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Anomalous electrical properties of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$

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Two anomalies are observed in the temperature dependencies of the electrical conductivity and the thermoelectric power of ferrimagnetic manganese ferrites: a magnetic anomaly at the Néel temperature which can be explained with a model proposed previously and a second anomaly at 620 K which is due to a cation redistribution process.

The electrical properties of manganese ferrites ($\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$) were investigated by a number of authors but the basic concept of the conduction process has been proposed by Lotgering.¹ For manganese concentrations lower than $x = 1.0$ the conduction is due to the electron exchange between ferrous and ferric ions on the octahedral sites and above $x = 1.0$ due to the electron exchange between Mn^{2+} and Fe^{3+} ions on octahedral sites. At temperatures between 500 and 1000 K additional nonlinearities are reported in the $\log \sigma - 1/T$ plot for which no unanimous explanation is found in literature. Belov, Popova, and Talalaeva² have assumed a band conduction mechanism and attributed the anomaly to the magnetic ordering. Rosenberg, Nicholas, and Bunget,³ however, have proposed a polaron hopping process and have explained the decrease in the activation energy in terms of splitting of the energy levels by an exchange interaction in the ferrimagnetic region. One of the present authors⁴ has suggested that the higher activation energy above the Néel temperature might be due to the cation migration between the tetrahedral and octahedral sublattices of the spinel. Such a migration has indeed been proved to occur at temperatures of 620 K and higher⁵ and is responsible for a thermally activated concentration of octahedral Mn^{2+} ions. These ions act as donor levels for the conductivity in the case of Mn concentrations $x \geq 1.0$. Since the Néel temperatures of the manganese ferrites are within the same temperature range where the ionic migration between the spinel sublattices can occur, previous data on the electrical conductivity and thermopower do not enable us to decide whether there is a magnetic anomaly in the electrical properties or not. In this paper we present additional evidence which offers a possible solution to this problem.

Thermoelectric power and resistivity measurements have been carried out on single crystals $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ with compositions $0 \leq x \leq 1.2$. Details of the experimental procedures and specimens can be found in Refs. 4–8.

Previous measurements of resistivity and the thermoelectric power of nickel ferrites $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ have yielded results which are not complicated by cation exchange between the sublattices, at least in the temperature range between 300 and 1000 K, and have therefore enabled us to conclude that the anomalies in ρ and θ are of magnetic origin. We have explained these magnetic anomalies in terms of a mean-field "two-band" model, in which the electron energy levels are split by the internal exchange field below the Néel temperature.⁷ The conductivity can be analyzed using the empirical

formula $\sigma = \Gamma T^{-3/2} \exp(-W/kT)$, where W is an activation energy and Γ a constant. The positive cusp in the $G(\sigma T^{3/2}) = d \ln \sigma T^{3/2} / d(1/T)$ vs T curve and the step in the θ vs T curve are clear indications of the onset of the magnetic disorder in the nickel ferrites. It is also very revealing to analyze the present conductivity data for the manganese system in terms of the quantity $G(\sigma T^{3/2})$ which can be calculated from the experimental conductivity data as described in Ref. 7. In Fig. 1 the quantity G is plotted versus T for two compositions $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and $\text{Mn}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and in Fig. 2 the Seebeck coefficient θ is plotted against temperature for various manganese concentrations. The indicated Néel temperatures T_N have been determined independently by magnetization measurements. For manganese ferrites with an excess of ferrous ions, $x < 1.0$, the cation distribution can be presented by the formula $\text{Mn}_{x-y}^{2+}\text{Fe}_{1-x+y}^{3+}[\text{Mn}_y^{2+}\text{Fe}_{1-x}^{2+}\text{Fe}_{1+x-y}^{3+}]\text{O}_4$. The exchange of electrons between octahedral sites is the dominant conduction process.¹ For low enough concentration x the $[\text{Mn}^{2+}]$ donor centers will have little influence on the population of the conduction electrons, which should be simply

FIG. 1. $G(\sigma T^{3/2}) = d \ln \sigma T^{3/2} / d(1/T)$ (σ in $\Omega^{-1} \text{cm}^{-1}$) for $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ plotted against temperature.

FIG. 2. Thermoelectric power θ ($\mu\text{V/K}$) for $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ plotted against temperature.

proportional to $(1-x)$. This suggests that the anomalies in the $G(T)$ and $\theta(T)$ curves at T_N are not caused by a temperature dependent cation distribution but are directly related to the magnetic transition. The anomalies in G and θ for $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ with $x \leq 0.5$ are similar to those observed in the nickel ferrous ferrite system, i.e., there is a positive cusp in G and a step in θ . Referring to Fig. 1, we observe that the positive cusp in G is quite small and almost suppressed in the $x = 0.5$ sample. This small cusp is superimposed on an overall increase in G occurring between, say, 400 and 1000 K, which is believed to be due to an increase in disorder due to cation (Mn) redistribution and is also due to the percolative and polaronic properties of the hopping process.⁷ In a recent paper⁷ the magnetic anomalies in nickel ferrite have been discussed in terms of a "two-band" model associated with magnetically ordered spin up and spin down states. We believe that this model provides a satisfactory description of the Mn ferrites with $x < 0.5$.

For higher Mn concentrations $x > 0.8$ the divergences of $G(\sigma T^{3/2})$ observed at T_N turn out to be negative, in contrast to the positive cusp observed in the equivalent concentrations of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$.^{7,8} The negative divergence in G for MnFe_2O_4 has been explained⁸ in terms of a mean-field model which is consistent with a previously proposed "two-band" model of the magnetic anomalies in nickel ferrous ferrite and in which the $[\text{Mn}^{2+}]$ donor binding energy is influenced by magnetic ordering. Therefore, the presence of a negative divergence in G for $x = 0.8$ (Fig. 2) and $x = 0.9$ (observed, but not shown) suggests that the conduction electrons originating from the donor levels play a surprisingly important role in samples of the composition range $0.5 < x < 1.0$.

For manganese concentrations $x \geq 1.0$, the electrical properties are dominated by the octahedral Mn^{2+} ions, which do not contribute directly to the conduction, but which act as donor centers and which provide the electrons

FIG. 3. Dimensionless thermoelectric power $e\theta/k$ and $\ln \rho/T^{3/2}$, where ρ is the resistivity in $\Omega \text{ cm}$ of $\text{Mn}_{1.075}\text{Fe}_{1.925}\text{O}_4$, plotted against reciprocal temperature.

for the conduction over the Fe levels.¹ Since at temperatures above 620 K a redistribution of Mn ions among the two sublattices in the spinel structure can occur, additional anomalous effects are expected to be seen in the temperature

FIG. 4. $G(\sigma T^{3/2})$ and $e/k d\theta/dT$ plotted against temperature for the specimen $\text{Mn}_{1.075}\text{Fe}_{1.925}\text{O}_4$. (a) and (b) are the results of the heating run, after the quenching of the specimen, (c) and (d) of the cooling run and the following cycles.

dependence of the electrical properties. To separate the magnetic anomaly and the effect of the cation redistribution, detailed measurements were carried out on a single crystal $\text{Mn}_{1.075}\text{Fe}_{1.925}\text{O}_4$, which was quenched from 800 °C to room temperature. In Fig. 3 the results are plotted against the reciprocal temperature, and it can be seen that below 620 K there is a difference between the heating and cooling run. The data of the first cooling run can be reproduced by heating a second time.

In Fig. 4, plots of $G(\sigma T^{3/2})$ and $(e/k)d\theta/dT$ vs T reveal the presence of two minima in G and in the $d\theta/dT$ curve: one at the Néel temperature and another at a temperature T_{cd} , which has to be associated with the cation redistribution. The appearance of the second minimum at T_{cd} in the first heating run indicates that cation redistribution is the cause of this anomaly. In the quenched specimen, an excess of manganese ions is frozen on the octahedral sites; these ions remigrate partially to the tetrahedral sites when the specimen is heated near T_{cd} ,⁵ where the diffusion rate is fast enough to achieve thermal equilibrium. During the subsequent cooling run and the second cycle, the departures from the thermal equilibrium are much smaller than those obtained during the initial quenching run and therefore the minima at T_{cd} will disappear. The small minima at T_N re-

main, which proves that we are dealing with the magnetic anomaly. The negative divergence at T_N although small compared with the cation diffusion anomaly, is consistent with the negative cusp found for manganese ferrite with $0.8 \leq x \leq 1.0$ and can also be described by the previously proposed mean-field model for the magnetic anomalies.^{7,8}

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