

Magnetic Resonance of the $M_x\text{Mn}_{1-x}\text{S}$ Compounds ($M = \text{Cu}, \text{Cr}$)

A. M. Vorotynov^{a,*}, G. M. Abramova^a, V. V. Sokolov^b, and O. V. Vorotynova^c

^a Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia

* e-mail: sasa@iph.krasn.ru

^b Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Akademika Lavrentieva 3, Novosibirsk, 630090 Russia

^c Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660041 Russia

Received April 3, 2012

Abstract—Cation-substituted manganese monosulfide $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Cu}, \text{Cr}$) has been investigated using the electron paramagnetic resonance method. The temperature and concentration dependences of the width and shape of the magnetic resonance line have been considered using the Van Vleck method of moments. It has been shown that, if the Mn^{2+} ions are substituted by the copper and chromium ions, the change of the effective exchange interaction in the system that substantially affects the magnetic resonance spectra takes place.

DOI: 10.1134/S1063783412110327

1. INTRODUCTION

The search, synthesis, and investigation of new compounds remain among important problems of physics of the solid state and magnetism. One method for the search and formation of substances with new physical properties is the method of cation (anion) substitution, which is used to synthesize solid solutions. The selection of matrices for such investigations is determined, in addition to other conditions, by the solubility of the substitution cation in this matrix.

Manganese monosulfide MnS with the Néel temperature of 150 K belongs to Mott dielectrics [1]. It is a convenient model system for the investigation of the influence of substitution of the Mn^{2+} ions by other ions of the series of $3d$ metals. Interest in such investigations is caused, on the one hand, by the possibility of this substitution without changing the crystal lattice of the starting component in a sufficiently broad concentration range (up to $x = 0.3$). On the other hand, the possibility appears to control such interesting properties of manganese monosulfide as the giant magnetostriction and the metal–dielectric transition [2–4].

Polycrystalline sulfides of the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ system synthesized based on manganese monosulfide were investigated in [5–8].

Sulfides of the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ system are known poorly [3]. As a rule, the cubic phase (alpha) of manganese monosulfide is compared with manganese monoxide MnO ($Fm\bar{3}m$, NaCl). In contrast with MnO , copper monosulfide CuO (d^9) [9] has a monoclinic structure, which is the distorted variant of the

NaCl cubic lattice, in which manganese monosulfide and monoxide are crystallized. It is assumed that the Cu^{2+} ion causes the distortion of the NaCl structure due to the Jahn–Teller effect.

Despite the growing interest in pure and substituted manganese monosulfides, magnetic and especially resonant properties of compositions $\text{Mn}_{1-x}\text{M}_x\text{S}$ ($M = \text{Cu}, \text{Cr}$) remain poorly known.

In this paper, we present the investigation of the $M_x\text{Mn}_{1-x}\text{S}$ single crystals ($M = \text{Cu}, \text{Cr}$) by the magnetic resonance method in order to reveal the influence of substitution by the Cr^{2+} ions and the Jahn–Teller Cu^{2+} ions on the physical properties and the Mott state in manganese monosulfide.

2. SYNTHESIS TECHNOLOGY

Synthesis technology of the samples and attestation techniques of the $M_x\text{Mn}_{1-x}\text{S}$ crystal structure ($M = \text{Cr}, \text{Cu}$; $0 \leq x \leq 0.29$) are described in detail in [2, 3]. The structural properties of polycrystalline and single-crystal samples are investigated using diffractometers DRON ($\text{CuK}\alpha$ radiation) and D8-ADVANCE ($\text{CuK}\alpha$ radiation, θ – 2θ scanning) with a VANTEC linear detector. The scanning step along angle 2θ is 0.016° , and the exposure is 0.3 s per step. According to [2, 3], the formation region ($0 < x < X_c$) of the $M_x\text{Mn}_{1-x}\text{S}$ homogeneous solid solution with the NaCl cubic structure depends on the number of d electrons of the substitution cation. In this work, we present only the samples with compositions $x < X_c$.

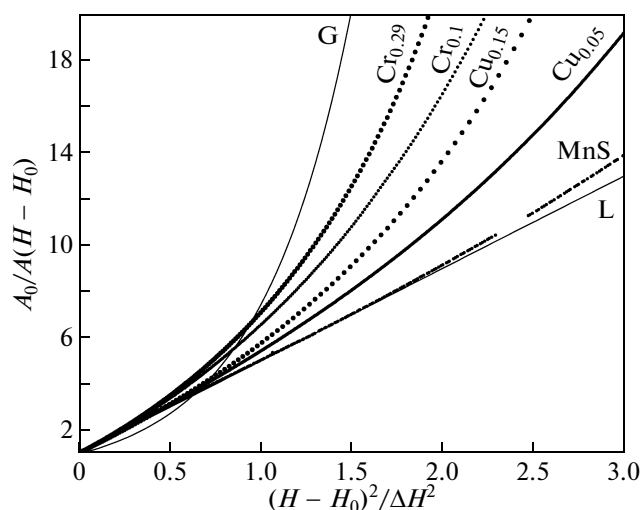


Fig. 1. Dependences of the change in the shape of the magnetic resonance line on the type and concentration of substituting ion. L and G are the Lorentzian and Gaussian line shapes, respectively; H_0 , A_0 , and ΔH are the resonant field, the maximal line amplitude, and the line width, respectively.

To study the resonant properties of sulfides $\text{Cu}_x\text{Mn}_{1-x}\text{S}$, we used single-crystal samples with compositions $x = 0.01, 0.07$, and 0.15 . The substances were the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ homogeneous solid solutions with a cubic structure of the MnS matrix; as the degree of substitution increased, the cubic lattice parameter decreased from 5.224 \AA ($x = 0$) to 5.214 \AA ($x = 0.15$).

To study the influence of the cation substitution in the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ system on the resonant properties, we used single-crystal samples with compositions $x = 0.10$ and 0.29 . The X-ray diffraction patterns of the samples were characteristic of the NaCl structure of manganese monosulfide with cubic symmetry $Fm\bar{3}m$. As the degree of cation substitution increased and the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ solid solution formed, lattice compression according to its expected behavior upon the substitution of the divalent manganese ions by the divalent ions Cr^{2+} in octahedral sites was observed. For example, the lattice parameter of the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ single crystal with $x = 0.29$ was $a = 5.17 \text{ \AA}$, which is close to the expected value $a = 5.172 \text{ \AA}$ for this composition of the solid solution.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic resonance spectra were recorded using an Elexsys E580 spectrometer operating in the X-band in a temperature range of $100\text{--}300 \text{ K}$. We studied the temperature dependences of the width and shape of the absorption line with an arbitrary orientation of the external magnetic field on the type of the substituting ion and its concentration. Figure 1 pre-

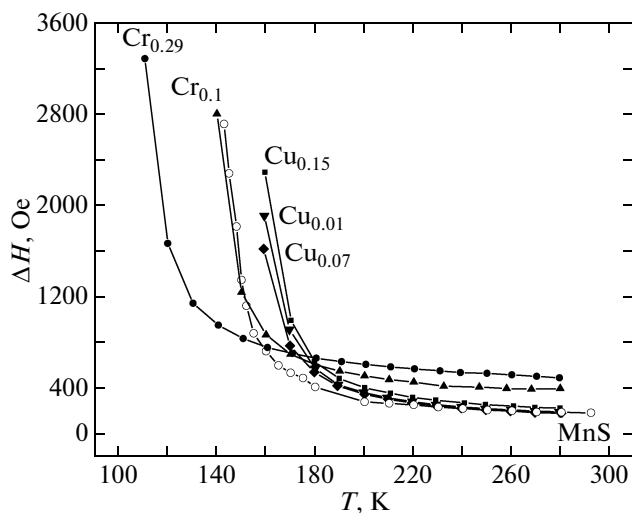


Fig. 2. Temperature dependences of the width of the magnetic resonance line for the substituted samples and pure MnS.

sents the dependences of the shape of the magnetic resonance line for samples $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ and $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ at room temperature.

We observed a single symmetric magnetic resonance line over the entire temperature range and for all the compositions.

The line shape for pure MnS is close to the Lorentzian. It is found that under the substitution, irrespective of the type of the substituting ion, the line shape deviates from the Lorentzian and approaches the Gaussian shape. This deviation manifests itself stronger for the substitution of the manganese ions by chromium ions rather than by copper ions.

The temperature dependence of the line width for the samples with chromium and copper is shown in Fig. 2. It is noteworthy that as the concentration of copper ions increases to 0.15 , the room-temperature line width remains invariable, while for chromium-containing compounds, it increases monotonically as their concentration increases. According to the magnetic resonance data, the Néel temperature for the copper-containing compounds increases compared with pure MnS (150 K) to 160 K ; thus, it is almost concentration-independent. However, for the compositions with chromium, it decreases to 110 K for $x = 0.29$.

It is convenient to perform the analysis of the change in the width of the magnetic resonance line with increasing concentration and depending on the type of the substituting ion using the method of moments [10].

Let us start our consideration with the unsubstituted MnS. In the case of the dipole–dipole interac-

tion only, the second moment of a polycrystalline sample is [10]

$$M_2 = 208.14 \frac{1}{a^6} \frac{g^4 \mu^4}{3h^2} S(S+1), \quad (1)$$

where a is the lattice constant, g is the g factor, μ is the Bohr magneton, h is the Planck constant, and S is the ion spin. Thus found second moment is $M_2 = 10.27 \times 10^6 \text{ Oe}^2$. It is clear that this quantity for the single-crystal sample depends on the orientation of the external magnetic field. Calculations show [10] that this spread for the face-centered cubic lattice is about 10%. It is shown by Kubo and Tomita that in the case of the exchange interaction, the width of the magnetic resonance line and the second moment are connected by the relationship [11, 12]

$$\Delta H = M_2 / \langle J \rangle, \quad (2)$$

where $\langle J \rangle$ is the average exchange interaction in the system. Using the experimental room-temperature line width for MnS and the calculated second moment, we find $|\langle J \rangle| = 7.4 \text{ K}$. The magnitudes of exchange interactions for MnS can be also found using the molecular field method described in [13]. Using the Curie paramagnetic temperature $\Theta = -465 \text{ K}$ [13] and the Néel temperature $T_N = 154 \text{ K}$ [13], we have the magnitudes of exchange interactions for the first and second neighbors $J_1 = -5.3 \text{ K}$ and $J_2 = -4.3 \text{ K}$, respectively. From here, taking into account the number of nearest neighbors, $|\langle J \rangle| = 5 \text{ K}$, which agrees rather well with the value found from (2).

To determine experimentally the second moment of pure MnS, the shape of the magnetic resonance line for which is close to the Lorentzian, it is necessary to take into account the wings of the absorption line to increase the accuracy. In our experiment, the second moment was determined upon scanning the field to $6H_0$, where H_0 is the resonant field

$$M_2 = \frac{\int (H - H_0)^2 f(H) dH}{\int f(H) dH},$$

where $f(H)$ is the Lorentzian function of the line shape.

Evaluations show that the error is about 10% in this case. Thus experimentally determined second moment is $M_2 = 3 \times 10^6 \text{ Oe}^2$.

It is rather complicated to calculate theoretically the second moment for the samples with the substitution by chromium and copper ions. This is associated with the circumstance that, first, the shape function of the magnetic resonance line is intermediate between the Gaussian and Lorentzian. This indicates that the resonance line becomes inhomogeneously broadened. Second, if ions of various sorts are present in the sample, the exchange interaction between them gives the contribution to the second moment. In this case, in

view of closeness of g factors of different ions ($g_{\text{Cu}} \approx 2.1$, $g_{\text{Cr}} \approx 2$, and $g_{\text{Mn}} \approx 2$ [11]), the line is unresolved.

However, we can make definite conclusions from the concentration dependence of the line width. It is clear that the addition of ions of another sort into pure MnS should lead to an increase in the contribution to the second moment (and, consequently, to the width of the magnetic resonance line) of the dipole–dipole interaction in any case. This is associated with the difference in g factors and spins of dissimilar ions as well as with a monotonic decrease in the lattice constant upon increasing the concentration of chromium or copper ions.

This situation is observed for the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ compounds, where the width of the room-temperature magnetic resonance line increases from $\Delta H(x=0) = 180 \text{ Oe}$ to $\Delta H(x=0.29) = 490 \text{ Oe}$ (Fig. 2). Such a behavior and a decrease in the Néel temperature from $T_N(x=0) = 150 \text{ K}$ to $T_N(x=0.29) = 110 \text{ K}$ (Fig. 2) indicates that with the substitution of the Mn ions by the Cr ions, the effective exchange interaction in the $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ system decreases as concentration x increases.

An inverse situation is observed upon doping of MnS by copper ions. Although the line shape for $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ deviates from the Lorentzian as the concentration of copper ions increases, this variation is substantially weaker than for $\text{Cr}_x\text{Mn}_{1-x}\text{S}$ (Fig. 1). In addition, the room-temperature line width remains almost constant for $0 < x < 0.15$. This fact and a small increase in the Néel temperature (Fig. 2) evidence in favor of the fact that upon the substitution of the Mn ions by the Cu ions, the effective exchange interaction in the $\text{Cu}_x\text{Mn}_{1-x}\text{S}$ system increases as concentration x increases.

4. CONCLUSIONS

We studied the temperature behavior of the line width and the concentration dependence of the shape of the magnetic resonance line for the cation-substituted compounds of manganese monosulfide. It is shown that, irrespective of the type of the substituting ion (Cr^{2+} or Cu^{2+}), the shape of the magnetic resonance line deviates from the Lorentzian and becomes intermediate between the Lorentzian and Gaussian. The degree of deviation increases as the concentration of substituting ions increases. This fact indicates the presence of inhomogeneous broadening in the sample. On the other hand, the variation in the width of the magnetic resonance line behaves variously depending on the type of substituting ions. It is shown that the substitution of the manganese ions by copper ions strengthens the effective exchange interaction in the system and enhances the exchange narrowing effect. To the contrary, the addition of chromium ions into the system weakens the effective exchange interaction and, as a consequence, leads to a significant change in

the shape of the magnetic resonance line, increases its room-temperature width, and decreases the Néel temperature.

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Translated by N. Korovin