0.6$) were prepared by the precipitation method. This method has

proved to give more homogeneous and stoichiometric final products than the usual ceramic technique (Gyehna *et al* 1966). All data in previous work were obtained on samples prepared by the ceramic method. To compare between the results with samples, that were prepared by both methods, one of the compositions ($x = 0.6$) was obtained by the ceramic method. Samples were prepared at the Faculty of Chemistry, Moscow State University.

The temperature dependence of resistivity ρ and thermo-emf α in a wide range lower and higher than transition temperature was obtained using a method described elsewhere (Ghani & Miryasov 1972, Ghani & Ahmed 1976).

3. RESULTS

Figures 1 and 2 give the temperature dependence of ρ and α for all samples. For compositions 1, 2 and 3, which were prepared by the precipitation method, an increase in the activation energy of resistivity is found on passing through the Curie point T_c . The thermo-emf expressed in units of $2.3 k/e = 198 \mu\text{V}/\text{deg}$, loosely depends on temperature in the whole range without observable changes in the region around the transition temperature.

Figure 2 shows also a comparison between the behaviour of ρ and α for sample No. 3 which was obtained either by the precipitation or by the ceramic technique.

In Table 1 we give the values of the activation energy for all samples in the ferromagnetic region E_F , in the paramagnetic region E_p , the change of this activation energy ΔE , values of the Curie temperatures T_c and the exchange energy $E_i = kT_c$ (k being the Boltzmann constant).

4. DISCUSSION AND CONCLUSION

(a) Results for samples No. 1, 2 and 3

With these compositions the increase of activation energy for conduction in the paramagnetic region ranges from about 0.01 e.v. to 0.13 e.v. (see table 1). These values of ΔE are comparable with those found for Cu-Cd ferrite (Ghani & Miryasov 1972) and are more than two times larger than the corresponding values for simple ferrites (Reslescu 1969). Relatively large ΔE for ferrites containing appreciable amounts of Zn or Cd ions may be explained as follows :

It is well known that in cubic ferrispines there are two magnetically non-equivalent tetrahedral or A and octahedral or B sublattices. The magnetic order is due to superexchange interaction mechanism occurring between metal ions in A and B sublattices through the separating oxygen ions. There are three types of interactions namely the ($A-A$), ($A-B$) and ($B-B$) interactions. Non-magnetic Zn and Cd ions occupy positions in the A -sublattice. This causes a decrease of the intensity of ($A-A$) and ($A-B$) interactions. As was confirmed

by the Mossbauer study (Petitt 1963, Satya Murthy *et al* 1968) the (*B-B*) exchange interaction on the contrary increases with the increase of Zn content in Ni-Zn ferrites.

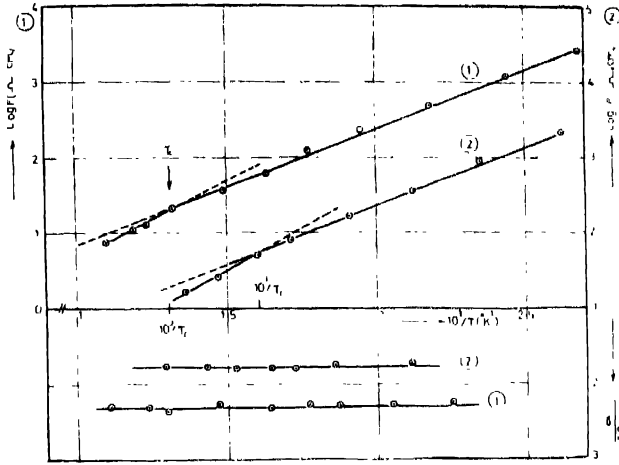


Fig. 1. Temperature dependence of resistivity ρ and thermo-emf α for samples 1 and 2 (see Table 1).

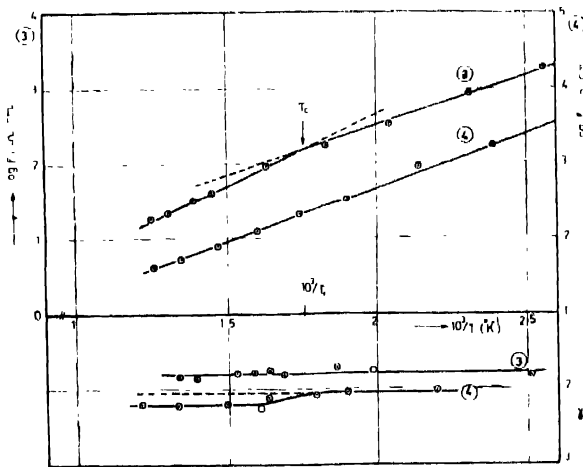


Fig. 2. Temperature dependence of resistivity ρ and thermo-emf α for samples 3 and 4 (see table 1).

The conductivity in ferrites occurs also through the B -sublattices due to the exchange of electrons between Fe^{2+} and Fe^{3+} ions. This exchange mainly occurs through the separating oxygen ions. The activation energy for the transfer of carriers in ferrites is lower in the magnetically ordered phase. This may be due to the fact that in this region there exists a certain correlation between the directions of electrons spin. Ferrites containing Zn and Cd have relatively strong (B - B) interaction i.e., strong correlation between directions of electronic spins in the ferrimagnetic region. For temperature higher than T_c this correlation vanishes. In this case we may therefore expect an enhanced change of activation energy for exchange of electrons between equivalent sites on the B -sublattice.

The thermo-emf for these samples weakly depends on temperature without observable changes in the region around the transition temperature. This behaviour of α means that the concentration of charge carriers remains constant in the whole temperature region and consequently the activation energy for conduction is totally consumed in the hopping process of these carriers between energetically equivalent sites (Austin & Mott 1969, Ghani & Ahmed 1976). Those results of α therefore give a further evidence which favours a localized rather than a band picture for conductivity in ferrites.

(b) *Results for samples 3 and 4*

Results in figure 2 show that for sample No. 3 (precipitation method) ΔE = 0.11 e.v, while for sample No. 4 (ceramic method) ΔE vanishes. An opposite behaviour is found for α . The thermo-emf for sample No. 3 shows no variation in the whole temperature range. For sample No. 4, α gradually increases with temperature in the vicinity of T_c and remains constant for other temperatures. This change in α is about +8% of the observed value for temperature lower than T_c . A similar decrease of α was previously reported (Ghani & Murzasov 1972) in the case of Cu-Cd ferrite containing about 0.05 Fe^{2+} ions per molecule. Another corresponding change was found (Griffiths *et al* 1970) for magnetite which have only Fe^{2+} and Fe^{3+} ions in B -sublattice. This change was about +13% of the observed value at T_c . We may consider therefore that the change $\Delta\alpha$ at the transition point is connected with the presence of Fe^{2+} ions in the composition of the ferrite.

We may refer to the theoretical calculations due to Heikes *et al* (1963). These calculations concern the behaviour of α at the transition temperature of antiferromagnetic semiconductor type NiO. This predicts a change $\Delta\alpha$ which depends on the concentration of the charge carriers. Moreover, $\Delta\alpha$ vanishes if the concentration of the charge carriers is lower than 0.01 per molecule. If we apply the conclusions of this theory to our results, we may attribute the difference between the samples No. 3 and No. 4 to a small increase of Fe^{2+} ions

in sample No. 4. The origin of the excess Fe²⁺ for sample No. 4 which was prepared by the ceramic method may be due to .

- (i) Small amounts of iron eroded from the ball mills (Heikes *et al* 1963) during the milling process. (Samples prepared by the precipitation method are not subject to this process).
- (ii) Sintering of this sample at 1350°C, which is 100°C higher than sintering temperature of sample No. 3.

The question of the dependence of ΔE on charge-carrier concentration was discussed in previous work (Ghani & Miryasov 1972), where the double exchange mechanism occurring between charge carriers was considered.

We conclude that, the behaviour of conductivity and thermo-emf during the transition to the paramagnetic state depends on the concentration of Fe²⁺ ions which might be present in the ferrite. Relatively large increase of the activation energy for conduction process ($\Delta E = 0.01-0.13$ e.v.) was obtained on highly stoichiometric samples of Ni-Zn ferrites and was attributed to the fairly strong (*B-B*) exchange interaction in these ferrites. The observed change of thermo-emf was explained using a theory given by Heikes *et al* (1963).

Table 1. Comparison between the changes in activation energy of conductivity ΔE during transition to the paramagnetic state and values of exchange energy for some compositions of the system Ni_{1-x}Zn_xFe₂O₄.

Sample No.	<i>x</i>	<i>E</i> _v ⁺ e.v.	<i>E</i> _p e.v.	ΔE e.v.	<i>T</i> _c °K	<i>E</i> _v k <i>T</i> _c e.v.	$\Delta E/E_v$
1	0.2	0.31	0.40	0.09	753	0.065	1.38
2	0.4	0.31	0.44	0.13	623	0.054	2.41
3	0.6	0.27	0.38	0.11	473	0.041	2.68
4	0.6	0.28	0.28	-	473	0.041	-

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