Magnetocapacity of manganese sulphides substituted by thulium ions

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Abstract. The capacity and the dielectric loss tangent of a Tm$_x$Mn$_{1-x}$S ($x=0.05$, $x=0.1$) solid solution in the frequency range (1–300) kHz without field $H=0$ and in a magnetic field of $H=8$ kOe in the temperature range (80–500) K were measured. The increase of dielectric permittivity and the maximum of dielectric losses at high temperatures were found. The shift of the maximum of the imaginary part of the permittivity towards high temperatures with increasing concentration is found. The magnetocapacitance effect for two compositions and change the sign of magnetocapacity with increasing concentration were revealed. The magnetocapacity is explained in terms of the model with orbital electron ordering.

1. Introduction

Materials based on solid solutions, which show the relationship of magnetic and dielectric properties are interesting both from fundamental and practical standpoints. Of a particular attention are materials that demonstrate magnetoelectric properties at room and higher temperatures due to their practical application in microelectronics for data recording and storage [1].

Among such studied materials is BiFeO$_3$ bismuth ferrite [2]. The giant magnetocapacitance effect was observed in LuFe$_2$O$_4$ at room temperature and was explained by fluctuations of charges with different values of spins in Fe$^{2+}$ and Fe$^{3+}$ [3] ions as a result of splitting between two types of the charge order by an external magnetic field.

Orbital degeneracy in manganese sulfide MnS can occur as a result of the substitution of the divalent manganese ion with trivalent thulium ion at n-type doping. Thulium sulfide TmS is a metal and has the same crystal and magnetic structure as that of the MnS semiconductor. Orbital ordering is possible due to strong electron correlations in MnS.

Nonuniform electrical system with orbital degeneration can be obtained by the substitution of trivalent thulium ions for bivalent manganese ions. The manganese sulfide MnS is semiconductor and thulium sulphide TmS is degenerate semimetals, the electrical resistances of which differ by factors of $10^6$–$10^9$ [4].

Thulium sulphide TmS and manganese sulphide MnS have an antiferromagnetic structure of the second-type ordering with the Neel temperatures $T_N = 63$ K and $T_N = 137$ K respectively. The spin-orbital and the Jahn–Teller interactions split $t_{2g}$ – electronic states and induce the spin splitting of the spectrum of electron excitations. As a result, the dielectric properties can be controlled by electric and magnetic fields [5].

The aim of this work is to establish the effect of the magnetic field on the dielectric properties in the spin-disordered region in solid solutions Tm$_x$Mn$_{1-x}$S.
2. Experimental results and discussion

The Tm$_{x}$Mn$_{1-x}$S solid solutions were synthesized by the solid-phase reaction method described in [6] from powders of the initial compounds in evacuated quartz ampoules in a single-zone resistance furnace. The phase composition and the crystal structure of the Tm$_{x}$Mn$_{1-x}$S samples were studied at 300 K using a DRON-3 diffractometer with CuK$_\alpha$ – radiation. The X-ray diffraction data showed that the synthesized compounds have a NaCl-type face-centered cubic (fcc) structure typical of manganese monosulphide. As the concentration of cation (X) increases, unit cell parameter $a$ increases from $a$ = 0.5440 nm for MnS to $a$ = 0.5520 nm for Tm$_{0.1}$Mn$_{0.9}$S [7, 8].

Figure 1. The real Re($\varepsilon$) (a, b) and imaginary Im($\varepsilon$) (c, d) components of the permittivity from temperature for the sample Tm$_{0.05}$Mn$_{0.95}$S at without field $H$ = 0 at frequencies of $\omega$ = 1 (1), 10 (5), 100 (9) kHz (a, c) and $\omega$ = 5 (3), 50 (7), 300 (11) kHz (b, d) and in a magnetic field of $H$ = 8 kOe at frequencies of $\omega$ = 1 (2), 10 (6), 100 (10) kHz (a, c) and $\omega$ = 5 (4), 50 (8), 300 (12) kHz (b, d).

The capacity and the dielectric loss tangent (tg $\delta$) were measured using an AM-3028 component analyzer in the temperature range 80–500 K in a zero magnetic field H=0 and in a magnetic field of H = 8 kOe. The magnetic field was applied parallel to the capacitor sheets [9, 10]. The magnetocapacitance effect $\delta \varepsilon = (\text{Re}(\varepsilon(H)) - \text{Re}(\varepsilon(0))/\text{Re}(\varepsilon(0)$ is determined as a result of the studies of the complex dielectric permittivity.

The spectral and temperature dependences of the dielectric constants can be used to the observation of the dipole electric moment and the determination of its characteristics, even when we are dealing with a local dipole moment in small clusters without a long-range order. The dielectric properties also give information of the charge transport and the processes of the charge ordering. The response of the dielectric properties on the action of a magnetic field gives a possibility of determining the main mechanisms that determine the correlation of the dielectric and the magnetic properties [11-13].

Figure 1 shows the temperature dependences of the real Re($\varepsilon$) (a, b) and imaginary Im($\varepsilon$) (c, d) parts of the dielectric permittivity of the Tm$_{0.05}$Mn$_{0.95}$S. sample. The real part of the dielectric
permittivity is increased and the maximum of dielectric loss is shifted at $T > 400$ K to high temperatures with frequency increasing.

Figure 2. The real $\text{Re}(\varepsilon)$ $(a, b)$ and imaginary $\text{Im}(\varepsilon)$ $(c, d)$ components of the permittivity from temperature for the sample $\text{Tm}_{0.1}\text{Mn}_{0.9}\text{S}$ a without field $H = 0$ at frequencies of $\omega = 1$ (1), 5 (3), 10 (5) kHz $(a, c)$ and $\omega = 50$ (7), 100 (9), 300 (11) kHz $(b, d)$ and in a magnetic field of $H = 8$ kOe at frequencies of $\omega = 1$ (2), 5 (4), 10 (6) kHz $(a, c)$ and $\omega = 50$ (8), 100 (10), 300 (12) kHz $(b, d)$.

Magnetocapacity is shown in figure 3a and attend 18% for composition $\text{Tm}_{0.05}\text{Mn}_{0.95}\text{S}$. The magnetocapacity is decreased and reaches a minimum of about 20% at the temperature $T=400$ K for all frequencies. The decrease in the dielectric permittivity in the magnetic field is caused by the spin-orbit interaction and the formation of a dipole glass.

Figure 2 shows the temperature dependences of the real $\text{Re}(\varepsilon)$ $(a, b)$ and imaginary $\text{Im}(\varepsilon)$ $(c, d)$ parts of the dielectric permittivity of the sample $\text{Tm}_{0.1}\text{Mn}_{0.9}\text{S}$. The dispersion of inhomogeneous electronic states and local magnetic fields is growth at increasing of the concentration of thulium ions. Temperatures maximum of the imaginary part of the dielectric permittivity for $x = 0.1$ (figure 2) practically do not shift in a magnetic field, and the value of dielectric losses increases. The dielectric permittivity increases in the magnetic field (figure 2a), the magnetocapacity is positive for all temperature range (figure 3b).

The imaginary part $\text{Im}\varepsilon$ has an inflection point at $T = 580$ K without magnetic field at low frequencies for composition $\text{Tm}_{0.1}\text{Mn}_{0.9}\text{S}$ (figure 2c). At heating the imaginary part $\text{Im}\varepsilon$ decreases with increasing frequency (figure 2d) and the dielectric permittivity increases at the magnetic field.
Figure 3. Dependence of magnetocapacity $\delta \varepsilon$ on temperature $T$ for samples $\text{Tm}_x \text{Mn}_{1-x} \text{S}$ with concentrations $x = 0.05$ (a), 0.1 (b) a without field $H = 0$ and in a magnetic field of $H = 8$ kOe at frequencies of $\omega = 1$ (1), 5 (2), 10 (3), 50 (4), 100 (5), 300 (6) kHz.

The relative change in the dielectric permittivity $\delta \varepsilon = (\text{Re}(\varepsilon(H)) - \text{Re}(\varepsilon(0)))/\text{Re}(\varepsilon(0))$ at the magnetic field as a function of temperature for the sample $\text{Tm}_0.1 \text{Mn}_{0.9} \text{S}$ is shown in figure 3b. Magnetocapacity $\delta \varepsilon$ for composition $\text{Tm}_0.1 \text{Mn}_0.9 \text{S}$ reaches a maximum of 40% at $T = 500$ K. This effect is explained by the pinning of conduction electrons at the Mn-Tm interface and the large electronic contribution to the dielectric permittivity.

3. Conclusion
Measurements of dielectric permittivity in solid solutions of $\text{Tm}_x \text{Mn}_{1-x} \text{S}$ were carried out, a magnetocapacity effect was found at temperatures of 80–500 K at frequencies of 1–300 kHz. The experimental data are explained in terms of model with the orbital ordering. At temperatures lower than the Debye temperature, polarons are pinned at the interface with the formation of the orbital magnetic moment at a site and the dielectric permittivity anisotropy.

The orbital «glass» is created for thulium ion concentrations less than the percolation concentration and a long-range orbital order is induced at the interface at higher concentrations. The change in the orbital correlations of the magnetic angular moment at magnetic field lead to change in the dielectric permittivity anisotropy.

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