RAMAN SPECTROSCOPY OF CUBIC HgS:Fe*

W. Szuszkiewicz, B. Witkowska

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland

AND M. Jouanne

Laboratoire de Physique des Solides de l'Université Pierre et Marie Curie (URA 154)
4, Pl. Jussieu, 75252 Paris Cedex 05, France

From the Raman spectra performed at temperatures from 10 K to 295 K for $Hg_{1-x}Fe_xS$ crystals containing up to a few percent of iron the phonon energies for selected high-symmetry points of the Brillouin zone have been determined. A very high ionicity of these mixed crystals has been found. The TO phonon frequency value for β-HgS at Γ point, equal to about 177 cm^{-1}, suggested previously in the literature, has been confirmed.

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Mercury chalcogenides crystallizing in the sphalerite (zinc blende) structure have been intensively investigated in the past due to their attractive physical properties, resulting from the zero-gap band structure. In particular, the values of the optical phonon energies at the center of the Brillouin zone have been determined for HgTe and HgSe a long time ago from the infrared reflectivity spectra ([1] and [2], respectively), and from the Raman scattering data ([3] and [4]). The phonon dispersion relations for HgTe and HgSe have been also investigated by the neutron scattering measurements [5]. Due to all these data the values of phonon energies for selected high symmetry points of the Brillouin zone are well known for these semiconducting compounds. Moreover, the theoretical calculations of the phonon dispersion relations in a whole Brillouin zone have also been published [5, 6]. The third semiconductor under consideration (β-HgS) is a metastable modification of this compound. Due to serious problems with this crystal growth in the past the lattice dynamics has never been studied in β-HgS (and have not been analyzed theoretically) till now. The only exception is an information given in the literature that TO phonon frequency value equal to 177 cm^{-1} has been determined from the reflectivity investigations of thin evaporated β-HgS slabs [7]. Nevertheless, the corresponding reflectivity spectrum has never been published and. e.g., the phonon damping and the oscillator strength parameter values are not known.

New method of β-HgS crystal growth has been recently found in the Institute of Physics, PAS. Idea of this method takes advantage of β-HgS metastable

crystal structure stabilization by the mercury sulphide doping with small amount of the transition metal impurity. The $Hg_{1-x}Fe_xS$ mixed crystals (containing up to a few percent of Fe) have been obtained by this method. The crystal structure investigations by means of the electron microscopy and X-ray diffraction measurements demonstrate that it is possible to obtain by the above-mentioned method big size good quality monocrystals without any precipitations or inclusions of the second (cinnabar) phase [8]. Successful growth of new materials obtained on the basis of β-HgS enable us to investigate the lattice dynamics in order to complete the experimental data corresponding to different mercury chalcogenides.

Samples used for the optical measurements were selected from two ingots with the nominal crystal compositions equal to $x = 0.02$ and $x = 0.04$. Raman scattering experiments were performed in a quasi-backscattering geometry on a few crystal slices taken from each ingot. The real crystal composition values determined by energy dispersive X-ray fluorescence (EDXRF) method did not differ more than about 0.002 for the given set of slices. Resulting from it a possible frequency shift of the observed Raman peaks did not exceed the experimental error related to the optical measurements. Under the circumstances the average real crystal composition values, corresponding to each set of slices (equal to $x = 1.1$ and $x = 3.7$, respectively) were chosen for the presentation of the results. Structures found in the Raman spectra obtained on cleaved and chemically polished unoriented crystal faces of the slices taken from the same ingot were quite similar. The Raman spectra were recorded using a double monochromator equipped with holographic grating and a S20 photomultiplier. More than one millimetre thick samples were mounted on the cold finger of the continuous flow helium cryostat, the measurements were performed at few different temperatures from 10 K to 295 K. The thermal expansion coefficient for β-HgS is not known but as we suppose due to the high sample thickness the possible strain effect on the results obtained can be neglected.

The Raman spectra were excited with Ar^+ laser lines (corresponding to wavelengths equal to 457.9 nm and 514.5 nm), a spherical lens was used to focus the laser beam on the sample surface. In order to avoid the heating of the sample by the incident light a power level value equal to 100 mW was chosen. The fact that possible both strain and heating effects can be neglected in our case was confirmed by the supplementary Raman scattering measurements, performed on the well-known and widely investigated semiconducting compound (HgTe). The frequency positions of the structures observed by us for HgTe samples correspond within the experimental error to these known from the literature.

A very rich structure in the Raman spectra was found at every temperature. The intensity of the Raman signal was very low (tens times smaller than that e.g., obtained for GaAs), but due to the low value of the scattered light background the structures under consideration were well seen. Typical results of the Raman scattering measurements performed in the high frequency range at $T = 10$ K on $Hg_{0.989}Fe_{0.011}S$ sample are shown in Fig. 1. The present interpretation of the results obtained, limited to the high-energy part of the spectra, is given in Table.

The most intense peak in the spectrum has been assigned to LO-phonon excitation. The second much less intense peak observed at frequency range close to the
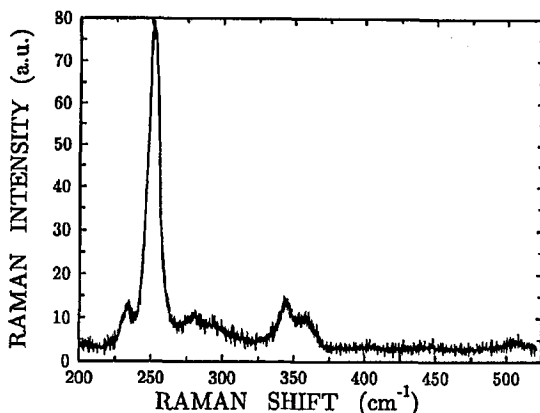
Fig. 1. High-frequency part of the Raman scattering spectrum taken at $T = 10$ K on the $Hg_{1-x}Fe_xS$ sample with $x = 0.011$.

TABLE

Identification of the structures (related to "HgS-like" lattice excitations) observed by the Raman scattering measurements for two sets of $Hg_{1-x}Fe_xS$ samples. The experimental errors are higher than 1 cm^{-1}.

Frequency [cm^{-1}]				Assignment
$x = 0.011$		$x = 0.037$		
$T = 295$ K	$T = 10$ K	$T = 295$ K	$T = 10$ K	
175	–	178	–	TO
247	252	247	253	LO
341	344.5	350	343	$2TO(\Gamma)$
	358.5		360	$2TO(L)$
–	507	–	–	2LO
278	280	285	289	TO("FeS") ?
289 ?	293.5	302	311	LO("FeS") ?

suggested in the literature value 177 cm^{-1} was attributed to TO phonon excitation. The observation of characteristic structures related to the double frequencies of TO and LO phonons confirm these assignments. The low temperature difference value of TO and LO phonon frequencies determined for the lowest $Hg_{1-x}Fe_xS$ mixed crystal composition under investigation ($x = 0.011$) is equal to about 75–80 cm^{-1}. Such extremely high ratio of the frequency separation of the above--mentioned lattice modes to LO frequency value, even not comparable to the similar values known for other II–VI semiconductors crystallizing in the sphalerite (zinc blende) structure, confirms the high ionicity of the investigated material. It

should be mentioned that we have observed a very rich structure in the Raman spectra in spite of a very high free-carrier concentration found in the samples under investigation (however, it should be also stressed that the Raman scattering spectra, taken by us for comparison for the transition metal doped HgTe or HgSe, do not reveal such numerous structures).

Small double structure just above the LO phonon frequency could correspond in our opinion to TO and LO branches of "FeS-like" local phonon. The structure under consideration changes more rapidly with the increasing Fe content than other parts of the spectrum. If the assignment presented above is quite correct a significant (above 10 cm^{-1}) splitting of Fe local mode into TO and LO branch observed for the same sample with $x = 0.011$ is also an argument supporting a high mercury sulphide ionicity.

Structure observed in the low-frequency part of the spectra are related to the "disorder activated" acoustic phonon excitations, difference processes etc. (disorder activated excitations can be observed even for the mixed crystal composition as low as $x = 0.03$, as it has been demonstrated for $Zn_{1-x}Mn_xS$ system [9]). In order to interpret all the structures in the Raman scattering spectra the supplementary measurements performed on the oriented faces of crystals are necessary. The transverse and longitudinal lattice excitations can be distinguished by such measurements. There also exists the clear need of the independent determination of phonon frequencies (e.g., by means of the neutron scattering measurements and phonon dispersion calculations).

Acknowledgments

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