

Heat Capacity and Thermal Conductivity of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ Single Crystals

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Abstract—This paper reports on the results of investigations of the thermal properties and thermal conductivity of single crystals of homogeneous solid solutions $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ with a cubic NaCl structure, which have been prepared by the cation substitution for divalent manganese ions in manganese monosulfide. It has been revealed that the heat capacity and thermal conductivity exhibit anomalies in the range of the magnetic transition. The cation substitution is accompanied by an increase in the phase transition temperature.

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1. INTRODUCTION

Investigations of solid solutions synthesized from matrices with different crystal structures allow one to reveal methods for controlling physical properties of materials by using the cation (or anion) substitution for host atoms. Examples of the most extensively studied solid solutions are provided by oxide compounds of the perovskite class. Unlike oxides, magnetic sulfide compounds have not been adequately investigated in view of the complex technology used for their preparation. However, the data obtained recently (see, e.g., [1]) make it possible to consider sulfides as a new class of materials promising for practical applications. Our earlier investigations of single crystals [2, 3] allowed us to establish that compounds in the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ system with compositions $0 \leq x \leq 0.29$ synthesized on the basis of the antiferromagnetic semiconductor MnS are single-phase solid solutions and have a cubic NaCl structure typical of the α manganese monosulfide. The cation substitution of iron ions for manganese ions leads to a contraction of the cubic lattice, which is accompanied by the concentration electron transition with a decrease in the electrical resistance by five orders of magnitude in the paramagnetic state, as is the case in MnS at 300 K under pressure. This paper reports on the results of investigations of the thermal properties, magnetic properties, and thermal conductivity of single crystals in the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ system. Most attention has been focused on the study of the thermal properties.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Single crystals in the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ system, which were characterized in our previous work [2], served as the objects of investigation. At room temperature, the materials had a cubic crystal structure with the unit-cell parameter that decreased with an increase in the degree of iron substitution from 5.22 Å ($x = 0$) to 5.17 Å ($x = 0.29$). The thermal properties were measured by differential calorimetry (DMC) in the temperature range 80–300 K with the use of powders prepared from the single crystals. The heat capacity and thermal conductivity of the single crystals were measured on a Quantum Design VSA PPMS 9 universal setup in the temperature range 2–300 K. The magnetic susceptibility was measured on a SQUID magnetometer in the temperature range 4.2–270.0 K in a magnetic field of 500 Oe.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the studies of the magnetic properties of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals by SQUID magnetometry show that, as the degree of cation substitution increases, the Néel temperature of the solid solution (the temperature of the magnetic susceptibility at the maximum) increases from $T_N = 150$ K at $x = 0$ to $T_N = 198$ K at $x = 0.29$ (Fig. 1), which agrees with the data of neutron diffraction studies [3].

The thermal properties of the manganese monosulfide near the magnetic transition were studied in [4, 5]. It was revealed that the magnetic transition in MnS is

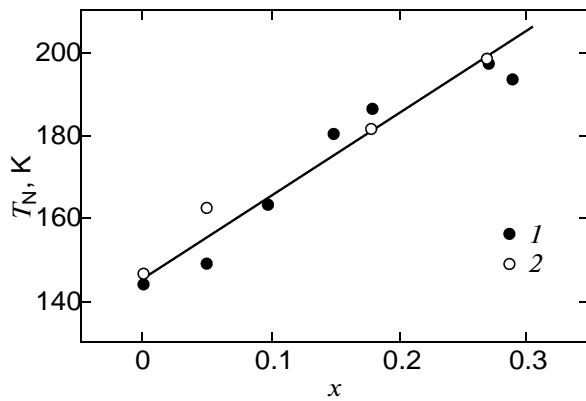


Fig. 1. Concentration dependence of the magnetic transition temperature for $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals: (1) results of investigation of the magnetic properties by SQUID magnetometry and (2) data obtained from neutron diffraction in [3].

accompanied by a λ -type anomaly of the heat capacity. The phase transition temperature was found to be 147 [4] and 152 K [5].

Figure 2a shows the results of our studies of the manganese monosulfide by using differential calorimetry. It was established that a phase transition temper-

ature of 144 K corresponding to the temperature of the maximum of the heat capacity anomaly is close to the data obtained in [4]. The heat capacity anomaly is extended in the temperature range 120–152 K. This indicates that a completely ordered state in MnS exists at temperatures below 120 K. The relatively broad maximum of the magnetic susceptibility that corresponds to the magnetic transition temperature is observed at $T_N = 150$ K.

Figures 2b and 2c show the temperature dependences of the excess heat capacity for ground single crystals of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions. As the degree of substitution increases, the phase transition temperature increases from 146 ($x = 0.05$) to 175 K ($x = 0.18$). The temperature range in which the phase transition occurs is wider (from 100 to 200 K) in the cation substituted samples than that in pure MnS. The wide temperature range in which the phase transition occurs could be assumed to be due to the microstructure of the powder samples. However, the study of the heat capacity of the single crystal confirms the data obtained for the powder samples. Figure 3 shows the temperature dependence of the heat capacity (curve 2) measured on the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystal with $x = 0.18$. For comparison, the data for pure manganese monosulfide MnS available from the literature (curve 1

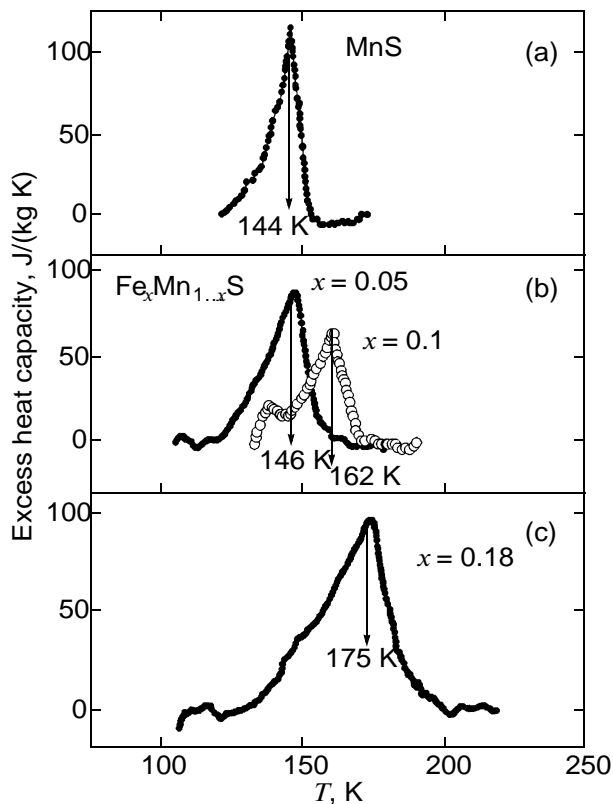


Fig. 2. Temperature dependences of the excess heat capacity of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ powders with different compositions x .

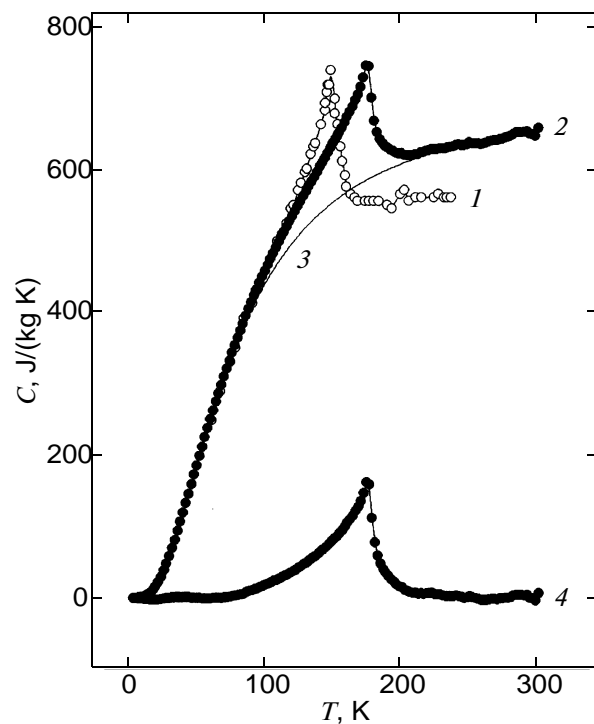


Fig. 3. Temperature dependences of (2) the heat capacity, (3) the phonon contribution to the heat capacity, and (4) the excess heat capacity of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.18$) single crystal. Data taken from [5] for MnS (presented for comparison).

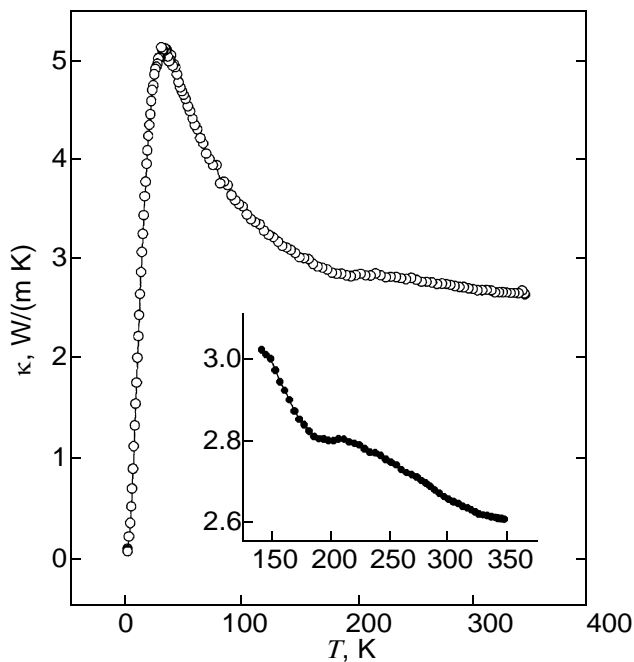


Fig. 4. Temperature dependence of the thermal conductivity coefficient of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.29$). The inset shows the portion in the vicinity of the magnetic transition.

[5]) are also presented in the plot. Curve 3 (obtained by extrapolation using the Debye–Einstein formula for regions which do not contain the anomalous part) corresponds to the temperature dependence of the phonon contribution to the heat capacity of the iron–manganese sulfide. Curve 4 is the temperature dependence of the excess heat capacity (difference between the total and the lattice heat capacities). A comparison of the data presented in Figs. 2 and 3 shows that the heat capacity anomaly in the single-crystal sample is also extended over a wide temperature range (100–200 K). Thus, the more correct method of studying on the perfect single crystal confirms the preliminary data measured by the express method (DMC). Taking into account this fact, the temperature range $T < 100$ K can be considered as the temperature range in which a long-range magnetic order forms over entire bulk of the sample.

According to the Dulong–Petit law, the heat capacity is limited at high temperatures, and it is 573 J/(kg K) for MnS, which is close to the experimental value 560 J/(kg K) [4] observed in the paramagnetic state. With the complete cation substitution ($x = 1$) in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$, the expectation Dulong–Petit heat capacity for a hypothetical cubic structure is $C(\text{FeS}) = 570$ J/(kg K). The experimental heat capacity of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ with $x = 0.18$ in the high-temperature paramagnetic state is 660 J/(kg K). The obtained Debye temperature $\Theta_D = 268$ K for the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ samples ($x = 0.18$) is close to the values characteristic

of manganese monosulfide ($\Theta_D = 272.6$ K [6]). The increase in the heat capacity in the paramagnetic state as compared to the expectation value is likely due to an increase in the lattice disordering as the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solution forms. Based on an analysis of the data presented in Fig. 2, we stated that a change in the entropy (in units of R , R is the gas constant) actually increases with increasing iron concentration from $\Delta S = 0.04R$ at $x = 0$ to $\Delta S = 0.16R$ at $x = 0.18$, which is explained by an increase in the configuration entropy related to the increasing structural disorder. At $x > 0.18$, the entropy decreases; this result agrees with the data of [2] and demonstrates the formation of the higher-ordered solid solution.

Important information on the heat capacity and thermal physical properties of a material can be obtained as its thermal conductivity is studied. At high temperatures exceeding the Debye temperature Θ_D , the temperature dependence of lattice thermal conductivity is mainly determined by the phonon mean free path that varies in inverse proportion to the temperature, and the thermal conductivity coefficient is $\kappa \approx 1/T$ at $T > \Theta_D$. In insulators, at temperatures below the Debye temperature, as temperature decreases, the thermal conductivity increases exponentially due to the umklapp processes violating the quasi-momentum conservation law and decreasing the heat flow. As temperature decreases further, the T^3 contribution becomes predominant characterizing the phonon scattering by lattice defects, impurities, and edges of a finite sample. This brings about the appearance of a maximum in the temperature dependence of the thermal conductivity characteristic of all materials.

Figure 4 depicts the temperature dependence of the thermal conductivity of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.29$). The magnetic transition temperature of the sample is 198 K. At room temperature, the thermal conductivity is 2.67 W/(m K). For comparison, the typical values of the thermal conductivity of an insulating NaCl are 7 and 27 W/(m K) at temperatures of 83 and 273 K, respectively [7]. It is seen from Fig. 4 that the thermal conductivity coefficient increases as temperature decreases and exhibits anomalous behavior near the magnetic transition (the inset to Fig. 4). For sulfide $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.29$), the typical thermal conductivity maximum due to a change in phonon scattering mechanisms is at the temperature $T_{\text{max}} = 35$ K. The processing and analysis of the obtained experimental data allowed us to state that the temperature dependence of the thermal conductivity in the temperature range $T_{\text{max}} < T < \Theta_D$ is not described by the exponential dependence typical of the lattice component of the thermal conductivity. At room temperature, the electrical resistance of the sulfide $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.29$) measured simultaneously with the thermal conductivity is 18.4 Ω cm. This value is two orders in magnitude lower than the characteristic electrical resistance of pure manganese monosulfide. As known, the contri-

bution of charge carriers to the thermal conductivity of a crystal at temperatures $T > \Theta_D$ can be estimated using the Wiedemann–Franz law (for metals). The estimations give the value of 3.9×10^{-5} W/(m K) that is five orders in magnitude lower than the experimental value of the thermal conductivity. Since the thermal conductivity anomaly is fairly pronounced near the magnetic transition, we can assume that, in the magnetically ordered state of the sample, along with the lattice contribution, additional contributions of phonon scattering occur, e.g., due to spin–phonon interaction [8]. A rhombohedral distortion of the NaCl lattice was earlier detected in pure manganese monosulfide [6].

4. CONCLUSIONS

Thus, the studies of the thermal properties of iron–manganese sulfide $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions allowed the statement that the transition to the magnetically ordered state is accompanied by the λ -type anomaly of the heat capacity and the thermal conductivity anomaly. An increase in the degree of cation substitution x in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ causes an increase in the critical phase

transition temperature and a broadening of the temperature range in which the phase transition occurs.

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