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# LATTICE DYNAMICS OF ZnO AND BeO

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Phonon dispersion in ZnO has been mapped for frequencies up to $4 \times 10^{12}$ c/sec. A postulated low frequency mode does not exist, and the results are in good agreement with the predictions of a simple shell model. Mean square vibrational amplitudes in ZnO and BeO are calculated.

ELECTRON diffraction patterns from thin plates of ZnO show fairly strong diffuse streaks along [101] and [$\bar{1}$01] directions through (0, 0, 2$l$) reciprocal lattice points, and along [001] through (2$h$, 0, 0) points.[1] Such streaking can be produced by a low frequency vibrational mode. Furthermore, neutron scattering results[2] indicated the presence of very low frequency optic modes in the isomorphous BeO, although no comparable streaks are seen in electron diffraction from this compound. (These modes were not found in reference 3).

Calculations of the lattice dynamics of wurtzite structures[4–6] have usually been complicated by the large number of parameters required. We have adopted a rather simple shell model[7] with nearest and second nearest neighbour compressional and shearing forces. The effective ionic charge, $Z^*$, is easily calculated for wurtzite from the splitting of the Raman frequencies due to a directional dependence of the coulomb dipole summation as $q \to 0$. We obtain

$$\omega_L^2 - \omega_T^2 = (Z^*)^2\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{e^2}{v_c}\,4\pi C_0,$$

where $\omega_L$ is the Raman frequency for $q \to 0$ in the direction for which the mode is longitudinal, and $\omega_T$ that when the $q$-direction is such that the mode is transverse: $m_1$, $m_2$ are the atomic masses, $e$ the electron charge, and $v_c$ the volume per ZnO molecule. $C_0 = (\epsilon + 2)^2/9\epsilon \quad 1$ where $\epsilon$ is the 'isotropic' high frequency dielectric constant. Furthermore, the equation should give the same result for the splitting of the $A_1$ character mode as for that of character $E_1$. When the Raman frequencies[8] are substituted, this is found to be true within experimental error, with the result $Z^* = 1.03$: this compares well with values found by other methods.[9] Taking $Z = 2$ we calculate the mechanical polarizability, and assuming only oxygen polarizable, the oxygen shell charge for a given shell spring. The four short-range force parameters and oxygen shell spring were chosen to fit the Raman frequencies and elastic constants.[10] We found that for this model (Fig. 1), there are no exceptionally low frequency modes, and all modes are stable for small changes in the force parameters. Dynamic structure factors were also calculated.

The experiment was performed on the triple axis spectrometer at Lucas Heights with the active co-operation of Drs. A.W. Pryor and M.M. Elcombe. A large (1cm × 1cm × 0.4cm) ZnO crystal was available from AIRTRON of New Jersey, U.S.A. Very low intensities prevented the mapping of the phonon dispersion above about $4 \times 10^{12}$ c/sec., but this was sufficient to demonstrate the absence of a mode of unusually low frequency. Furthermore, quite

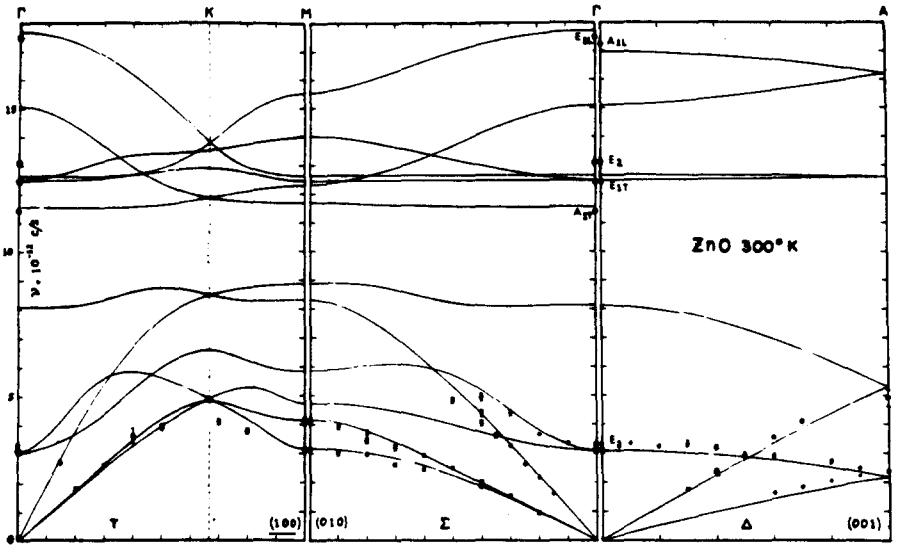


FIG. 1. Phonon dispersion in ZnO at 298°K predicted by a shell model based on elastic constants and Raman spectrum, with measured frequencies.

good agreement was obtained in this region with the previously calculated dispersion relation. A search in the positions of the electron diffraction streaks failed to reveal enhanced scattering in these directions, but because of the intensity problems and uncertainty in the spectrometer focussing conditions for this situation, we cannot unilaterally conclude that the streaking is peculiar to electron diffraction. It will be necessary to calculate in detail the diffuse scattering pattern expected from the model.

Further confirmation of the validity of the model, at least for the low frequency region, was obtained when mean square vibrational amplitudes were calculated for comparison with recent X-ray analysis [11] (Table 1). We confirmed that the vibration was almost isotropic as had been assumed in this analysis.

*Table* 1: ZnO *B-factors calculated at* 298°K.

| | $\bar{B}^{11}_{exp}$ | $B_{11} = B_{22}$ | $B_{33}$ |
|---|---|---|---|
| Zn | 0.63 ± 0.02 | 0.50 | 0.60 |
| O | 0.68 ± 0.07 | 0.54 | 0.63 |

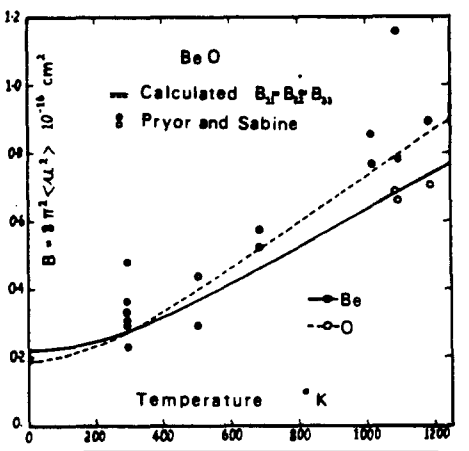


FIG. 2. BeO *B*-factors for a shell model with measurements of Pryor and Sabine.[14]

A similar model was then calculated for BeO, using available Raman frequencies [12] and elastic constants.[13] Fair agreement is obtained with some very recent neutron scattering:[3] again there is no low frequency mode. The comparison of the calculated vibrational amplitudes with an extensive neutron diffraction analysis [14] (Fig. 2) is very satisfactory, although we have neglected the temperature dependence of the $C_{ij}$.

The agreement between the models and experiment can be improved by fitting the parameters to the phonon data: as well, we have not included dielectric constant data in our calculations. In a forthcoming paper we will make quantitative comparisons of the lattice dynamics of wurtzite and blende, with particular attention to ZnS.

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## REFERENCES

1. COWLEY J.M., *Proc. Int. Conf. Electron Diffraction and Crystal Defects*, Melbourne, (1965).
2. BRUGGER R.M., STRONG K.A. and CARPENTER J.M., *J. Phys. Chem. Solids* **28**, 249 (1967).
3. OSTHELLER G.L., SCHMUNK R.E. and KEARNEY R.J., Preprint.
4. MERTEN L., *Z. Naturforschg.* **17a**, 65 (1961).
5. SULLIVAN J.J., *J. Phys. Chem. Solids* **25**, 1039 (1964).
6. NUSIMOVICI M.A. and BIRMAN J.L., *Phys. Rev.* **156**, 925 (1967).
7. WOODS A.D.B., COCHRAN W. and BROCKHOUSE B.N., *Phys. Rev.* **119**, 980 (1960).
8. DAMEN T.C., PORTO S. and TELL B., *Phys. Rev.* **142**, 570 (1966).
9. BERLINCOURT D., JAFFE H., SHIDZAWA L.R., *Phys. Rev.* **129**, 1009 (1963).
10. BATEMAN T.B., *J. appl. Phys.* **33**, 3309 (1962).
11. ABRAHAMS S.C. and BERNSTEIN J.L., *Acta Crystallogr.* **B25**, 1233 (1969).
12. LOH E., to be published in *Phys. Rev.*
13. CLINE C.F., DUNEGAN H.L. and HENDERSON G.W., *J. appl. Phys.* **38**, 1944 (1967).
14. PRYOR A.W. and SABINE T.M., *J. Nuc. Mat.* **14**, 275 (1964).

Phonon–Dispersion im ZnO wurde bis auf Frequenze von $4 \times 10^{12}$ Hertz beobachtet. Eine vorausgesetzte Kleinfrequenz-Schwingung wurde nicht beobachtet, und die Resultate übereinstimmen gut mit den Voraussagen des einfachen Schalenmodells. Die Mittelquadratamplituden für ZnO und BeO wurden berechnet.