Electrical resistivity of ferrites of the general formula $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ (t = 0.1, 0.3, 0.4, 0.5)

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The electrical resistivity of the ferrites $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ (t = 0.1, 0.3, 0.4, 0.5) has been measured in the temperature range of 30 to 300° C. A break in In ρ against 1/T around T_c has been observed. This break is associated with a change in the activation energy around the Curie temperature. The conductivity behaviour is discussed in terms of the cation distribution in these ferrites.

1. Introduction

The physical properties of cubic ferrites with the spinel-type crystal structure have been the subject of many investigations. High electrical resistivity and relatively easy preparation make these materials widely usable for the cores of intermediate and high frequency electromagnetic devices [1, 2]. The system of the general formula $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ $(0 \le t \le 1)$ has the spinel structure, and can be obtained by replacing the Fe³⁺ ions in MgFe₂O₄ by equal amounts of Mg²⁺ and Ti⁴⁺. In the past few years the aim of the magnetic measurements, that were carried out on this system, was to determine the influence of the heat treatment on the magnetic properties of such compounds [3, 4]. The cation distribution and the oxygen parameter for the above mentioned system for slowly cooled and quenched samples have been determined using the intensities of X-ray reflections [5, 6]. From a Mössbauer effect study [7] it was found that the ferrimagnetism in the system $Mg_{1+t}Fe_{2-2t}Ti_tO_4$, may not be described in terms of the Néel theory.

As far as we know the electrical properties of the above mentioned system has never been subjected to an extensive study. In this paper we report on the electrical resistivity of the above mentioned compounds as a function of temperature. The resistivity behaviour is explained in terms of the band picture with a change in the value of the energy gap as the system undergoes magnetic transition.

2. Experimental details

The electrical resistivity measurements were carried out on polycrystalline samples. The samples were prepared by a standard ceramic technique from pure mixtures of the corresponding oxides in calculated proportions, and then dry-ground into fine powder. The resulting powder was well mixed and then calcined at 850° C in air for 6 h soaking time. The mixture was compressed to form pellets with 12mm in diameter and 2.5mm thickness and sintered in air at 1200° C for 6 h soaking time. The samples were gradually cooled to room temperature with a rate of 1 degree per minute. The X-ray diffraction patterns showed that the samples are pure spinels and no extra lines indicative of the starting oxides or any other phases are present. The resistivity measurements were carried out using the two-terminal d.c. method in a range of temperature from 300 up to 600 K.

3. Results and discussion

In Fig. 1 we plot the relation between $\ln \rho$ against 1/T. The following points are to be noted:

1. The resistivity behaves according to the Arrhenius relation

$$o = \rho_0 e^{E/kT}$$

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Figure 1 Relation between $\ln \rho$ (resistivity) against absolute temperature.

where E is the activation energy, k is the Boltzman constant and T is the absolute temperature. From the above relation the activation energy E for the conduction mechanism is found to be in the range 0.4 to 0.7 eV.

2. For each measured sample there exists a break in $\ln \rho$ against 1/T, which takes place at a temperature which, when compared with the reported data, is identified as the Curie temperature.

3. Activation energies in the ferrimagnetic and paramagnetic regions were calculated from the plot $\ln \rho$ against 1/T and it was found that the observed values of the activation energies in the paramagnetic region are higher than those found in the ferrimagnetic region.

4. The resistivity at a given temperature increases with the increase of the titanium concentration.

The Curie temperatures and the activation energies are listed in Table I.

In the system $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ the general

formula of the cation distribution may be given by:

$$(\operatorname{Fe}_{1-x-y}\operatorname{Mg}_{x}\operatorname{Ti}_{y})[\operatorname{Fe}_{1+x+y-2t}\operatorname{Mg}_{1+t-x}\operatorname{Ti}_{t-y}]O_{4}$$

in which the cations enclosed by () occupy the A sites while those enclosed by [] occupy the B sites. However, there is evidence that the values of y are small [8] as the result of the maximum charge neutralization. In otherwords, the tetrahedral Fe³⁺ ions are mainly replaced by Mg²⁺ ions and the octahedral Fe³⁺ ions are replaced by Ti⁴⁺ ions. Therefore, it is reasonable to consider the cation distribution to be of the form:

$$(\mathrm{Fe}_{1-x}^{3+}\mathrm{Mg}_{x}^{2+})[\mathrm{Fe}_{1+x-2t}^{3+}\mathrm{Mg}_{1+t-x}^{2+}\mathrm{Ti}_{t}^{4+}]\mathrm{O}_{4}$$

TABLE I Values of T_{C} and the activation energies for t = 0, 1, 0.3 and 0.4

t	Т _С (К)	$E(T < T_{\mathbf{C}})$ (eV)	$E'(T > T_{\mathbf{C}})$ (eV)	Δ <i>E</i> (eV)
0.1	530	0.61	0.76	0.15
0.3	440	0.41	0.55	0.14
0.4	370	0.38	0.52	0.14



Figure 2 Relation between the Curie temperature $T_{\rm C}$ as obtained from different techniques against titanium concentration (t): (x) magnetic data, (•) authors data and (\circ) Mössbauer effect data.

The Curie temperature $T_{\rm C}$ is roughly proportional to the product of the concentrations of the Fe³⁺ ions in the A and B sites. Accordingly the Curie temperature $T_{\rm C}$ varies with t and x as

$$(1-x)(1+x-2t) = (1-x^2)-2t(1-x).$$

The temperatures at which the breaks in $\ln \rho$ against 1/T take place satisfy the above mentioned relation. In addition, they agree with the reported values of $T_{\rm C}$ [3, 7], see Fig. 2. Therefore we identify these temperatures as Curie temperatures.

The resistivity of the ferrites is controlled by the cation concentration in the B sites. Since the determined activation energy is in the range of 0.4 to 0.7 eV we assume that the conductivity is of an intrinsic nature and governed by the Fe³⁺ concentration in the B site. This explains the increase in resistivity with the decrease of the Fe³⁺ concentration in the B site. The conduction mechanism in ferrites is generally described either using the band picture or the hopping model. According to the band model, the temperature dependence of conductivity is mainly due to the variation of the charge carrier concentration with temperature, while in the hopping model, the change of their mobility with temperature is considered to constitute the conduction current by jumping or hopping from one iron ion to the next.

According to the theory of magnetic semiconductors one expects a decrease in the activation energy E due to the splitting of the conduction and valance bands below $T_{\rm C}$. Above the Curie temperature the bands are degenerate for the two spin directions. One therefore expects a reduction in the activation energy as the system undergoes transition from paramagnetic to ferromagnetic states. This result is also in agreement with the theory developed by Irkin and Turov [9].

Finally we find that the change $\Delta E = E' - E$ is associated with the ordering temperature $T_{\rm C}$ roughly given by the relation

$$\Delta E = qkT_{\mathbf{C}}$$

where E and E' are the activation energies below and above $T_{\rm C}$, respectively. The value of the proportionality constant q is found to be around 3.

In conclusion one may expect that the resistivity behaviour reflects the magnetic ordering that takes place in the system $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ with a change in the activation energy as the system becomes ordered. The electrical behaviour is determined by the concentration of Fe^{3+} ions in the B sites.

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