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LATTICE VIBRATIONS IN $FeIn_2S_4$ SINGLE CRYSTALS

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I. INTRODUCTION

The spinel structure compounds are one of the most important and most comprehensive studies of all structure types. The spinel structure compounds are used in photo-electronic and optical applications [1] due to the wide band gap observed in these structures. The studies of spinel structure compounds also have numerous applications in geophysics and magnetism [2–4]. The ferromagnetic properties of some spinels are also of great importance in solid state chemistry.

Lattice dynamical calculations is a valuable tool for the detailed analysis of the vibrational spectra, information on bonding, structure and the dynamics of the spinel structure compounds.

II. EXPERIMENTAL

The single crystals of $FeIn_2S_4$ were grown by the method of directional crystallization of an almost stoichiometric melt of this compound. The synthesis of $FeIn_2S_4$ crystals was carried out by the two temperature method from the parent elements of purity no less than 99.999 wt. %. To suppress the dissociation of the compound and obtain a composition of necessary stoichiometry, we created a pressure of sulfur vapors of ~1.5 atm. over the melt and conducted cooling of the $FeIn_2S_4$ melt in the regime of the switched off furnace. The ingot synthesized was ground and placed into a double quartz ampoule; the internal ampoule had a cylindrical capillary at its end, which ensured the formation of the single crystals seeding. After the evacuation of the ampoule to a residual pressure of ~10^{-3} Pa, it was placed into a vertical one zone furnace. The temperature in the furnace was increased at a rate of ~100 K/h to 1400 K and, for the homogenization of the melt, was maintained at this temperature for 2 h, after which the directional crystallization of the melt was conducted by reducing the temperature at a rate of ~2 K/s until complete solidification of the melt. For the homogenization of the ingots obtained, they were annealed at ~1020 K for 150 h. This regime made it possible to reproducibly grow single crystals ingots with a diameter of ~14 mm and a length of ~40 mm.

Raman and IR spectra of the $FeIn_2S_4$ compound were obtained on the Fourier spectrometer FIR–30 in the frequency range 50–500 cm^{-1} at room temperature with a resolution of 2–4 cm^{-1}.

III. VIBRATIONAL ANALYSIS

The crystal structure of spinel AB_2S_4, classified as the HI1 space group O_h^7 (Fd3m), is cubic and consists of a slightly distorted cubic close-packed arrangement of S–ions with the A and B–ions occuping 1/8 of the tetrahedral and 1/2 of the octahedral interstices, respectively (normal spinel) [5]. An inverse spinel has one half of the B–ions occuping the tetrahedral sites and the other half of the B–ions and the A–ions occupy the octahedral sites. In the present paper only normal spinel structure compounds are considered. In normal spinels, the deviation from the cubic close–packed structure consists of a displacement of the S–ions by an amount $\sqrt{3}\delta$ away from the occupied tetrahedral sites. For an ideal spinel $\delta = 0$.

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The rhombohedral primitive unit cell has a volume of V = a3/3 (a = lattice constant) and contains two formula units (14 atoms).

From a group theoretical treatment it is known that the optical zone–centre (Γ = 0) phonon modes can be resolved into 17 fundamental lattice vibration modes [6]. The representation of these modes at zero wave–vectors is expressed as

(1)

Here the A_{1g}, E_g, and $3F_{2g}$ modes are Raman–active and the F_{1u} modes are infrared-active modes. In the $5F_{1u}$ modes, one mode with frequency zero is a translation mode, and the other four modes are observed in the infrared region. There is one Raman-inactive mode, F_{1g}, while $2A_{2u}$, $2E_u$, and $2F_{2u}$ are infrared–inactive modes.

IV. RESULTS AND DISCUSSION

The study of the vibrational spectra of complex semiconductor in the far IR region provides information not only on optical modes, but also allows solving the problems of the structure and dynamic theory of the crystal lattice. Vibrational dispersion curves allow us to calculate the density of states from which we can determine the complete set of thermodynamic functions of the crystal.

Figure 1 shows the IR reflection spectra for FeIn2S4 single crystals. It can be seen that in the spectra of this compound, five bands of reflection are clearly manifested in the investigated frequency region at 72, 86, 190, 241 and 336 cm^{-1}.

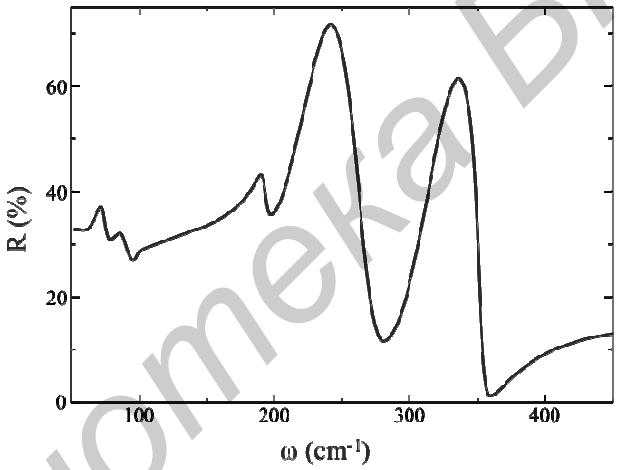

Figure 1 – IR spectra of $FeIn_2S_4$

The obtained IR reflection spectra were processed by the Kramers–Kronig sequential dispersion analysis (DA–K–K), which subsequently determined the frequencies of the longitudinal ωLO and transverse ωTO phonons, the attenuation coefficients gn, and the value of the high–frequency permittivity ε∞. The parameters that gave the best agreement for the $FeIn_2S_4$ are shown in Table 1 and Table 2.

Table 1 – Optical phonons parameters

Optical mode	ωLO, cm–1	ωTO, cm–1	gn	Sn
1	351	316	17,5	0,012
2	262	225	18,5	0,018
3	194	184	5,0	0,06
4	91	83	4,0	0,011
5	76	68	4,0	0,013

Table 2 – Dielectric permittivities and effective charges parameters

Parameter	ε∞	ε0	——	—	—	—	——
Value	6,8	8,2	0,77	0,89	–2,61	1,21	1,24

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Raman scattering spectra of $FeIn_2S_4$ single crystals are presented in Figure 2.

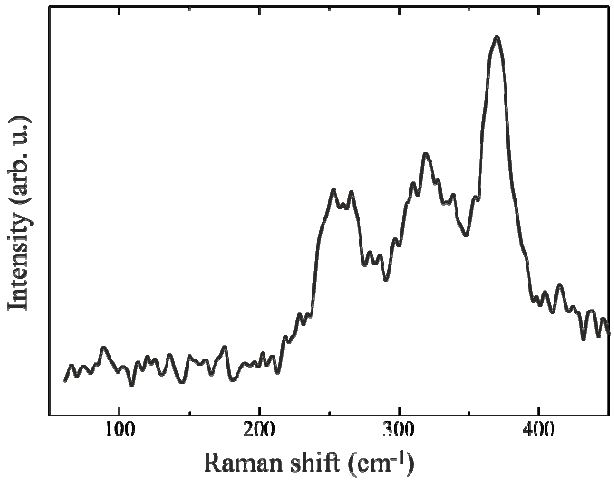

Figure 2 – Raman spectra of FeIn2S4

Raman spectra (Figure 2) in inverse spinels have complex behavior. The bands are broadened and partly more than five Raman bands (as predicted by group theory) are observed, with up to three $A1_g$ species instead of one. These findings probably arise from the lack of full translation symmetry in inverse spinels due to the random distribution of the bivalent metals and indium on the octahedral sites. The observed additional bands were assigned to $F1_u$ longitudinal phonon modes, which have been claimed to be enhanced by resonance effects. However, as an alternative explanation it must be borne in mind that the additional bands are defect-induced modes also due to the breakdown of the translation symmetry.

III. CONCLUSIONS

The Raman and IR spectra for $FeIn_2S_4$, have been obtained by means of the microprobe technique. This technique is very useful in the present case because large single crystals of these compound, as required for conventional Raman measurements, are not usually available. The analysis of the results allows us to clarify the controversy in reported data on spinel $FeIn_2S_4$.

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MECHANICAL PROPERTIES OF MEMS COMPONENTS BASED ON ANODIC ALUMINUM OXIDE

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I. INTRODUCTION

Devices based on microelectromechanical systems (MEMS) are widely used in industrial electronics, medicine, military and space hardware. MEMS combine both electric and mechanical components. Their functional characteristics are defined by mechanical properties of material, they are based on.

Nowadays, silicon and its modifications are the most used materials in MEMS technology, because of its good physical and mechanical properties. MEMS technology based on silicon doesn't always allow to

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