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Raman and infrared characterization of gadolinium-doped manganese sulfide

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ABSTRACT

Gadolinium manganese sulfide solid solutions are investigated by infrared and Raman spectroscopy. Longitudinal optical–transverse optical splitting of the manganese–sulfur bond vibration is observed in the vibrational spectra. The Raman spectra contain modes that are prohibited in the crystal structure of the alpha phase of manganese sulfide, which are associated with activation of the phonons from both the Brillouin zone center and its X and L points. The concentration dependence of transverse optical and longitudinal optical modes' frequencies is calculated within the frame of the modified random-element-isodisplacement model, being in good agreement with the experimental results. Both theory and experiment show that the solid solution under study exhibits a “one-mode” behavior.

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Introduction

Currently, researchers are paying great attention to the investigation of materials with a strong interconnection between electrical and magnetic properties, in relation to future applications in devices of next-generation electronics.^[1] According to earlier results,^[2,3] from the point of view of fundamental research, special attention is to be devoted to transition metal sulfide compounds containing rare earth elements, for example $Re_xMn_{1-x}S$, where $Re = Gd, Sm, Ho$, exhibiting phase transitions between the metal and the insulator, accompanied by the conductivity-type change from p-type to n-type, by the magnetic phase transformations including variations of magnetic properties within the same magnetic symmetry, providing the possibility of magnetoresistance effect under certain conditions. However, despite certain advances in the study of these compounds,^[4–7] the vibrational spectra of Re -doped manganese sulfides have still been studied insufficiently.

Doping of manganese sulfide with gadolinium leads to the formation of solid solution preserving face-centered crystal lattice of sodium chloride type. Magnetic ion Mn^{2+} is in the crystal field of the octahedral symmetry created by the sulfur environment. With increasing degree of cation substitution x , the parameter of the unit cell grows.^[2] Doping with rare earth gadolinium ion leads to local deformation of the structure associated with the difference in the ionic radii of manganese and gadolinium ($r = 0.83 \text{ \AA}$ for manganese, $r = 0.94 \text{ \AA}$ for gadolinium).

Raman and infrared spectroscopy are important tools for studying the relationship of the physical properties and structure of the matter. Therefore, it is attractive to study the influence of compositional change onto the phonon spectra for gadolinium-doped manganese sulfide. Similar solid

solutions are of interest from the point of view of manifestation of so-called “one-mode” or “two-mode” behavior type.^[8] In the class of solid solutions with “one-mode” behavior, each of the optical modes' frequencies with $k=0$ (infrared or Raman-active) vary continuously and approximately linearly with a solid solution content between the frequencies characteristic of the end members of the solid solution system.^[9] In the class of solid solutions with “two-mode” behavior, Raman lines intensity of these modes is proportional to the content of every constituent. Varying the content leads to intensity growth of one mode and to the decrease of another mode, while the modes' frequencies remain practically unchanged.

In this paper we will discuss the vibrational spectra of $Gd_xMn_{1-x}S$ ($x = 0.04, 0.1, 0.25$) solid solutions; the obtained values were compared to those calculated using the modified random-element-isodisplacement (MREI)^[9] model.

Experimental

The $Gd_xMn_{1-x}S$ crystals were synthesized in a quartz reactor from a melt of polycrystalline powders of sulfides. The reactor with a charge in the glass-carbon crucibles was pulled through a single-turn inductor of a high-frequency facility. As an inert medium, high-purity argon was used.^[10] $Gd_xMn_{1-x}S$ solid solution remains a single-phase system with the studied gadolinium content range. $x = 0.25$ is a critical concentration, exceeding of which results in the appearance of extra phases, verified by the additional peaks in the X-ray diffraction patterns. These additional peaks are indexed as those of the GdS system.

Analysis of scanning electron microscope images obtained with a Hitachi TM-3000 microscope proves that the sample

is featured by a microinhomogeneity associated with slight variation of the gadolinium content. All the investigated samples are polycrystals.

Raman spectra were recorded using a T64000 spectrometer (Horiba Jobin Yvon, France) in backscattering geometry, with a spectral resolution of 2 cm^{-1} in the range of $30\text{--}750\text{ cm}^{-1}$. Argon laser at wavelength $\lambda = 514.5\text{ nm}$ was used as a source of excitation radiation. The radiation power at the sample was $<5\text{ mW}$. Fourier spectrometer VERTEX 80 V (BRUKER, Germany) was used to obtain the far-IR (infrared) absorption spectra. IR spectra were obtained in the spectral range of $30\text{--}700\text{ cm}^{-1}$ at 0.2 cm^{-1} spectral resolution. Temperature scanning was performed using an Optistat TM AC-V 12a cryostat (Oxford instruments, UK) within the range from 5 to 330 K.

To perform the lattice dynamics simulation of pure α -MnS and gadolinium-doped manganese sulfides, the program package LADY (Smirnov, M. B.; Kazimirov, V.Yu. Dubna, Russia) was used. The atomic vibration frequencies were obtained using the modified random-element-isodisplacement model.^[9] Then we simulated the complete spectra of the crystals; interionic interactions between Mn-S, Gd-S, and S-S have been described in the fairly common model of “rigid-ion”, where the interatomic potential is considered as a sum of long-range Coulomb electrostatic:

$$V(r_{ij}) = \frac{1}{2} \sum_{ij} \frac{Z_i Z_j}{r_{ij}} + U(r_{ij}).$$

The short-range interaction potential was taken in the Buckingham form as follows:

$$U(r_{ij}) = \lambda \exp(-r_{ij}/\rho) - C/r_{ij}^6$$

where r_{ij} is the interatomic distance and λ , ρ , and C are the parameters characterizing the short-range pair interionic interaction. To find the model parameters, the special optimization program was written (Oreshonkov A. S., Krasnoyarsk, Russia) and tested for several compounds from different chemical classes.^[11–26]

Results and discussion

According to the group theory analysis for α -MnS (point symmetry group O_h), vibrational representation in the center of the Brillouin zone is as follows:

$$\Gamma_{\text{vibr}} = 2T_{1u}$$

and one of the triply degenerate modes is acoustic, while the other one is optical. For gadolinium manganese sulfide solid solutions, an additional T_{1u} mode should appear in the vibrational representation. This mode is the so-called “gap” mode,^[9] which is related to the Gd-S bond vibration. According to the selection rules, all the modes noted above are IR active, but not active in Raman spectra. Despite these considerations, we obtained the Raman spectra from these solid solutions.

Figure 1 shows the IR and Raman spectra of $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.04, 0.1, 0.25$), which are compared with the pure α -MnS. The IR spectra practically coincide in position and shape with the data for natural mineral Alabandite (α -MnS),^[27,28] the Raman spectrum of α -MnS coincides with the spectrum from the RRUFF database.^[29] The spectra in Fig. 1 are obtained in the equivalent experimental conditions and later they were normalized by the spectral contour area.

The observed frequencies of the vibrational modes in Raman and infrared spectra correspond to the phonons emerging from the center of the Brillouin zone, as presented in Table 1.

The rest of the peaks observable in the Raman spectra in Fig. 1 are the vibrational modes emerging from the boundaries of the Brillouin zone. Phonon dispersion curves along the W-L- Γ -X-W-K- Γ points of the Brillouin zone and the phonon density of states for α -MnS are presented in.^[30]

Emerging of vibrational modes from the Brillouin zone boundaries can be produced either by the defects of the crystal structure or by the local distortions of that structure induced by the Gd ions' doping. The spectral contour at 274 cm^{-1} may be associated with the activation of the LO (L) and LO (X) phonons. The peaks in the region of 200 cm^{-1} correspond to TO (L) and LA (L) vibrations. In the frequency range below

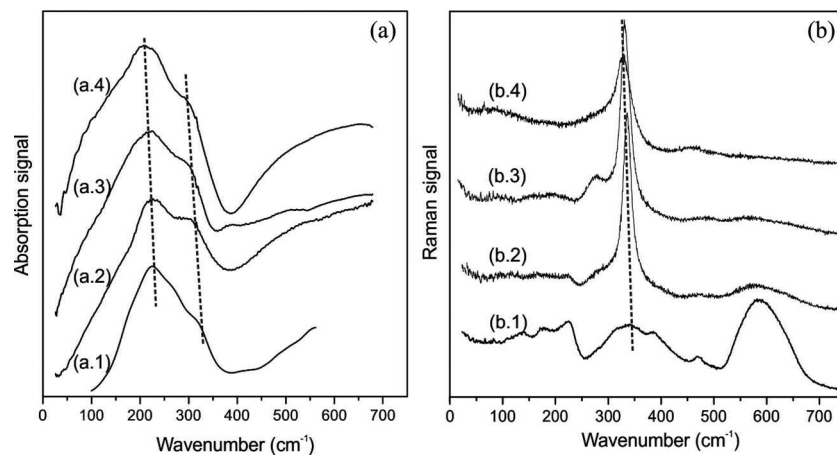


Figure 1. Infrared (a.1) and Raman (b.1) spectra of pure manganese sulfide and gadolinium-doped manganese sulfide with gadolinium content equal to 0.04 (a.2, b.2), 0.1 (a.3, b.3), and 0.25 (a.4, b.4).

Table 1. Experimental and calculated frequencies of modes in Raman and infrared spectra of pure α -MnS and gadolinium-doped manganese sulfide and their assignments.

Compound	TO			LO		
	IR	R	Calc.	IR	R	Calc.
MnS	225	226	222	321	340	340
Gd _{0.04} Mn _{0.96} S	224	224	221	316	335	337
Gd _{0.1} Mn _{0.9} S	216	–	220	305	331	336
Gd _{0.25} Mn _{0.75} S	209	–	216	289	327	322

180 cm^{-1} manifestation of LA (X), TA (L), and TA (X) modes is possible.^[30]

In addition to the features in Raman spectra discussed above, a wide bell-shaped band is observed near 600 cm^{-1} in the Raman spectra of α -MnS and (Mn,Gd)S solid solutions. The intensity of this band is maximum for α -MnS and drops down with gadolinium concentration. We attribute it to the double resonance of phonons from Brillouin zone boundaries, in analogy with the graphite Raman spectra.^[31] Increase in Gd content must lead to the decrease of anharmonicity of the Mn–S vibrations and to the observed decrease of this band height.

The calculated and measured TO and LO optical phonon modes are summarized in Fig. 2. On the whole, the predicted phonon frequencies are in good agreement with the experimental data.

The interpretation of the experimental data within the MREI model evidences that for the solid solution under study, the general situation of “one-mode” behavior is implemented. TO and LO optical mode frequencies vary continuously and approximately linearly with Gd concentration from the frequency of MnS to that of GdS,^[32] which are also shown in Fig. 1 by the dashed vertical lines.

Calculations show the presence of the triply degenerate gap mode of Gd vibration, which is split into two modes—the

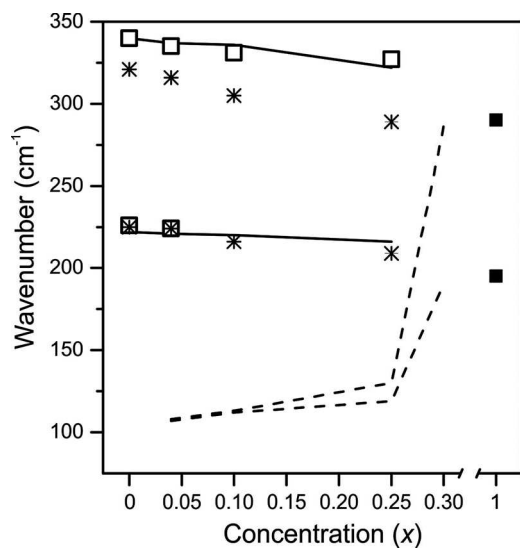


Figure 2. Phonon modes of cubic gadolinium manganese sulfide solid solutions. The solid lines represent calculations of longitudinal optical and transverse optical frequencies of gadolinium-doped manganese sulfide, dashed lines are longitudinal optical and transverse optical “gap” modes of gadolinium. The open squares symbols and snowflakes symbols refer to measured Raman and infrared data, respectively. Black squares are experimental Raman values of gadolinium sulfide (32).

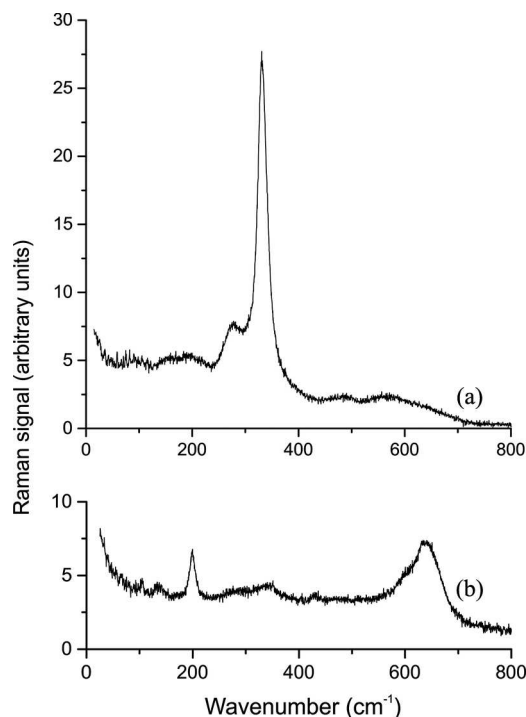


Figure 3. Raman spectra of gadolinium-doped manganese sulfide ($x = 0.1$) (a), Raman spectra of the undamaged sample; (b) Raman spectra recorded from the burnt crater.

transverse and the longitude ones. Increase of Gd content results in the increase of gap mode splitting. The crystal structure of $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ preserves stability up to $x = 0.25$. Upon further increase in Gd content, the system becomes less stable, and it is more energetically favorable for this system to release the excess of Gd in the form of GdS. The TO and LO gap modes of solid solution at x above 0.25 are transformed into TO and LO modes of pure GdS, as shown in Fig. 2 by the bending of the dashed lines.

At excessive power of the laser beam, the formation of burnt craters on the surface of (Gd, Mn)S samples is observed. In analogy with paper,^[33] we observe the disappearance of Raman peaks corresponding to $\text{Gd}_{0.1}\text{Mn}_{0.9}\text{S}$ structural vibration is practically absent at burnt spots, and the Raman spectra recorded from these spots correspond to the known spectra of MnO_2 ,^[34] Fig. 3.

No anomalies due to restructuring were revealed upon decrease of temperature, and all solid solutions preserve O_h symmetry down to 5 K.

Conclusion

We investigated the solid solutions of $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ ($x = 0.25, 0.1, 0.04$) using infrared absorption and Raman scattering. LO–TO splitting of the manganese–sulfur bond vibration is observed in the vibrational spectra. The Raman lines forbidden by the selection rules are manifested in the spectra due to the violation of the local symmetry of the crystal. The solid solutions under study exhibit “one-mode” behavior that was successfully described by the MREI model. The critical concentration of gadolinium for preserving the stability of the cubic MnS crystal lattice is 0.25.

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