P. Nicolau
I. Bunget
M. Rosenberg
I. Belciu

Transport Properties of Iron-nickel Ferrites

Abstract: The mechanism of electrical conduction in the magnetic semiconductors $Ni_xFe_{3-x}O_4$ with $0.6 < x \leq 1$ was investigated. The electrical properties of these compounds are extremely sensitive to the presence of α-Fe_2O_3 as a second phase. The exponential temperature dependence of the electrical resistivity ρ and the temperature-independent thermoelectric power θ are in good agreement with an electron-hopping model. The electrical conduction occurs by thermally activated electron hopping between octahedral Fe^{2+} and Fe^{3+} ions with an activation energy q. The values of ρ, q and θ depend on the Fe^{2+} concentration only, and are not sensitive to small deviations from stoichiometry due to the presence of cation or anion vacancies.

Introduction

The electrical properties of $NiFe_2O_4$ and of other compositions of the $Ni_xFe_{3-x}O_4$ system have been investigated and reported by several authors.[1-13] Although many of these favor a hopping mechanism for conduction within the composition range $0.6 < x \leq 1$, the lack of information concerning the chemical composition of the investigated samples leaves much doubt whether the experimental data are in better agreement with a hopping or a band model. On the other hand, some Hall-effect data[5,9,11] provide support for a band-conduction mechanism, and this type of model was used recently by Jefferson and Baker[11] for $Ni_{0.6}Fe_{2.4}O_4$.

This paper deals with the investigation of the electrical properties of 13 chemically well-defined compositions in the $Ni_xFe_{3-x}O_4$ system ($0.6 < x \leq 1$). The results are in fairly good agreement with an electron-hopping mechanism of conduction.

Experimental technique

Polycrystalline samples of 13 compositions (Table 1) in the $Ni_xFe_{3-x}O_4$ system were sintered from oxydic powders prepared in three ways: a) ball-milling of mixtures of NiO and α-Fe_2O_3 (samples 5, 8, 11 and 12); b) co-precipitation of hydroxides followed by firing at 500°C (samples 1 and 9); and c) co-precipitation of mixed oxalates followed by firing at 500°C (samples 2, 3, 4, 6, 7, 10 and 13).

The powders were isostatically pressed at 2000 kg/cm^2 and sintered in the temperature range 1400 to 1450°C in air (samples 1 through 10) or argon (samples 11 through 13), and slow cooled in air (samples 1 through 8) or argon (samples 9 through 13). All 13 compositions were monitored metallographically as well as by x-ray diffraction, and all were identified as single-phase, cubic spinel structures. The "concentrations" (numbers of ions for the $Ni_xFe_{3-x}O_4$ formula unit) of the divalent iron, [Fe^{2+}], the total iron, [Fe], and the nickel, [Ni], were determined chemically[15] and the resulting valency formulas are given in Table 1. The densities of the samples varied from 82 to 94% of the theoretical values; the best results (> 90%) were obtained for the samples prepared from co-precipitated oxalates. The temperature dependences of the dc electrical resistivities ρ and Seebeck coefficients θ (against platinum) were investigated in the interval 20 to 400°C.

Results and discussion

For all the samples the temperature dependence of the electrical resistivity was exponential, described by $\rho = \rho_\infty \exp(q/kT)$. The dependence of ρ, q and θ on the concentration of divalent iron ions is shown in Fig. 1.

In all cases the Seebeck coefficient θ was temperature independent, in disagreement with the results of Samokhvalov and Rustamov,[9] who reported a small decrease in θ with increasing temperature. We did observe this weak temperature dependence of θ in all cases in which the sample was not single phase and in which some α-Fe_2O_3 was detected. Probably the presence of α-Fe_2O_3 as a second phase could explain the anomalous results.

Figure 1 shows that the electrical parameters depend very strongly on the concentration of Fe^{2+} ions. Some scatter of the values due to the presence of oxygen or metallic vacancies in the samples does not severely affect the dependence on [Fe^{2+}].

P. Nicolau is located at the Institute of Physics, Calea Victoriei 114 Bucharest, Romania; I. Bunget and M. Rosenberg are in the Physics Department at the University of Bucharest, Romania; and I. Belciu is at the Politechnical Institute of Bucharest, Romania.

Table 1 Electrical properties of samples in the $Ni_xFe_{3-x}O_4$ system.

Sample	*Composition (valence formula)*	*Mobility μ ($cm^2/V\text{-}sec$)*	*Carrier concentration N ($10^{20}/cm^3$)*	*Transition frequency ν_0 (THz)*
1	$Fe^{3+}(Ni^{2+}\ Ni^{3+}_{0.002}\ Fe^{3+}_{0.998})\ O_4$ [a]	4.08×10^{-9}	1.87	21
2	$Fe^{3+}(Ni^{2+}_{1.04}\ Fe^{2+}_{0.007}\ Fe^{3+}_{0.953})\ O_{3.977}$ [a]	1.37×10^{-8}	0.96	48
3	$Fe^{3+}(Ni^{2+}_{1.03}\ Fe^{2+}_{0.035}\ Fe^{3+}_{0.935})\ O_{3.968}$ [a]	2.97×10^{-5}	4.8	2.04
4	$Fe^{3+}(Ni^{2+}\ Fe^{2+}_{0.04}\ Fe^{3+}_{0.96})\ O_{3.98}$	1.22×10^{-5}	5.5	2.68
5	$Fe^{3+}(Ni^{2+}_{0.918}\ Fe^{2+}_{0.049}\ \square_{0.011}\ Fe^{3+}_{1.022})\ O_4$	2.44×10^{-5}	6.74	1.16
6	$Fe^{3+}(Ni^{2+}_{0.98}\ Fe^{2+}_{0.053}\ Fe^{3+}_{0.967})\ O_{3.974}$	2.92×10^{-5}	7.28	1.66
7	$Fe^{3+}(Ni^{2+}_{0.88}\ Fe^{2+}_{0.06}\ \square_{0.02}\ Fe^{3+}_{1.04})\ O_4$	1.825×10^{-4}	7.98	1.67
8	$Fe^{3+}(Ni^{2+}_{0.84}\ Fe^{2+}_{0.115}\ \square_{0.015}\ Fe^{3+}_{1.03})\ O_4$	3.1×10^{-4}	15.8	2
9	$Fe^{3+}(Ni^{2+}_{0.99}\ Fe^{2+}_{0.12}\ Fe^{3+}_{0.89})\ O_{3.945}$	5.04×10^{-4}	16.5	1.57
10	$Fe^{3+}(Ni^{2+}_{0.89}\ Fe^{2+}_{0.142}\ Fe^{3+}_{0.968})\ O_{3.986}$	5.12×10^{-4}	19.85	1.8
11	$Fe^{3+}(Ni^{2+}_{0.856}\ Fe^{2+}_{0.144}\ Fe^{3+})\ O_4$	5.6×10^{-4}	19.8	1.37
12	$Fe^{3+}(Ni^{2+}_{0.92}\ Fe^{2+}_{0.205}\ Fe^{3+}_{0.875})\ O_{3.94}$	1.23×10^{-3}	28.1	1.78
13	$Fe^{3+}(Ni^{2+}_{0.637}\ Fe^{2+}_{0.38}\ Fe^{3+}_{1.017})\ O_{3.992}$	7.45×10^{-3}	60	1.72

[a] Calculated from the Seebeck coefficient.

The exponential temperature dependence of ρ and the lack of any temperature dependence of θ can be explained using an electron-hopping mechanism of conduction.[14] In this model an Fe^{2+} ion contributes, above room temperature, a mobile electron that moves among the octahedral-site iron atoms and has a thermally activated mobility. Under such an assumption the values of θ can be correlated with those of the concentrations of the octahedral Fe^{2+} and Fe^{3+} ions of the spinel lattice by means of the formula

$$\theta = \frac{k}{e}\left(\log_e \frac{[Fe^{3+}]}{[Fe^{2+}]} + a\right), \qquad (1)$$

where a is the kinetic term that takes values in the range 0 to 1. In the case of high-resistivity and low-mobility semiconductors the value of a is small and in most cases can be neglected. Indeed, good agreement between experimental and calculated values of θ was obtained (Fig. 1) for $0 < [Fe^{2+}] \leq 0.2$ by neglecting a.

If the Fe^{2+} concentration is assumed to be the carrier concentration (Table 1, column 4), the room-temperature values of the mobility (Table 1, column 3) can be obtained from the relation $\sigma = ne\mu$ for a diffusion-like hopping process; here

$$\mu = (eS\nu_0/kT)\exp(-q/kT), \qquad (2)$$

S is the average surface for carrier diffusion, and ν_0 is the maximum frequency of the transition between two neighboring octahedral sites. Taking for S a value corresponding to the crystallographic data of $NiFe_2O_4$, we also computed the frequency ν_0 (Table 1, column 5).

For all of the n-type samples the values of ν_0 are concentrated in a narrow range between 1.16 THz and 2.68 THz. These values are close to the first two vibrational frequencies of 1.8 THz and 7.2 THz detected by Waldron[16] in the infrared absorption spectrum of $NiFe_2O_4$. This narrow range of ν_0 values corresponds to a basic requirement of the theory of the hopping mechanism of conduction. The very weak dependence of ν_0 on $[Fe^{2+}]$ is probably due to the fact that the total concentration of the divalent ions, $[Ni^{2+}] + [Fe^{2+}]$, on octahedral sites is the same for all the n-type samples investigated, so that the interaction coefficients are not strongly affected by changes in composition.

As ν_0 is relatively constant, the composition dependence of the carrier mobility is basically due to changes in the activation energy q with the carrier concentration. The most dramatic decrease of q occurs for $0 < [Fe^{2+}] < 0.2$. It is to be expected that q is less sensitive to changes in carrier concentration above that concentration for which, on the average, there is at least one carrier in the first metallic coordination sphere of an Fe^{2+} ion. This con-

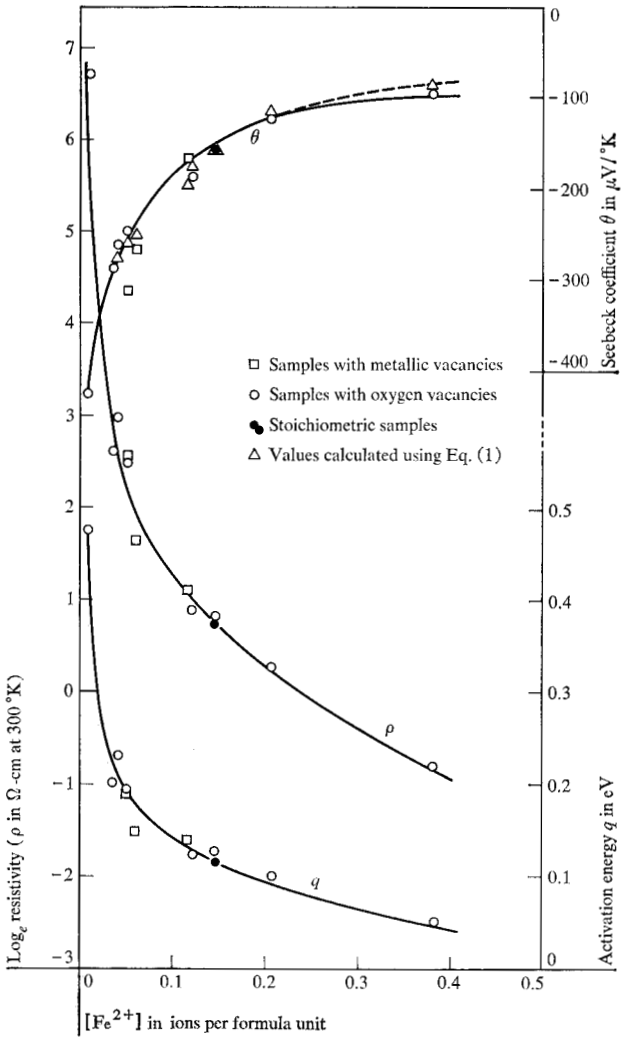

Figure 1 Electrical resistivity ρ, activation energy q, and Seebeck coefficient θ plotted as functions of the concentration [Fe^{2+}] of the iron ions.

centration corresponds to a value of [Fe^{2+}] of about 0.3, which is close to the value above which the composition dependence of θ begins to differ from that given by Eq. (1). This disagreement probably indicates that, above the range of concentration $0.2 < [Fe^{2+}] < 0.3$, the conditions for applicability of small polaron theory are no longer fulfilled.

It should be pointed out that a difference of an order of magnitude exists between our drift mobility and the Hall mobility reported by Lavine[5] for $Ni_{0.75}Se_{2.25}O_4$. This discrepancy can be understood in the frame of the theory of the Hall effect in the polaron model.[17]

Sample 1 (see Table 1) has a positive but very small Seebeck coefficient, $\theta \approx +550\ \mu V/°K$. The plus sign can be ascribed to electron jumps between the Ni^{2+} and Ni^{3+} ions; the low value of the mobility is characteristic of a hopping process involving localized holes in ferrites.[14]

Summary

The results of the investigation of the electrical properties of the $Ni_xFe_{3-x}O_4$ system in the composition range $0.6 < x \leq 1$ can be explained with a hopping mechanism of conduction and a small polaron model for the more limited range $0.8 < x \leq 1$. Preliminary results show that for $0 < x < 0.6$ one does not find satisfactory agreement with hopping-model theory; the discrepancy increases for lower values of x, i.e., as the composition approaches that of Fe_3O_4.

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