Connection of Thermopower, Magneto Thermopower with Resistivity and Magnetoresistivity in Nd\(_{(1-x)}\)Sr\(_x\)MnO\(_3\) and Sm\(_{(1-x)}\)Sr\(_x\)MnO\(_3\) Manganites

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Abstract: An experimental study of thermopower, magneto thermopower, magnetoresistivity and magnetization of Nd\(_{(1-x)}\)Sr\(_x\)MnO\(_3\) and Sm\(_{(1-x)}\)Sr\(_x\)MnO\(_3\) with 0 ≤ \(x\) ≤ 0.3 was conducted. A steep rise of thermopower as well as giant values of magneto thermopower and magnetoresistivity were observed near Curie temperature \(T_C\) in compounds with 0.15 ≤ \(x\) ≤ 0.3. On the other hand, no special features were found in case of \(x\) = 0. It has been known that compounds with 0.1 ≤ \(x\) ≤ 0.3 consist of ferromagnetic clusters of ferron (magnetic polaron) type located in A-type antiferromagnetic matrix. An increase of thermopower near \(T_C\) is caused by ferrons as with the application of magnetic field or temperatures higher than \(T_C\) thermopower falls sharply due to the destruction of ferrons. So, the value of thermopower is directly connected to the number of magnetic polarons in sample. Therefore, thermopower in doped magnetic semiconductors is determined by level of doping and volume of the sample.

Keywords: Manganites, Thermopower, Magneto Thermopower, Magnetoresistance, Magnetic Polaron, Magnetization

1. Introduction

At present, the practical application of thermoelectricity is mostly limited to temperature measurement elements and thermoelectric cooling modules, which are used in various areas from cooling systems for electronics to medical and home coolers and fridges (for example, coolers in cabins of train drivers). Thermoelectricity is rarely used in large cooling devices due to low energy conversion efficiency (ECE), which could be calculated for thermoelectric material as:

\[ ZT = S^2\sigma / k \]  

where \(S\) is thermopower, \(\sigma\) – specific electric conductivity, \(k\) – coefficient of thermal conductivity. Presently, \(ZT\) of the best thermoelectric materials does not surpass one. From the last century, Bi\(_2\)Te\(_3\) with various additions or prepared using special processes is considered the most promising thermoelectric material. In this paper, it was demonstrated that the value of thermopower in magnetic semiconductors could be significantly enhanced via doping and increment of the volume of sample. Similar results were reported in earlier paper [1].

Increased value of \(S\) which reached hundreds of mV, was observed in some manganites near Curie temperature \(T_C\) [2-4]. Authors of this works linked it to the formation of polarons with small radiuses (small polarons) near \(T_C\). It is known that the small polarons are observed in non-magnetic semiconductors, and their occurrence only near Curie temperature in magnetic semiconductors is not discussed in [2-4]. Moreover, sizes of studied samples are not provided in
works mentioned above, so no investigations concerning dependence of thermopower on volume were carried out. It should be brought to attention, that before work [1], it was believed that thermopower doesn’t depend on sample sizes.

As is seen from short report [1], thermopower in magnetic-semiconductor system Sm$_{1-x}$Sr$_x$MnO$_3$ (0.15 ≤ $x$ ≤ 0.3) could be widely regulated by doping level and sample size. In this work, it was provide results from measurements of thermopower, magneto thermopower, electric resistivity and magnetoresistance along with other properties of Nd$_{1-x}$Sr$_x$MnO$_3$ (0.15 ≤ $x$ ≤ 0.3) system. This result support conclusions reached in [1].

The interest in magnetic semiconductors has been inspired by the observed phenomenon of colossal magnetoresistance and volume magnetostriction in the vicinity of $T_c$ [5-7]. Most researchers now explain these effects as being results of the existence of special magnetic-impurity states called ferrons, the theory of which has been developed in [8-12]. The idea of a “ferron” consists of the notion that an electron of a donor (or a hole of an acceptor) creates around the impurity a microscopic ferromagnetic region, a ferron, due to a gain in the s–d exchange energy.

Figure 1. Temperature dependence of magnetization M(T) for Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ in various magnetic fields and different cooling conditions (ZFC – zero field cooling, FC – field cooling).

Figure 2. Temperature dependence of magnetization M(T) for Sm$_{0.7}$Sr$_{0.3}$MnO$_3$ in various magnetic fields.
Explaination of results, obtained for both systems studied in this work, is based on existence of ferrons in these systems. Inside ferrons the crystalline lattice is compressed as discussed in [11, 12]. In ferromagnetic semiconductors, magnetic polarons exist only near \( T_C \), where the long-range ferromagnetic order is partly or completely broken, and rapidly disappear with further increase in the temperature. In antiferromagnetic semiconductors, the electron density is increased near impurities (compared to other regions of the crystal), so the crystal consists of antiferromagnetic matrix in which ferromagnetic spheres (collective ferrons) with increased electron density are symmetrically located. Through study of data from neutron and electron scattering as well of magnetic properties of \( \text{Sm}_x\text{Sr}_{1-x}\text{MnO}_3 \) system provided in [13-16], it has been shown that in compounds with \( x \leq 0.33 \) clusters of ferron type located in A-type antiferromagnetic matrix are present. Whereas in the compounds with \( 0.45 < x < 0.5 \) are clusters with antiferromagnetic charge-orbital ordering in which the lattice parameters reduce. In these compositions in the Neel temperature of the CE-type antiferromagnetic clusters is discovered, the maximum of the thermopower and giant negative magnetothermopower [17-19].

2. Experiment

Rectangular single-crystalline samples of \( \text{Nd}_{1-\alpha}\text{Sr}_\alpha\text{MnO}_3 \) (with \( x = 0, 0.15, 0.2, 0.3 \)) and \( \text{Sm}_{1-\alpha}\text{Sr}_\alpha\text{MnO}_3 \) (\( x = 0, 0.15, 0.2, 0.25, 0.3 \)) were prepared through crucible-less floating zone melting method. Phase composition and lattice parameters were controlled with x-ray diffractometer Siemens D5000. Single-phase samples had the structure of perovskite with orthorhombic structure (Pnma group). A temperature gradient of 5 K across the sample for the thermopower \( S \) and magneto-thermopower \( \Delta S/S \) measurements was created using the electrical furnace (thin constantan wire) located on one end of the sample. Three copper-constantan thermocouples were used to measure temperature difference between hot and cold ends of the sample and temperature \( T \) at the middle of the
sample. The voltage difference between ends of the sample was determined using an analog-to-digital NI-9211 module with input impedance of 20 MΩ capable of measuring small voltages with a typical relative error of 0.5%. Sample was placed into a specially constructed insert from which the air was pumped to avoid condensation of vapor and submerged in liquid nitrogen. Temperature was set using electrical furnace wound on the inner surface of the insert. Influence of different magnetic fields \( H \) on thermopower was studied using an electromagnet. The magnetization \( M \) was measured by a SQUID magnetometer. The electric resistivity \( \rho \) and magneto-resistance \( \Delta \rho / \rho \) were determined using the four-point-probe method. Measurements of thermopower, resistivity and magnetization were conducted on two samples cut from single crystal in the shape of identical parallelepipeds in a way that the longest edge was parallel to \( c \) axis (or \( ab \) plane) of orthorhombic structure. \( C \) axis or \( ab \) plane were orientated parallel to magnetic field during measurements. \( M(T) \), \( M(H) \) and also \( S(T) \), \( S(H) \); \( \Delta S/S(T) \), \( \Delta S/S(H) \) and \( \rho(T) \), \( \rho(H) \) were almost identical for the pair of each compound. This indicates small magnetic and crystallographic anisotropy.

### 3. Results and Discussions

Figures 1 and 2 show the temperature dependence of magnetization \( M(T) \) for \( \text{Nd}_{0.85}\text{Sr}_{0.15}\text{MnO}_3 \) and \( \text{Sm}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \) measured in various magnetic fields and different cooling conditions (ZFC – zero field cooling, FC – field cooling). From these dependencies, the following conclusions can be reached that the transition from ferromagnetic to paramagnetic state is heavily blurred and occurs in a temperature range of about 100 K. It should be noted, that in homogeneous ferromagnetics this transition usually happens during a little degrees K. Moreover, in low magnetic fields, there is a difference between the magnetizations of FC and ZFC samples. The following was observed for both compounds: in case of low temperatures and strong magnetic fields (maximum value of magnetic field reached 50 kOe) magnetic moment per chemical unit is lower by order of magnitude compared to the value achieved in fully ferromagnetically ordered moments of \( \text{Mn}^{3+} \) and \( \text{Nd}^{3+} \) ions (or \( \text{Mn}^{3+} \) and \( \text{Sm}^{3+} \) ions). Samples with other doping levels exhibited similar temperature dependences of magnetization \( M(T) \). ZFC and FC curves are also similar to the ones presented on Figure 1 and Figure 2 for \( x = 0.3 \). However, in case of \( T < 30 \text{ K} \) and strong magnetic fields \( M(T) \) dependence is different for \( \text{Nd}_{0.85}\text{Sr}_{0.15}\text{MnO}_3 \) system and \( \text{Sm}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \) system. From comparing Figure 1. and Figure 2, it will be obvious that \( \text{Nd} \) system shows a steep rise of magnetization as the temperature gets lower, while in \( \text{Sm} \) system magnetization at some point reaches saturation and does not change with further fall of temperature. It was established that experimental dependencies \( M(T) \) for \( \text{Nd} \) sample in temperature range of \( T \leq 30 \text{ K} \) satisfy the following equation that describes magnetization of superparamagnetic materials:

\[
M = L \left( \mu_c H \right)
\]

where \( L(x) = ch(x) - \frac{1}{x} \) is a Langevin function (2).

Magnetic moments of superparamagnetic clusters \( \mu_c \) for all \( \text{Nd} \) compounds were obtained by selecting suitable \( \mu_c \) in equation (2) to fit experimental curve \( M(T) \) for \( T \leq 30 \text{ K} \). The results are shown in table 1 along with the number of molecular units per cluster for ferromagnetic (FM) and ferrimagnetic (FIM) ordering of \( \text{Nd} \) and \( \text{Mn} \) ions. Apparently, magnetization in this temperature range is caused only by orientation of magnetic moments of superparamagnetic clusters by magnetic field. It should be noted, that results of earlier works [20-24] dedicated to study of magnetization in \( \text{Nd} \) manganites indicate that saturation was not reached in fields of several Tesla that is caused by slanted or ferrimagnetic ordering of \( \text{Nd} \) and \( \text{Mn} \) magnetic moments. Study of neutron diffraction in neodymium manganites showed that \( \text{Nd} \) and \( \text{Mn} \) sublattices tend to order ferromagnetically [21].

![Figure 6. Temperature dependence of magneto thermopower \( \Delta S/S(T) \) in various magnetic fields for \( \text{Nd}_{0.85}\text{Sr}_{0.15}\text{MnO}_3 \).](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic moment of single cluster, ( \mu_n )</th>
<th>Magnetic moment of single molecule, ( \mu_n )</th>
<th>Number of molecules in cluster in case of FM ordering of ( \text{Nd} ) and ( \text{Mn} )</th>
<th>Number of molecules in cluster in case of FIM ordering of ( \text{Nd} ) and ( \text{Mn} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Nd}<em>{0.85}\text{Sr}</em>{0.15}\text{MnO}_3 )</td>
<td>43</td>
<td>4.227</td>
<td>5</td>
<td>24</td>
</tr>
<tr>
<td>( \text{Nd}<em>{0.8}\text{Sr}</em>{0.2}\text{MnO}_3 )</td>
<td>64</td>
<td>4.006</td>
<td>6-7</td>
<td>32</td>
</tr>
<tr>
<td>( \text{Nd}<em>{0.4}\text{Sr}</em>{0.6}\text{MnO}_3 )</td>
<td>44</td>
<td>4.268</td>
<td>4-5</td>
<td>22</td>
</tr>
</tbody>
</table>

On the other hand, when temperature is higher than 30 K, as shown on Figure 1, superparamagnetic clusters containing \( \text{Nd} \) are no longer present and magnetization curve \( M(T) \) is mostly caused by ions of \( \text{Mn} \). A difference between FC and ZFC curves is observed in this temperature range. This indicates the presence of microregions with frustrated bonds.
The transition from this type of magnetization to paramagnetic state is blurred and occurs in a temperature range of about 100 K, while in homogeneous ferromagnets this transition is abrupt and happens during a couple degrees K. This magnetically-inhomogeneous state is caused by the existence of magnetic impurities – ferrons, that form near impurities – ions of $\text{Sr}^{2+}$ [8-10]. These ferromagnetic microregions are located in antiferromagnetic matrix of NdMnO$_3$ in the first system and SmMnO$_3$ in the second system. It is evident that Curie temperatures of compounds with $0.1 \leq x \leq 0.3$, presented in [24, 16], are conditional, as they represent temperatures at which ferrons near impurities cease to exist. All Curie temperatures for compounds studied in our work were determined by the position of minimum on $dM(T)/dT$ curves in low magnetic field of 100 Oe, as shown on Figure 3 for Sm$_{0.7}$Sr$_{0.3}$MnO$_3$. They coincide with $T_C$ values from works [24, 16].

Figures 4, 5a demonstrate temperature dependence of thermopower $S(T)$ in various magnetic fields for Nd$_{0.85}$Sr$_{0.15}$MnO$_3$ and Sm$_{0.2}$Sr$_{0.8}$MnO$_3$ samples with the sizes of 11 mm x 2.5 mm x 3 mm. As can be seen from these graphs, a maximum occurs near Curie temperatures of 120 K for the first sample and 87 K for second sample. Moreover, thermopower reaches a giant value of 18 mV/K in case of the second sample. Temperature dependence of magneto thermopower $\langle\Delta S/S\rangle(T)$ for various magnetic fields is presented on figures 6 and 7. Magneto thermopower is negative and its absolute value reaches 63% in the first sample near $T_C$ and 94.5% in the second (for magnetic field of 13.23 kOe). Similar behavior of thermopower and magneto thermopower curves was also observed in all other samples studied in this works. Maximum values of $S$ and $|\Delta S/S|$ measured near $T_C$ are presented in table 2. All samples exhibited giant values of these properties.

![Figure 7. Temperature dependence of magneto resist ance $\langle\Delta \rho/\rho\rangle(T)$ in various magnetic fields for Nd$_{0.85}$Sr$_{0.15}$MnO$_3$.](image)

Figure 7 shows temperature dependency of magnetoresistance $\langle\Delta \rho/\rho\rangle$ in various magnetic fields for Nd$_{0.85}$Sr$_{0.15}$MnO$_3$. It can be seen, that giant negative magnetoresistance was recorded near $T_C$. This effect is common for doped magnetic semiconductors and most researches explain it by existence of ferrons. Maximum values of $\rho$ and $|\Delta \rho/\rho|$ observed during measurements of all samples are presented in table 2.

![Figure 8. Schematic representation of magnetic polarons (ellipsoids) and their role in creation of thermopower in magnetic semiconductors.](image)

It must be emphasized that curves: $\rho(T)$ and $S(T)$, $\langle\Delta \rho/\rho\rangle(T)$ and $\langle\Delta S/S\rangle(T)$ show similar behavior. This indicates that thereof similarities were caused by the same reason – existence of ferrons. Giant thermopower and negative magneto thermopower implies that thermopower in these compounds is primarily caused by ferrons. This is further confirmed by the fact that thermal or magnetic destruction of ferrons causes a sharp decrease of thermopower. As shown on Figure 8, thermopower $S_I$ appears on every single ferron under the influence of local temperature gradient $\Delta T_I$, caused by total temperature gradient $\Delta T$. Each such microregion contributes
Nd power conservation law temperature gradients be greatly increased by enlarging of the volume of the magnetization curves of temperature in the compositions temperature. Superparamagnetic behavior of the observed giant negative magnetoresistance near the Curie which represents the antiferromagnetic A-type matrix which 

measurements of undoped NdMnO$_3$ to the thermopower of AFM matrix without ferron. Our measurements of undoped NdMnO$_3$ (also presented in table 2) showed that thermopower is almost nonexistent in this sample with the maximum value of 0.2 µV/K. So, contribution from ferrons defines the effective thermopower of the whole sample. Consequently, thermopower in doped magnetic semiconductors is defined by concentration of doping agent and volume of the sample. Moreover, due to power conservation law temperature gradients $\Delta T_i$ on ferron microregions are created from heat transferred into sample to create gradient $\Delta T$. Thus, coefficient of thermal conductivity of the whole sample is lowered as a substantial part of the whole sample. As known, in nonmagnetic semiconductors thermopower does not depend on the sample's volume. As known, in nonmagnetic semiconductors thermopower does not depend on the sample’s volume.

4. Conclusion

1. Curves of magnetization with temperature for compositions Nd$_{1-x}$Sr$_x$MnO$_3$ and Sm$_{1-x}$Sr$_x$MnO$_3$ manganites indicate a magnetically inhomogeneous state, which represents the antiferromagnetic A-type matrix which contains a ferromagnetic microregions. These ferromagnetic microregions of ferron type, since in these materials is observed giant negative magnetoresistance near the Curie temperature. Superparamagnetic behavior of the magnetization curves of temperature in the compositions Nd$_{1-x}$Sr$_x$MnO$_3$ below temperatures of 25 K was observed from which the magnetic moment of a superparamagnetic cluster was determined. It can be attributed as the ferromagnetic and the ferrimagnetic ordering of the moments of the ions Nd and Mn.

2. In the compositions near the Curie temperature discovered high thermopower and giant negative magneto thermopower, which are accompanied by high specific resistance and a maximum of giant negative magnetoresistance. It is shown that the thermopower is determined by the level of impurities and the sample volume.

3. Thus, in doped magnetic semiconductors, which include manganites, the value of thermopower can be significantly increased, in comparison with undoped one, by increasing the concentration of impurities and the volume of the sample. Furthermore, thermomaterials based on magnetic semiconductors should be characterized by specific thermopower, that is the value of thermopower per unit volume.

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References


