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LATTICE DYNAMICS OF CUBIC ZINC SULFIDE*

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Dispersion curves for the acoustic phonons have been measured in the [100], [111], and [110] directions by neutron scattering. The zone boundary frequencies have been used to reassign multi-phonon events previously reported from infrared and Raman spectra. The data are compared with a preliminary six-parameter valence force model.

DISPERSION relations for the acoustic lattice vibrations of cubic ZnS have been measured in the [100], [111], and [110] directions by neutron inelastic scattering. The principal sample used was a natural crystal (light green in color) which in its original form was twinned about the [111] direction. This was cut to yield a much smaller crystal of 1.44 cm^3 volume, which appeared free of twins. One branch, the transverse (lowest) acoustic mode in the [110] direction, was measured using a second sample. This was a larger synthetic crystal grown by vapor deposition (kindly loaned by Eagle–Picher Industries).

The measurements were made on the University of Michigan triple axis spectrometer using constant-Q scans exclusively. Extensive use was made of the resolution formulation of Cooper and Nathans[1] to find reciprocal lattice positions where the intensity and width of observed phonon peaks were optimum. For the longitudinal phonons, it was found advantageous, for example, to deviate from the usual scans along lines passing through the origin of reciprocal space; phonons of the [001] LA branch measured from (1, 1, 3) to (1, 1, 4) were much superior to those measured between (0, 0, 4) and (0, 0, 5).

Dynamical structure factors were calculated on the basis of a simple rigid ion model, and proved to be essentially a perturbation of those for germanium.[2] Because of the small size of the available crystals, the optic branches have not yet been reliably observed. Lack of intensity also prevented observation of the [001] LA and [111] LA events exactly at the zone boundary.

The data are shown as solid circles in Fig. 1. The dashed lines are the sound velocities derived from the elastic constants of Berlincourt *et al.*[3] The solid curves represent a preliminary least squares fit to the data based on a six-parameter version of the shell model.[4] In our model the short range forces are given in terms of a valence force field.

The zone boundary acoustic mode frequencies compare poorly with those inferred from optical data reported earlier,[5–7] although the TA (L) frequency of 72 cm^{-1} deduced by Brafman and Mitra[8] from polytype analysis is in good

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agreement with our TA (L) value. However, the present neutron data provide a new basis for interpreting the multi-phonon optical events. A possible assignment, which is consistent with both sets of data (but not necessarily unique), is shown in Table 1. The open circles of Fig. 1 correspond to this assignment. For the Raman data, it appears necessary to assign at least two of the frequencies to one-phonon events, which under usual conditions are considered forbidden.

Further efforts to measure the optical branches and to refine the fitted model are in progress.

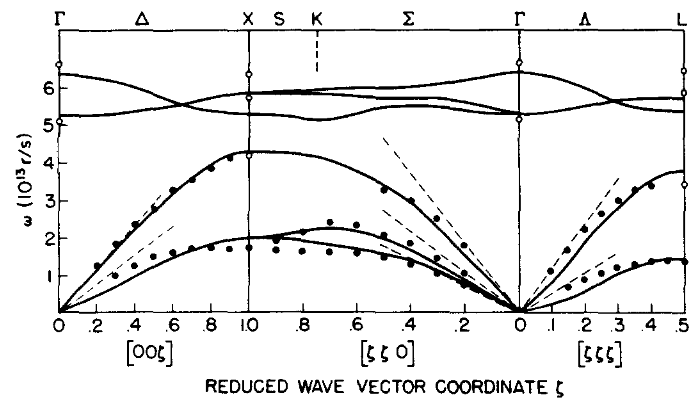

FIG. 1. Dispersion curves of cubic ZnS for the primary symmetry directions. The measured neutron points are the solid circles. Optical branch frequencies, shown as open circles, were deduced from optical experiments (cf. Table 1). The lowest open circles at X and L are extrapolations of the neutron data. The dashed lines are sound velocities based on measured elastic constants.[3] The solid curves represent a preliminary dynamical calculation.

Table 1. Branch assignments of phonon events observed in infrared absorption[5] *and Raman scattering*[7] *spectra*

Present assignment		Observed frequencies	
Frequency	Branch	Infrared[5]	Raman[7]
179 cm^{-1}	LA (L) or		176 (181) cm^{-1}
186	2 TA (X)		
222	LA (X)		219 (222)
304	LO (X)		295 (304)
352	LO (Γ)		352 (353)
397	LO (X) + TA (X)		386 (401)
415	TO (L) + TA (L)	415 cm^{-1}	
431	TO (X) + TA (X)	431	
444	2 LA (X)	455	448 (457)
491	LO (L) + LA (L)	491	
526	LO (X) + LA (X)	526	511 (525)
608	2 LO (X)	593 605	
624	2 LO (L)		612 (621)
642	LO (X) + TO (X)	642	636 (644)
676	2 TO (X)	677	665 (672)
737	LO (Γ) + LO (L) + TA (L)	733	
831	TO (Γ) + TO (X) + LA (X)	823	

The presently assigned frequencies are based on the set (in cm^{-1}): LO (Γ) 352, TO (Γ) 271, LO (L) 312, TO (L) 342, LA (L) 179, TA (L) 73, LO (X) 304, TO (X) 338, LA (X) 222, TA (X) 93. The values in parentheses are Nilsen's frequencies before his calibration correction.

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Les relations de dispersion, dans le cas de phonons acoustiques, furent mesurées par diffusion neutronique selon les directions [100], [111] et [110]. Les fréquences à la limite de la zone de Brillouin furent employées dans la redétermination de processus multi-phonons, récemment signalés dans les spectres infra-rouge et Raman. On compare, enfin, les résultats avec les prédictions d'un modèle préliminaire à six paramètres de force de valence.