
MAGNETISM
AND FERROELECTRICITY

Structure and Mössbauer Studies of Manganese Monosulfide Solid Solutions $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Cr}, \text{Fe}$)

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Abstract—This paper reports on the results of the synthesis and study of the diffraction patterns and Mössbauer spectra of single crystals of homogeneous $M_x\text{Mn}_{1-x}\text{S}$ solid solutions with a cubic NaCl structure prepared by the cation substitution of 3d elements for divalent manganese ions in manganese monosulfide. It has been shown that, similarly to the hydrostatic pressure, the substitution of 3d ions with a smaller ionic radius is accompanied by the contraction of the MnS cubic cell. The calculated lattice parameters agree with the experimental data. The homogeneous region of the formation of homogeneous solid solutions is limited in composition x , which depends on the choice of a substitutional cation.

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1. INTRODUCTION

One of the methods for controlling the physical properties of materials is the cation (anion) substitution used for synthesizing solid solutions. At present, multicomponent systems, such as 3d element oxides (manganites) and 3d element chalcogenides with a colossal magnetoresistance and Mott transition, have been studied extensively. In this case, the amount of experimental information on the structure of solid solutions in oxides is considerably larger as compared to information on the mechanisms of formation of solid solutions based on sulfide matrices. Since the electrical resistance is a parameter dependent on the structure, a clear view of formation of solid solutions is necessary to understand the physical phenomena associated with the change in this parameter. The “solid solution” concept describes a single-phase material [1–5] formed by substitution of atoms of some elements for a part of atoms of the initial matrix. The formation and change in the properties of the solid solution as compared to its prototype are determined by two (deformation and chemical) factors. The deformation factor is due to the difference between the geometric sizes of substitutional and “host” atoms. Solid solutions have been frequently analyzed using the Vegard law, which is an empirical law based on results of numerous studies of alloys of isostructural metals. According to this law, when an $A_{1-x}B_x$ solid solution is formed from initial materials A and B having the lattice parameters a and b , respec-

tively, the lattice parameter of the $A_{1-x}B_x$ solid solution varies linearly from a ($x = 0$) to b ($x = 1$). As a rule, experiments reveal some deviations from the Vegard law in the concentration dependences of the lattice parameter of real solid solutions. The mutual solubility of different compounds is dependent on their crystal structures. A continuous series of solid solutions can be synthesized using only isostructural compounds. Knowing the ionic radii R_x (cation) and R_a (anion), one can calculate the limiting ratio R_x/R_a at which the structure with a known coordination number will be stable. According to [6], for the NaCl structure with the coordination number $z = 6$, the limiting ratio is $R_x/R_a = 0.41$. The corresponding ratios R_x/R_a for the 3d element monosulfides MnS, FeS, NiS, and CoS are 0.5, 0.44, 0.406, and 0.43, respectively. In all cases, the R_x/R_a ratio is higher than the limiting value (0.41); however, the face-centered cubic NaCl structure is characteristic only of the manganese sulfide. Chromium, iron, and copper monosulfides, as well as other 3d element sulfides, crystallize in a hexagonal NiAs structure [7]. Taking into account substantial differences between the crystal structures of initial compounds of the MnS–MS series, a limited solubility of a 3d element (M) in the cubic lattice of the manganese monosulfide can be expected in the formation of $M_x\text{Mn}_{1-x}\text{S}$ solid solutions.

In this work, single crystals of manganese monosulfide solid solutions $M_x\text{Mn}_{1-x}\text{S}$ were synthesized and their crystal structures were studied using X-ray

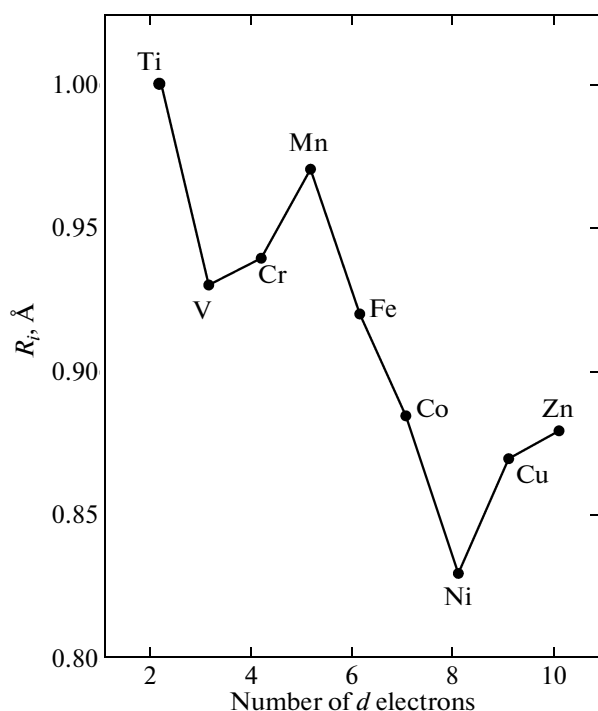


Fig. 1. Ionic radii of 3d elements.

diffraction and Mössbauer spectroscopy. Most attention was focused on the determination of the region of the formation of homogeneous solid solutions and the elucidation of the concentration dependences of the lattice parameters for various types of substitutional cations at their different contents in the material.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In this work, we studied materials in the $M_xMn_{1-x}S$ systems ($M = Cr, Fe, Ni, Cu$) with compositions $0 < x < 0.3$, which were synthesized for the first time. Polycrystals in the $Fe_xMn_{1-x}S$ system with $0.3 < x < 0.6$ were previously studied in [8]. According to the Mössbauer studies [9], these polycrystals contained the accompanying phase of the magnetic iron sulfide. To synthesize the $M_xMn_{1-x}S$ single crystals, we first synthesized powdered sulfides by sulfiding calculated mixtures of metal oxides and pure metals in a horizontal quartz reactor with the use of glassy-carbon boats as containers. The metal-oxide mixtures were heated to 700–800°C by halogen quartz lamps. Gaseous products of thermolysis of ammonium rhodanide NH_4CNS were used as sulfiding agents, and helium served as an inert gas carrier. The completeness of sulfiding of the samples was controlled by their weighting

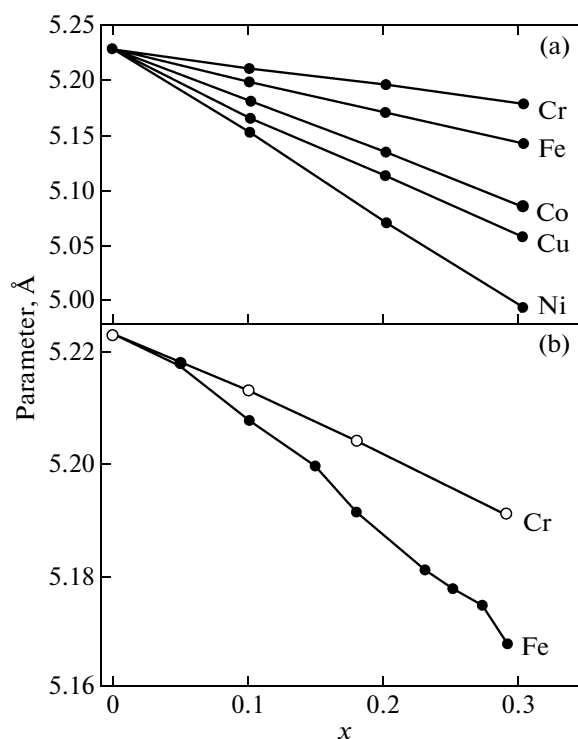


Fig. 2. (a) Expected and (b) experimental concentration dependences of the cubic unit cell parameter for the $M_xMn_{1-x}S$ solid solutions.

and X-ray diffraction. The single crystals were grown by zone melting from the melt of the powdered sulfides in sulfur vapors in the glassy-carbon container with the use of induction heating by moving the container through a one-turn inductor at a rate of 5–10 mm/h (vertical version).

The X-ray diffraction studies of the powders prepared by rubbing the single crystals were performed on single-crystal and DRON diffractometers (CuK_α radiation). The Mössbauer studies were carried out on a spectrometer with a $^{57}Co(Cr)$ source.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 presents the ionic radii of the 3d elements [10]. Knowing the Vegard law, the ionic radii of the 3d elements, and the lattice parameter of the initial matrix MnS used for synthesizing solid solutions $a = 5.22$ Å, we can preliminarily calculate the expected concentration dependence of the cubic lattice parameter for the solid solution synthesized with the manganese monosulfide. Figure 2a shows the calculated concentration dependences of the cubic lattice parameter for the $M_xMn_{1-x}S$ ($M = Fe, Cr, Co, Ni, Cu$) solid solutions. In our experiments, chromium, iron, nickel, and copper with the ionic radii smaller than the

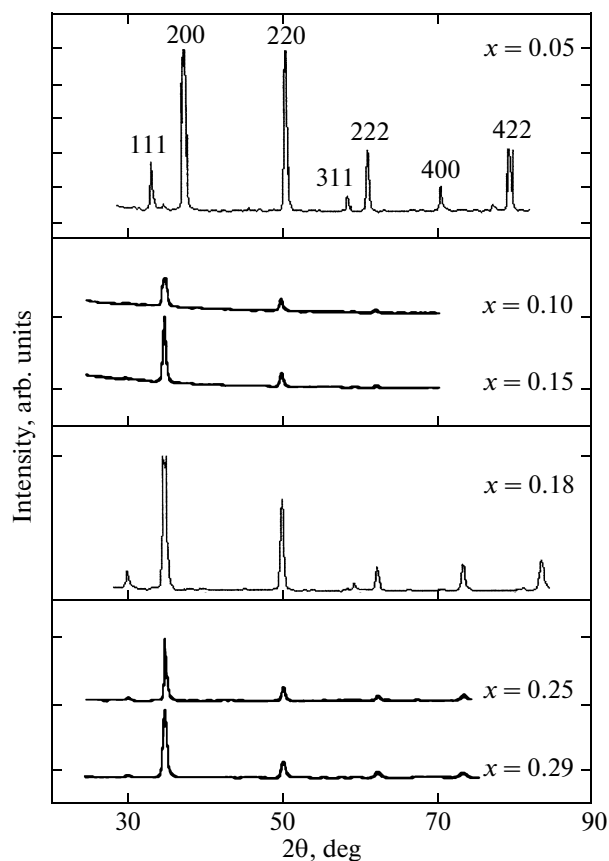


Fig. 3. X-ray diffraction patterns of the $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Fe}$) solid solutions.

ionic radius of the manganese ion were chosen as 3d elements for the substitutional cations M in the $M_x\text{Mn}_{1-x}\text{S}$ systems. This suggested that the cation substitution will cause changes in the crystal structure of the matrix similar to those produced by hydrostatic pressure.

As an illustration, Fig. 3 depicts the X-ray diffraction patterns of the $M_x\text{Mn}_{1-x}\text{S}$ samples synthesized, in which the iron ion is the substitutional cation. Similar X-ray diffraction patterns are observed for the $M_x\text{Mn}_{1-x}\text{S}$ solid solutions with $M = \text{Cr}$ and Cu . A specific feature of the X-ray diffraction patterns of the manganese sulfides is a high intensity of small-angle structural reflections as compared to the noise, which can lead to very substantial errors in the analysis of the phase composition. The presence of the noise with an intensity above 10% in the X-ray diffraction patterns (similar to that revealed in [11] for the system containing cobalt as the substitutional cation) is indicative of a sample imperfection. Figure 4 shows the X-ray diffraction pattern (cut in the reflection intensity) of the $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Fe}$) sample with the maximum magnetization in comparison with the X-ray diffraction pattern typical of the iron sulfide, which can accom-

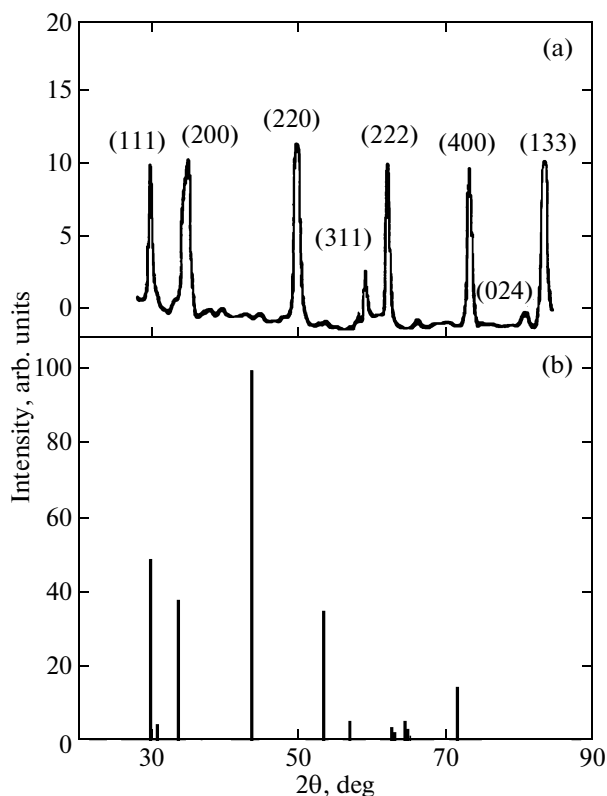


Fig. 4. X-ray diffraction patterns of (a) the $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Fe}, x = 0.18$) solid solution and (b) iron monosulfide.

pany iron manganese sulfides [9]. The structural reflections observed in the X-ray diffraction patterns (Figs. 3, 4a) are well indexed in a face-centered cubic structure of the NaCl type. The absence of any noise with an accuracy of up to 5% and additional structural

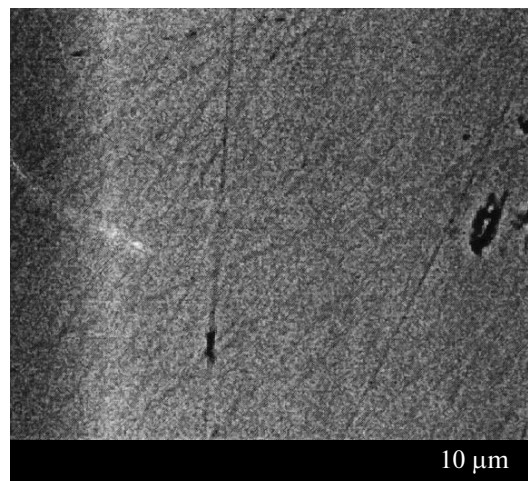


Fig. 5. Electron micrograph of the surface of the $M_x\text{Mn}_{1-x}\text{S}$ ($M = \text{Fe}, x = 0.1$) crystal.

0.29, which is evidenced by the singlet Mössbauer spectrum (see the inset to Fig. 6b). The spectra describe divalent iron ions in the octahedral positions, which indicates the isovalent cation substitution in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$; namely, divalent iron ions substitute for divalent manganese ions. The observed decrease in the isomer shift with an increase in the degree of substitution (Fig. 6a) indicates the change in the chemical bonding and an increase in the degree of covalency due to the enhancement of the $sp-d$ hybridization. At $x > 0.15$, a weak quadrupole splitting of the singlet appears and increases, which suggests a weak local distortion of octahedra. The sharpest change in the quadrupole splitting corresponds to the composition range $0.15 < x < 0.25$ (Fig. 6b). Taking into account [7] that the iron monosulfide (covalent compound) crystallizes in a hexagonal structure and the manganese monosulfide (ionic compound) crystallizes in a cubic structure, one can assume that the degree of covalency and the $sp-d$ hybridization (along with the geometric factor) play an important role in the mechanism of formation of the $M_x\text{Mn}_{1-x}\text{S}$ solid solutions synthesized from the manganese monosulfide and $3d$ elements.

Thus, the results of the study showed that the homogeneous solid solutions with the face-centered cubic NaCl-type structure characteristic of the alpha-manganese monosulfide upon cation replacement with $3d$ elements in $M_x\text{Mn}_{1-x}\text{S}$ are formed in a limited composition range. The increase in the degree of cation substitution brings about the contraction of the cubic cell of manganese monosulfide due to the change in the geometric size of the substitutional $3d$ ions and is similar to the action of the hydrostatic pressure. The composition range in which the homogeneous solid solutions with the cubic structure are formed depends not only on the geometric factor but also on the number of $3d$ electrons and the degree of covalency.

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