LATTICE DYNAMICS
OF CUBIC MERCURY SULPHIDE*

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The acoustic phonon dispersion of mercury sulphide of zinc-blende struc-
ture (β-HgS) was studied by inelastic neutron scattering. The measurements
were carried out at 19 K and 295 K on HgS crystals doped with Fe. A slight
decrease in phonon frequencies with increasing temperature was found, the
temperature dependence being the strongest for LA phonons with $[\xi, \xi, 0]$
propagation. From acoustic phonon dispersion the values of selected elastic
constants were determined for β-HgS.
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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 prop-
erties, resulting from the zero-gap band structure. The lattice dynamics of HgTe
and HgSe is relatively well known. In particular, in spite of the high neutron ab-
sorption cross-section of natural mercury and the high non-coherent scattering the
acoustic phonon dispersion curves were determined by inelastic neutron scattering
for both compounds, while the optical modes were investigated for HgTe only [1, 2].
The optical mode frequencies corresponding to the selected high symmetry points
of the Brillouin zone were determined for HgSe from both infrared reflectivity
and Raman scattering measurements (see, e.g., [3, 4]). The stable crystal structure
of third chalcogenide (mercury sulphide) is a hexagonal one (cinnabar, α-HgS).
However, as it was recently shown, good quality monocrystals of the metastable
sphalerite phase (β-HgS) can be obtained by doping mercury sulphide with small
amount (about 2%) of a selected transition metal [5].

Big size (above 1 cm^3) perfect monocrystals of β-HgS were grown in the Insti-
tute of Physics, Polish Academy of Sciences in Warsaw by the modified Bridgman

method (by doping mercury sulphide with Fe). As the samples two 1 millimeter thick slices with different crystallographic orientations (cut from as grown ingot) were used for the neutron measurements. The lack of detectable precipitations and other crystallographic phases in the samples was verified by X-ray diffraction methods. The chemical composition of the samples was determined by the energy dispersive X-ray fluorescence (EDXRF) analysis. Fe content in the samples under investigation corresponds to the mixed crystal $Hg_{0.982}Fe_{0.018}S$ composition. Such a small amount of Fe in the sample is not expected to affect strongly the lattice dynamics and to give rise to impurity-related modes (like a local, gap or resonant modes) of sizeable intensity in the neutron scattering measurements.

Inelastic neutron experiments were performed at the Orphee reactor in Laboratoire Léon Brillouin (LLB) in Saclay on a triple-axis spectrometer installed on a thermal source. Both the monochromator and the analyzer were pyrolytic graphite in (002) reflection. The scans were performed with constant final wave vector $k_\xi = 2.66$ Å^{-1}.

The acoustic phonon dispersion curves for β-HgS were determined at room temperature along the high symmetry directions [100], [110] and [111]. The set of measured branches is displayed in Fig. 1.
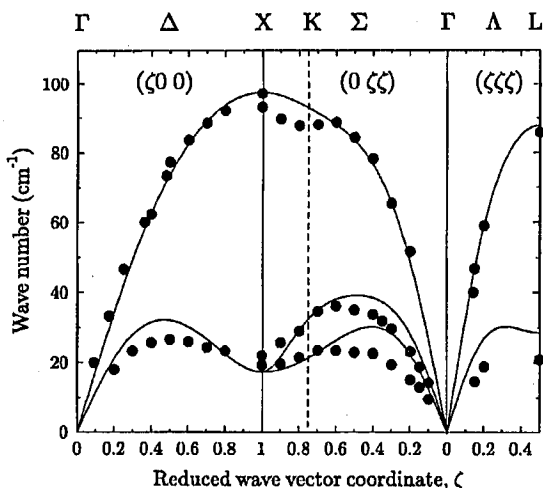

Fig. 1.   Acoustic phonon dispersion along the high symmetry directions in the Brillouin zone measured for β-HgS by inelastic neutron scattering at $T = 295$ K. Points — experimental data, solid curves — the dispersion relations calculated from the non-central version of the rigid ion model with the same values of the force constants as those used previously in the case of HgTe and HgSe [1, 2] (see text).

These results are in agreement with values obtained from recent Raman scattering measurements performed on the same crystals [6], for zone boundary modes at high symmetry points. The maximum value of 95 cm^{-1} obtained for the acoustic modes and the minimum value of 175 cm^{-1} for the optical modes at

$q = 0$ allow us to anticipate a wide gap in the one-phonon density of states, as the dispersion of the optic modes should be moderate. Such wide gap could result mainly from the large differences of Hg and S atomic mass values.

The influence of the temperature on the lattice dynamics was checked by repeating a part of the measurements at 19 K. Only a slight hardening of the acoustic modes was observed (more pronounced for LA modes than for TA ones for which the increase at low temperature does not exceed 1 cm^{-1}).

The theoretical phonon dispersion was calculated using non-central version of rigid ion model (RIM) (see, e.g., [7,8]). In this version both the first- and the second-neighbour interactions are described by tensor coupling parameters in their most general form. A reasonable agreement between the theoretical curves and experimental points was obtained when we used the values of RIM parameters previously applied for HgTe and HgSe [1,2] (except for the atomic masses, lattice parameter and effective charge values). We did not attempt to adjust the parameters of the model on the experimental data of the acoustic modes. Information on the optical branches is indeed necessary to get a reliable set of parameters.

From the analysis of the phonon dispersion the elastic constant values for β-HgS can be deduced. The values of c_{11} and c_{44} can be directly estimated with a reasonable accuracy from TA and LA dispersion along [001] direction. Table

TABLE

Selected elastic constant values (at 10^{10} N/m^2) for mercury chalcogenides at low temperatures.

	c_{11}	c_{44}	Comments
HgTe	5.971	2.241	[11], extrapolation to $T = 0$ K
HgSe	6.900	2.3073	[9], extrapolation to $T = 0$ K
	6.90	2.33	[10], extrapolation to $T = 0$ K
β-HgS	8.13	2.64	[12], theoretical predictions
	7.53 ± 0.20	2.28 ± 0.06	this work, $T = 19$ K

shows the comparison of the low-temperature values of c_{11} and c_{44} for β-HgS with the literature data taken for HgSe [9,10], HgTe (see [11] and the references therein) and the theoretical predictions for β-HgS given in [12]. As one can see, the estimated experimental values of selected elastic constants for β-HgS agree well with the data for other mercury chalcogenides. The possible high experimental error related to the determination of third elastic constant c_{12} (which could be estimated by indirect method only) does not allow the similar comparison on the basis of the present neutron scattering data. More experimental data for acoustic phonon dispersion along [111] high symmetry direction is necessary in order to determine precisely the value of c_{12}.

Non-monotonous LA dispersion along [110] direction (in the q wave vector range corresponding to the 0.5–0.8 of the q vector value for the X high symmetry point of the Brillouin zone) was found. This effect is related to the particular character of the atoms vibration in the unit cell (probably the dominant part of

the second-neighbour interactions is the central one). This "anomaly" is known, e.g., for IV–VI compounds but has not been reported till now for II–VI compounds crystallizing in the zinc-blende structure and, in particular, has not been seen for previously investigated HgSe and HgTe.

The peculiar properties of lattice dynamics of β-HgS resulting from both high ionicity of material and large difference of anion and cation mass should affect also a lot of the optical modes. It seems that from this point of view β-HgS could be the most interesting representative of mercury chalcogenides. This work is in progress and the results concerning LO and TO phonon dispersion will be soon published.

Acknowledgments

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