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LATTICE VIBRATIONS OF BeO*

R. M. BRUGGER†, K. A. STRONG†

Phillips Petroleum Company, AED, Idaho Falls, Idaho

and

J. M. CARPENTER

The University of Michigan, Department of Nuclear Engineering, Ann Arbor, Michigan

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Abstract—Parts of the dispersion relations for BeO have been measured. These relations are for waves moving in the [10$\bar{1}$0] direction with their polarization vectors in the (0001) plane. The initial slopes of the measured acoustical branches agree with those obtained from ultrasonics. Branch intercepts at the zone centers of 84 meV ($1{\cdot}27 \times 10^{13}$ rad/sec) and possibly 5 meV (8×10^{12} rad/sec) were found. The dispersion relations are correlated with infrared, Reststrahlen and "frequency spectra" measurements and proposed models.

THE following communication presents measurements of the dispersion relations for BeO. Although these are not complete they are of interest at this time because (a) they are for a new class of crystal, (b) quantitatively they are markedly different from the initial theoretical curves,[1] and (c) more complete measurements and complete theoretical curves from the MTR will not be available for 1–2 years. The data are being presented now so that they can be a guide to other theoreticians[2,3] who attempt to explain the dynamics of Wurtzite materials.

As dispersion relations for more crystals are measured and are calculated[4] the interest in crystals with structures other than cubic increases.[5] Several calculations[1-3] of the dispersion relations for crystals having the Wurtzite structure are now available, but measured curves were not available because of the increased complexity of the branches and the difficulty of obtaining a satisfactory sample. Dispersion relations were measured for the Wurtzite material BeO for waves propagating in the (0001) plane and these data are compared with infrared, Reststrahlen, and "frequency spectra" data and they indicate modifications of the theoretical curves.

In addition to being an example of a Wurtzite crystal, BeO's unique properties made it of interest in itself. It is a metal oxide ceramic[6] having a very high heat conductivity while having a very low electrical conductivity. It is one of the principal reactor moderating materials and this has stimulated great interest[7] in its physical properties as they pertain to its moderating capabilities.

Three models[1-3] have been developed for the motion of the atoms in Wurtzite crystals SULLIVAN'S[2] dynamical model is based on the shell model with the assumptions (i) that non-Coulomb forces extend only to nearest neighbors, and (ii) that the forces for the modes of motion in which the cation sublattices and the anion sublattice are vibrating as units is equivalent to the motion of a sphalerite crystal. YOUNG'S[1] model assumes that BeO is ionic and expresses the lattice potential as a repulsive core plus a Coulomb attraction. The Coulomb contribution to the dynamical matrix is determined by the Ewald method and the effective charge on the ions is selected to match the cohesive energy and the maximum of the frequency spectrum. No structure factors for inelastic scattering have been calculated.

BeO has the Wurtzite structure (hexagonal,

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† Presently with Idaho Nuclear Corporation, Idaho Falls, Idaho.

$a = 2{\cdot}698$ Å, $c = 4{\cdot}380$ Å with four atoms per unit cell[8]). It forms nearly perfect crystals, but large crystals are very difficult to obtain. AUSTERMAN[9] has developed methods of growing BeO crystals, large by X-ray diffraction standards, but small by neutron inelastic scattering standards. Initially it was thought that to have adequate intensity, 10–20 of the largest of these crystals would be needed to form an assembled and aligned sample. Two of Austerman's largest crystals, each a little less than 1 cm^3, were borrowed to explore the feasibility of measuring the dispersion relations for this material.

The dispersion relation measurements were made with inelastically scattered slow neutrons using the MTR phased chopper velocity selector.[10] The detectors were placed near scattering angle of 90° and 105° while the incident energies ranged between 30 and 65 meV. The two crystals were glued to movable aluminum bases and were aligned, first optically and then by matching their neutron Bragg scattering. The two crystals were aligned with the c axis vertical, so that the (0001) plane is parallel to the scattering plane and the observed phonons propagate in the (0001) plane with their polarization vector ξ in this plane. In aligning the crystals with Bragg neutron scattering no indication of mosaic spread or twinning in these crystals was detected. Crystals grown in a similar method have mosaic spreads of $\sim$40 sec.[11] Because of this small mosaic spread, little double Bragg+phonon scattering is expected.[12] All data were obtained with the sample at room temperature.

Because of the recently increased intensity of the MTR velocity selector[13] and the use of He^3 counters, the measurements with only two crystals were more favorable than expected and dispersion relations were measured. Figure 1 shows the measured dispersion relations in the $[10\bar{1}0]$ direction of BeO for the waves having a finite component of their polarization vector ξ in the (0001) plane. The wave vector of the phonon q is in reciprocal Angstroms and the energy of the phonon E is in meV. The lines are our best estimate of the positions of the branches, and the dashed lines are our guesses as to how the branches might continue. Since BeO has four atoms per primitive unit cell, there are 12 branches to the dispersion relations. In Fig. 1, since the curve is over determined in many areas, the spread in the points indicates the experimental error.

With four atoms per primitive unit cell, there are twelve branches to the dispersion relation, with no degeneracies for general q along $[10\bar{1}0]$. For this direction of high symmetry, Be and O polarizations are similar. The polarizations of the four transverse waves $T\|$ with their displacement vectors lying in the (0001) plane are uniquely defined by symmetry for all q along $[10\bar{1}0]$. Four modes with this polarization are shown in Fig. 1(a).

Among the eight remaining modes, the polarization of four transverse waves $T\perp$ with displacements perpendicular to the (0001) plane and the polarization of four longitudinal waves L are unique only at $q = 0$. At larger q, these eight modes have mixed $T\perp$ and L polarization. Two of these remain predominately $T\perp$ and since waves with this polarization cannot be excited in this experiment, they probably are two unobserved modes. Two waves remain predominately longitudinal, one of which is an acoustic mode; these are labeled LA and LO in Fig. 1(b).

Of the four remaining modes, two, which are longitudinal at $q = 0$, go over to $T\perp$ at the zone boundary, in accordance with YOUNG's[1] calculations. Two modes which are $T\perp$ at $q = 0$ may go over to L at the zone boundary. This is probably why the branches marked A and B could not be observed at the zone boundary and at $q = 0$, respectively. Clearly since only four modes are distinguishable in Fig. 1(b), two, which have a longitudinal component, have not been observed. Small structure factors under the conditions of the experiment may have precluded their observation. This would be the case for modes in which oxygens in each cell have displacements opposite in direction from the berylliums.

The separation of the longitudinal and transverse branches $T\|$ was made by analyzing the polarization factor $(Q\cdot\xi)$ where Q is the difference between the wave vectors of the incident and final neutrons. Double Bragg+phonon scattering might violate this condition but none is expected in this experiment because of the small mosaic spread of the crystals. Optical and acoustical branches were partially separated by a simplified, but not unique, consideration of structure factors.[14] Structure factors for inelastic scattering from Wurtzite structures have not been calculated yet. The

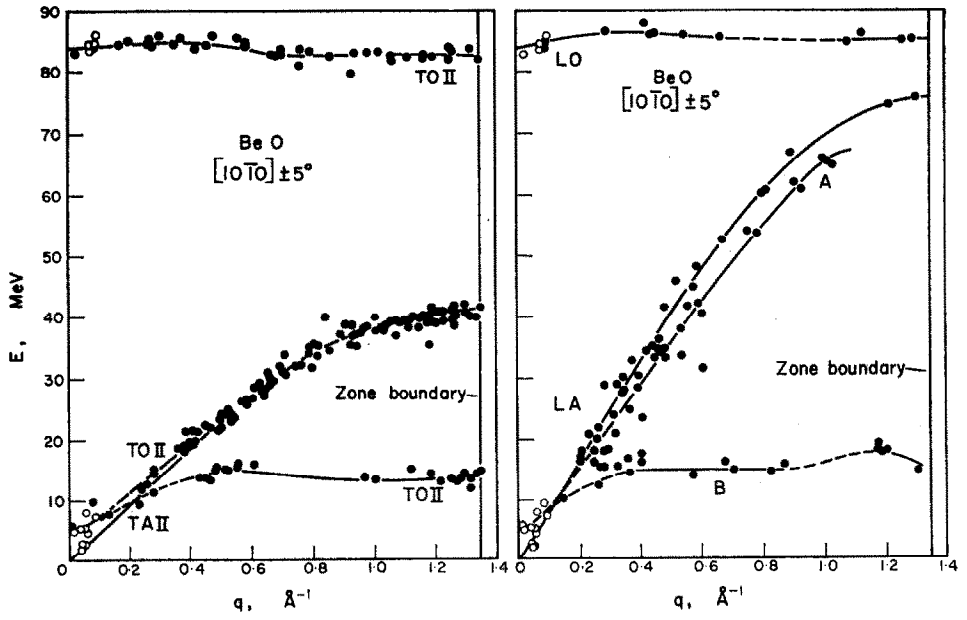

FIG. 1. The dispersion relations measured for waves traveling in the [10$\bar{1}$0] direction in BeO. The left-hand section (a) shows the transverse waves which have a uniquely defined polarization in the (0001) plane. The right-hand section (b) shows the parts of branches with a large component of the polarization vector parallel to $\boldsymbol{Q}$ such that they produce a measurable phonon peak. These branches are uniquely defined as longitudinal only at $q = 0$. The solid points are for phonons with q in the [10$\bar{1}$0] ± 5° direction while the open points are for q in the (0001) plane.

postulation in Fig. 1(a) of the $TO\|$ and $TA\|$ branches and in Fig. 1(b) of the LA and A branches is based on this simplified approach to structure factors. The calculated dispersion relations of YOUNG[1] qualitatively verify these postulations.

Two obvious intercepts were found, those at 84 meV for a longitudinal and a transverse branch. Following the predictions of YOUNG,[1] searches for intercepts between 50 and 70 meV and 10 and 20 meV were made but no intercepts were found. In fact no points were detected in the triangle ($q = 0$, $E = 15$ meV) ($q = 0$, $E = 80$ meV) ($q = 0{\cdot}9$ Å^{-1}, $E = 70$ meV) in any direction in the (0001) plane. Since there is no zone in the (0001) plane where Bragg scattering is forbidden, an optical intercept below 10 meV is difficult to observe because the intercept can be masked by Bragg scattering. In the data of Fig. 1, for $q < 0{\cdot}1$ Å^{-1}, points for q's in directions other than the [10$\bar{1}$0] have been plotted as open circles. There is some indication of an optical intercept at 5 meV and the optical branches near 15 meV probably have this low lying $q = 0$ intercept.

The two lines of Fig. 1 at small q starting at $E = 0$ are the slopes of the acoustical branches determined from BENTLE'S[15] elastic constant measurements. The initial slopes of the measured acoustical branches agree well with these. The TA branch is closely approximated by a sine function which suggests nearest neighbor forces only for this type of shear wave. The lack of optical intercepts between 10 and 84 meV agree with the infrared[16] measurements in which no bands were observed between 240 cm^{-1} and 700 cm^{-1}. Reststrahlen and dielectric constant[17] measurements confirm the 84 meV intercept.

The almost flat optical branches at 84 meV will produce a sharp peak in the frequency distribution. This agrees with the peak observed by SINCLAIR[18] in the "frequency spectrum" of BeO. These flat optical branches are similar to what is expected in ZrH_2[19] and suggest that, for this type

of motion, each Be (or O) in its tetrahedron of O's (or Be's) experiences an isotropic force. Sinclair observed no sharp peak near 50 meV or near 65 meV in his "frequency spectrum"; peaks would be present if nearly flat optical branches were at 50 meV or 65 meV as suggested by YOUNG.[1] The measured dispersion relations indicate no such branches. Because of his limited resolution Sinclair would have had difficulty observing a peak in his frequency spectrum arising from the flat optical branches at 15 meV.

These dispersion relation measurements suggest that the calculated dispersion relations of Young must be modified. The initial slopes of the LA and $TA\|$ branches must match these data and that of Bentle. The LO branch which intersects $q = 0$ at 86 meV and decreases as q increases must be flattened and intersect $q = 0$ at 84 meV. The second LO branch near 65 meV must be lowered to near 15 meV. Of the two flat $TO\|$ branches near 65 meV, one must be raised to 84 meV and the other lowered to 15 meV. These data do not indicate where the "$T\perp$" branches occur, but Bentle's elastic constants give an initial slope for the $TA\perp$ branch. The lack of peaks in the "frequency spectrum" of Sinclair indicate that there are no flat $TO\perp$ branches near 50 meV and 65 meV.

The data for this paper agree with data from other sources where comparisons are possible. In addition, these data give a clearer, but not yet complete, picture of the lattice motion for the determination of the forces. Measurements in other symmetry directions are needed but these were not started because the velocity selector was needed for another experiment. When the MTR triple axis spectrometer is in operation the $T\perp$ branches in the [10$\bar{1}$0] and the branches in the [0001] direction will be mapped.

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