# Effect of conduction electrons on exchange interactions in single crystals of the $Mn_xFe_{3-x}O_4$ system

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The effect of conduction electrons on the exchange interaction in manganese ferrite film single crystals is investigated by using the method of contact potential difference. The influence of conduction electrons on saturation magnetization and on the Neél temperature is shown experimentally. An interpretation is given for the observed effect.

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It was shown theoretically[1] that the indirect exchange interaction of transition-element cations via conduction electrons may be important at concentrations of the

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latter of the order of $10^{25}-10^{26}$ m$^{-3}$. The indirect exchange effect was studied experimentally in materials with a high concentration of carriers-rare-earth oxides and chalcogenides.[2]

The purpose of this work is to verify experimentally the effect of conduction electrons on the exchange interactions in manganese ferrite single crystals, for which $n$-type conductivity is characteristic.

The method of potential contact difference is used to measure the concentration of conduction electrons in the bulk of a magnetic semiconductor. In the physics and technology of ordinary semiconductors, this method has been widely used to produce regions of space charge (RSC) in the contact zone of materials with different work functions. It is convenient to combine this method with the film geometry of the samples (the RSC are propagated in the bulk).

Film single crystals of $Mn_xFe_{3-x}O_4$ with $x = 0.7$ and 1.5 and a thickness of 1 $\mu$m, which were grown epitaxially on the surface of a manganese oxide crystal by the chemical transport reaction technique, were investigated. The 0.05 to 0.1-$\mu$m-thick platinum films were deposited on the (001) surface of $Mn_xFe_{3-x}O_4$ single crystals by thermal sputtering in vacuum. The choice of metal was predicted by a record high value of the work function ($\sim$6 eV).

The chemical composition and thickness of the films were controlled by x-ray spectrum fluorescence analysis. The magnetic measurements were carried out by the method of mechanical moments in a constant magnetic field of 8–16 kOe.

Measurements of $M_S$ and $T_N$ were carried out for a series of samples obtained in a single prepared batch and in different batches. Unambiguous results were obtained in all the cases: the $M_S$ and $T_N$ for the two-layer systems $Mn_{1.5}Fe_{1.5}O_4$-Pt are always less than for individual films. Qualitatively, the results were somewhat different for a number of samples from different prepared batches, which accounts for the different contact surface finish (not controlled in the experiment). The effect of the contact field on the exchange characteristics of single crystals of $Mn_{0.7}Fe_{2.3}O_4$ was not evident.

According to Ref. 3, the $Fe^{2+}$ and $Fe^{3+}$ ions of different valence are located simultaneously in the octahedral positions of the $Mn_xFe_{3-x}O_4$ spinel It is clear that the donor $Fe^{2+}$ ions are the source of the conduction electrons. Their density can be estimated by the equation

$$n \approx N \exp(-E/kT),$$

where $N$ is the concentration of the $Fe^{2+}$ ions and $E$ is the activation energy of the impurity conductivity.

Using the experimental data for the activation energy of manganese ferrite,[4] we obtain $n \cong 0.5\times10^{22}$ m$^{-3}$ for $Mn_{1.5}Fe_{1.5}O_4$ and $n \approx 0.2\times10^{27}$ m$^{-3}$ for $Mn_{0.7}Fe_{2.3}O_4$. The average depth of the RSC, according to Ref. 5, is

$$d \approx (2V_C \epsilon_0 \epsilon/en)^{1/2},$$

where $V_C$ is the potential contact difference, $\epsilon_0\epsilon$ is the absolute dielectric constant, and $e$ is the electron charge.

For $Mn_{1.5}Fe_{1.5}O_4$ the depth of the RSC is $d \approx 7\times10^{-7}$ m; for $Mn_{0.7}Fe_{2.3}O_4$ we

TABLE I

| Sample | $M_S$, G | $T_N$, K |
|---|---|---|
| $Mn_{1,5}Fe_{1,5}O_4$ | 172 ± 6 | 480 ± 5 |
| $Mn_{1,5}Fe_{1,5}O_4$ – Pt | 62 ± 2 | 423 ± 5 |
| $Mn_{0,7}Fe_{2,3}O_4$ | 280 ± 9 | 690 ± 5 |
| $Mn_{0,7}Fe_{2,3}O_4$ – Pt | 280 ± 9 | 690 ± 5 |

have $d \approx 7 \times 10^{-10}$ m. The large concentration of conduction electrons in manganese ferrite with $x = 0.7$ does not vary significantly the magnetic properties, since in this case the donor ions in one- and two-atomic layers become ionized. For $Mn_{1.5}Fe_{1.5}O_4$ the situation is better: of the order of $10^3$ atomic layers of the semiconductor are ionized.

Therefore, the conduction electrons in manganese ferrite at concentrations of the order of $10^{22}$ $m^{-3}$ have an important effect on the exchange interaction. We can validly assume that the indirect exchange via the conduction electrons (at given concentrations of the latter) does not occur in the entire volume of the crystal, but in certain microregions within it. It is known that for compositions $1 < x < 1.8$ the manganese ferrite has a tendency to break down into microregions (clusters) enriched with $Mn^{3+}$ ions with a local tetragonal symmetry while maintaining the overall cubic symmetry of the crystal.[6,7] It was concluded in Ref. 6 on the basis of the measurements of the temperature variation of the Seebeck coefficients and of the electrical resistivity, that the conduction electrons are concentrated in these microregions. Therefore, they have an enhanced concentration of electrons, which is sufficient for the indirect exchange. The indicated microregions and the interaction between them contribute to the magnetic properties of the crystal.


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