

Magnetic and Electric Properties of $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ Alloys

S. S. Aplesnin^{a, b}, A. M. Kharkov^a, O. B. Romanova^{a, b}, K. I. Yanushkevich^c,
A. I. Galyas^c, and V. V. Sokolov^d

^aSiberian State Aerospace University, Krasnoyarsk, 660014 Russia

^bKirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

^cScientific and Production Center for Materials Science, National Academy of Sciences of Belarus, Minsk, 220072 Belarus

^dInstitute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Abstract—Results from investigating the structural, magnetic, and electrical properties of $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ alloys ($0 \leq x \leq 0.2$) synthesized on the basis of manganese monosulfide are presented. Substituting manganese for ytterbium increases the concentration of charge carriers and lowers the activation energy. The observed anomalies in the temperature dependence of resistivity are explained by an impurity semiconductor model with donor $4f$ levels.

DOI: 10.3103/S1062873813100031

INTRODUCTION

Materials that reveal the relation between electric and magnetic properties are attractive due to their possible use as elemental bases in microelectronics, spintronics, and sensor facilities. Compounds with variable valence exhibit metal–dielectric and magnetic phase transitions, including variations in their magnetic properties while the magnetic symmetry remains the same. Ytterbium sulfide (YbS), which displays anomalous magnetic and kinetic properties, is one such compound. The presence of $4f$ and $5d$ orbitals that are close in energy determines certain specific properties of this compound. Under normal pressure, ytterbium sulfide is a semiconductor with a direct gap of ~ 1.3 eV in the spectrum of electron excitation and an indirect gap of ~ 1.0 eV [1] between the completely occupied $4f$ state and free sd band states located 4 eV above than the $3p$ valence band of sulfur. Under the effect of pressure, the gap shrinks monotonically: $dE_g/dP = -6 \pm 1$ eV/Pa; at $P = 8$ GPa, the bands overlap and the metal state appears. Quantum resonance is observed, i.e., the superposition of $f^{13}d$ and f^{14} states and a change in valence 2.4 at $P = 10$ GPa [3]; i.e., the carrier density per one ytterbium ion is $0.4/\text{Yb}$.

We might expect that after replacing manganese cations with ytterbium, the pressure exerted by the immediate environment would change the valence of the ytterbium ions and lead to the formation of metal bonds. If we assume the metal valence to be +3 and that of sulfur to be -2 , the four electrons not included in an Me-S bond will be contained in each cell containing four YbS formula units. These electrons will be incorporated into the Me-Me bond and collectivized. In addition to Me-Me bonds, however, six Me-S bonds appear in the unit cell and the compound becomes preferentially ionic.

Variations in the electron structure of the solid solution can also occur as a result of the formation of chemical bonds between the ytterbium and manganese ions. As a result, variations in the electron structure lead to changes in their magnetic and transport properties.

The aim of this work was to establish a correlation between magnetic and electric properties upon replacing manganese ions with ytterbium (an element with variable valence), and to reveal the mechanism associated with internal chemical pressure or with the prevalent influence of exchange effects.

EXPERIMENTAL

$\text{Yb}_x\text{Mn}_{1-x}\text{S}$ crystals ($0 \leq x \leq 0.2$) were grown via crystallization from a melt of powder sulfides in glassy carbon crucibles and a quartz reactor in argon by pulling the reactor through the single-turn inductor of a high-frequency installation [4]. X-ray structural analysis of the $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ compositions identified a face-centered cubic (fcc) lattice structure of the NaCl type. The unit cell size in the $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ alloy grew linearly as the concentration of the substituting element increases, as is shown in Fig. 1.

RESULTS AND DISCUSSION

Specific magnetization and magnetic susceptibility in the temperature range $80 \text{ K} < T < 800 \text{ K}$ was investigated ponderomotively in a magnetic field of 0.86 T. The temperature dependence of inverse magnetic susceptibility for a composition with $x = 0.1$ in field $H = 0.86 \text{ T}$ is given in Fig. 2 (the insert in Fig. 2). For most alloys, a maximum of magnetic susceptibility is observed whose temperature is associated with the Néel temperature. Magnetic susceptibility is described

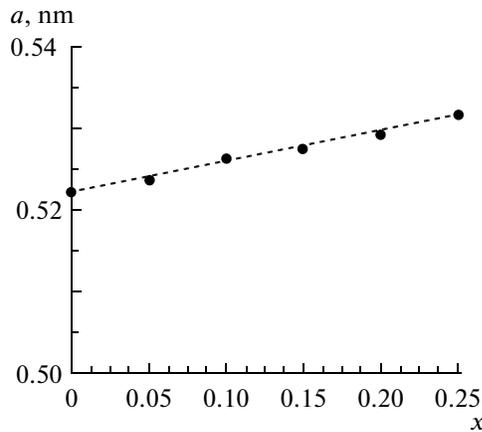


Fig. 1. Concentration dependence of the lattice parameter for our $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ solid solutions.

by the Curie–Weiss law $1/\chi(T) = (T + \theta)/C$ with negative paramagnetic Curie temperature θ for all compositions.

Concentration dependences of the Néel temperature and the Curie paramagnetic temperature were determined from the magnetic susceptibility. Magnetic measurements confirmed the presence of trivalent ytterbium ions with high magnetic moments for compositions with $x > 0.1$.

Resistivity was measured via the dc compensation four-probe method in the temperature range of 77–1100 K. The temperature dependences of resistivity for $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ solid solution with $x = 0.15$ are presented in Fig. 3. These are typical semiconductors, and temperature T^* can be determined for substitution concentrations $x \leq 0.1$ in the temperature range $T_N < T < 800$ K, at which the activation energy rises. For a composition with $x = 0.05$, the activation energy grows by a factor of 1.7 at $T = 440$ K; as the concentration increases, the variation in activation energy declines, and T^* shifts to lower temperatures. Replacing manganese with ytterbium raises the concentration of charge carriers and lowers the activation energy. The absence of plateau-like segments in the temperature dependence of resistivity $\rho(T)$ in a solid solution with $x \leq 0.1$ indicates that upon transitioning from impurity states, the electron concentration in the conduction band exceeds the concentration of intrinsic charge carriers.

A correlation between the temperature behavior of resistivity and susceptibility can be established for the composition with $x = 0.15$. A jump in resistivity is observed at $T = 288$ K; resistivity grows by a factor of 2, while the inverse susceptibility and Curie paramagnetic temperature rise by a factor of 1.6. A maximum in resistivity is observed in the high-temperature region of $880 < T < 1020$ K (the insert in Fig. 3). For the composition with $x = 0.2$, the maximum disappears, and a jump with resistivity varying by a factor

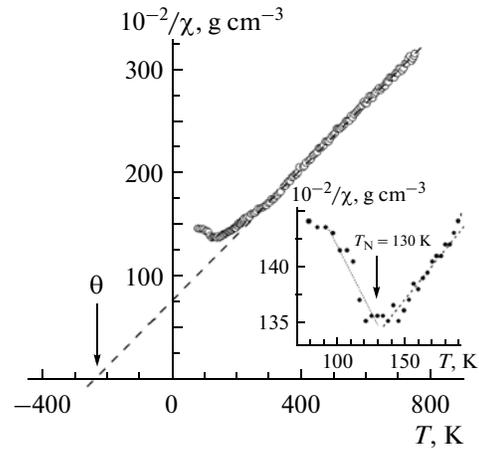


Fig. 2. Temperature dependence of magnetic susceptibility measured for the $\text{Yb}_{0.1}\text{Mn}_{0.9}\text{S}$ sample. The temperature dependence of magnetic susceptibility for the same sample in the region of 70–190 K is in the insert.

of 3 at $T = 700$ K is observed. Two temperature ranges, $110 \text{ K} < T < 150 \text{ K}$ and $325 \text{ K} < T < 460 \text{ K}$, can be distinguished for this composition, in which resistivity is independent of temperature, as is characteristic of semiconductors of the impurity conduction type. In the vicinity of Néel temperature $T_N = 102$ K, the derivative of resistivity with respect to temperature $d\rho(T)/dT$ has the maximum characteristic of spin polarons. It is possible that the jump in resistivity at $T = 700$ K is not associated with the elastic lattice and structural characteristics, variations in which should lead to anomalies in magnetic susceptibility, but they

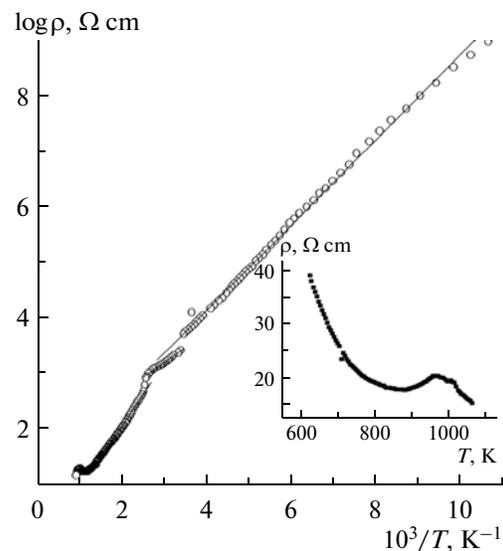


Fig. 3. Temperature dependences of the resistivity of the $\text{Yb}_x\text{Mn}_{1-x}\text{S}$ sample with $x = 0.15$. The temperature dependence of resistivity for $x = 0.15$ in the region of 500–1100 K is in the insert.

are unobservable for this composition. Jumps in resistivity are caused by the chemical potential shifting from the bottom of the conduction band to the middle of the band gap upon an increase in temperature and intersecting with the $4f$ level; i.e., at low temperatures, the $4f$ level is partially populated and located below the chemical potential, while at high temperatures it enters the conduction band where sd band electrons are scattered, producing the resistivity maximum.

CONCLUSIONS

The anomalies in $\rho(T)$ can be explained by the impurity semiconductor model with donor $4f$ levels for compositions with concentrations $x < 0.1$.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 12-02-00125_a,

11-02-98018_p_sibir'_a; and jointly by the Russian Foundation for Basic Research and Belarusian Republic Foundation for Basic Research, project no. 12-02-90004_Bel_a.

REFERENCES

1. Syassen, K., Winzen, H., Zimmer, H.G., et al., *Phys. Rev. B*, 1985, vol. 32, p. 8246.
2. Adhikari, D.R., Upadhyay, R.K., Singh, V.K., and Joshi, G.C., *Indian J. Theor. Phys.*, 2002, vol. 50, p. 119.
3. Matsunami, M., Okamura, H., Ochia, A., and Nanba, T., *Phys. Rev. Lett.*, 2009, vol. 103, p. 237202.
4. Aplesnin, S.S., Ryabinkina, L.I., Romanova, O.B., et al., *Fiz. Tverd. Tela*, 2009, vol. 51, p. 661.

Translated by N. Korovin