RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 12 15 JUNE 1985

High-pressure Raman study of the optic-phonon modes in BeO

G. A. Kourouklis,* A. K. Sood,† and H. D. Hochheimer
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

A. Jayaraman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 5 March 1985)

The shift with pressure of the transverse optic-phonon-mode frequencies in BeO has been measured up to 20 GPa at 25 K by Raman scattering, using a diamond anvil cell. The mode Grüneisen parameters have been determined from the pressure data and are compared with the systematics observed in III-V and other II-VI compounds. The total energy calculations of Chang and Cohen predict a pressure-induced transition from wurtzite to NaCl-type phase at about 20 GPa. Unfortunately the pressure limit in the present study is inadequate to demonstrate this transition, for it stops just near the predicted transition pressure, which would almost surely require considerable overpressure.

I. INTRODUCTION

The effect of high pressure on the optic-phonon modes in several diamond–zinc-blende materials have been investigated in recent years by Raman spectroscopy, using the diamond anvil cell.[1-5] (See, for example, Ref. 2 for GaAs and InP; Ref. 3 for AlN, BN, and BP; Ref. 4 for GaSb, InAs, and InSb; Ref. 5 for ZnS, ZnSe, and ZnTe.) From these studies, the mode Grüneisen parameter γ, and in the case of compound semiconductors the transverse effective charges as a function of pressure, have been obtained, the latter from the LO-TO splitting. These results have been compared with the effective charges calculated using the bond-orbital model[6] as well as the dielectric-matrix pseudopotential method[7] and are found to be in reasonable agreement.

As for the wurtzite structured compounds, the pressure dependence of the optic phonons in ZnO and CdS have been investigated[8,9] by Raman spectroscopy. Mitra, Brafman, Daniels, and Crawford,[8] who were the first to study these compounds up to a pressure of 1 GPa reported a correlation between the γ_{TO} and the ionicity expressed in terms of Szigetti effective charge. In the case of CdS, Venkateswaran, Chandrasekar, and Chandrasekar[9] carried out Raman measurements to 4.2 GPa. They attributed the presence of the wurtzite lattice phonon beyond the wurtzite to NaCl-type phase-transition pressure of 2.7 GPa, to the coexistence of both the phases over a considerable pressure range. They obtained Grüneisen parameters in good agreement with the previous studies by Mitra, Brafman, Daniels, and Crawford.[8]

Our motivation to study BeO at high pressure by Raman spectroscopy was for two reasons.

(1) A recent total-energy calculation,[10] using the pseudopotential method and the density functional formalism by Chang and Cohen, has predicted a phase transition from wurtzite to an insulating rock-salt structure in BeO around 20 GPa.

(2) We thought it would be worthwhile to compare the pressure dependence of the phonon frequencies of BeO, which is more ionic in nature compared to the III-V and other II-VI compounds, with the systematics observed for the large class of diamond–zinc-blende structure semiconductors. In this study we have carried out Raman measurements on BeO up to 20 GPa using the diamond anvil cell, at three different temperatures (25, 100, and 295 K). The three observable optic phonons are seen even at 20.6 GPa, the limit of pressure reached in the present study, and this would indicate that the wurtzite phase is dominant. The mode Grüneisen parameters obtained correlate well with the Szigetti effect charge. These results will be presented and discussed in this paper.

II. EXPERIMENTS

A gasketed diamond anvil cell[11] (DAC) was used to generate hydrostatic pressure. The well-known ruby-fluorescence technique[12] was used to determine the pressure in the sample chamber. For the room-temperature measurements (300 K) the standard 4:1 methanol-ethanol mixture was used as the pressure-transmitting medium and for the low-temperature measurements argon was used.[13] For argon filling, the DAC was mounted in an optical crysostat, the central block of which is cooled by coils circulating liquid helium. After cooling the cell, argon was admitted into the gasket region and condensed into the gasket hole until it was filled. The pressure chamber was then sealed and the excess argon pumped out. Then the He contact gas was admitted. The outer jacket of the cryostat was continuously pumped to maintain high vacuum. Pressure was applied by turning the screw thread mechanism of the DAC by two long rods suitably coupled to the cell and coming out of the vacuum region through neoprene gasket seals. In this setup pressure could be changed while the cell was at low temperature, by turning the long rods with the special wrench from outside the cryostat. The cell temperature in the gasket region was monitored with a germanium resistance thermometer, placed inside the DAC in the vicinity of the gasket region.

The spectra were recorded using a conventional Raman double monochromator with a band pass of ~4 cm^{-1}. Both 488- and 514.5-nm laser lines from an argon-ion laser were employed for excitation, in the backscattering geometry. The power level for the laser line was about ~800 mW. The Raman frequencies were determined from a computer fit of the observed lines to a Gaussian profile.

The BeO crystals were flux grown and were kindly made available to us by Dr. K. Nassau. They were small elongated pieces, colorless, and transparent, with natural faces. Small fragments obtained by breaking the crystals were used for the pressure study. A fragment of suitable size having as nearly a smooth surface as possible was selected for mounting inside the gasket hole. The crystal fragments were therefore of random orientation and hence no polarization studies were attempted.

III. RESULTS AND DISCUSSION

BeO crystallizes in the wurtzite structure and belongs to space group C_{6V}^4 ($P6_3mc$) with two formula units in the primitive unit cell. There are thus nine optical branches to the phonon dispersion[14]

$$\Gamma = A_1(\mathrm{ir,R}) + 2B_1 + E_1(\mathrm{ir,R}) + 2E_2(\mathrm{R}) \ ,$$

where ir and R denote the infrared and Raman activity of the mode. Since A_1 and E_1 are both ir and R active, LO and TO modes are nondegenerate and can be observed by Raman spectroscopy. Unfortunately in our experiments A_1(LO) and E_1(LO) could not be observed with BeO in the diamond anvil cell, due to their weak-scattering efficiencies. The A_1(TO) and E_2(TO) modes are very close in frequency ($A_1 = 681$ cm^{-1}, $E_2 = 687$ cm^{-1}) at atmospheric pressure and hence E_2 could not be well resolved at ambient pressure and at low pressure. However, these two modes are well separated for $p \geqslant 2$ GPa, due to the difference in their pressure response. Figure 1 shows the typical Raman spectra for three different pressures at 25 K. As expected, the Raman signal is stronger at low temperatures and hence the different modes can be followed easily up to high pressures.

The phonon frequencies for A_1, E_1, and E_2 modes are plotted as a function of pressure in Fig. 2. The solid lines are the least-squares-fitted curves to $\omega = \omega(0) + bP$, with ω_0 and b as two adjustable parameters. The mode Grüneisen parameters defined as

$$\gamma_i = -\frac{B}{\omega_i(0)} \frac{d\omega_i}{dP} \ ,$$

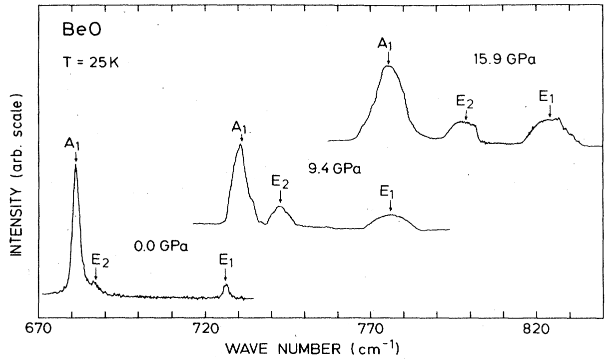

FIG. 1. The transverse optic-phonon modes of BeO at three different pressures and at 25 K, recorded with the sample in the diamond anvil cell. At low pressure the E_2 is almost coincident with A_1. The broadening of the Raman peaks at higher pressures may be associated with the presence of some nonhydrostatic components.

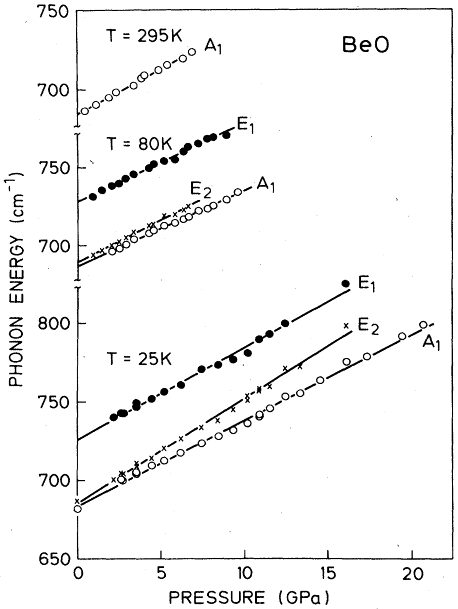

FIG. 2. A plot of the phonon frequency as a function of pressure at 295, 80, and 25 K. For $T = 295$ K only the A_1 is clearly seen up to 7 GPa. At higher pressures it becomes too weak to be seen.

where B is the bulk modulus, are given in Table I for all the three modes at the three temperatures. The value of B used[10] was 249 GPa. The values of γ_i have errors within ±5%. The temperature dependence of γ_i shown in Table I is quite peculiar and we have no explanation for it at the present time. It is not connected with any uniaxial stress because the slopes were obtained from the low-pressure region, where solidified argon behaves quite hydrostatically. More experiments are needed at different temperatures to establish the temperature dependence of γ. Such a study would be interesting to decipher the relative contributions of the quasi-harmonic and -anharmonic interactions to phonon frequencies.

We next come to the comparison of the γ with other compounds. This can be best illustrated in terms of the correlation diagram[8] between the γ_{TO} and the Szigetti effective charge per cation valence electron, $q_S^*/Z_c e$. The Szigetti effective charge q_S^* is related to Born's transverse effective charge q_T (Ref. 15) by the relationship

$$q_S^* = \frac{3q_T}{\epsilon_\infty + 2} \ .$$

TABLE I. Mode Grüneisen parameters γ for BeO. γ values were calculated using $B_0 = 249$ GPa (Ref. 10) and $\omega_i(0)$ values taken from the fitting (intercept).

Temperature phonon (cm^{-1})	25 K	80 K	295 K
A_1(681)	1.952	1.724	2.035
E_2(687)	2.375	1.919	
E_1(725)	1.967	1.693	

q_T in turn is given by

$$q_T^2 = \frac{\Omega M_r}{4\pi} \epsilon_\infty (\omega_{\rm LO}^2 - \omega_{\rm TO}^2) \quad ,$$

where Ω is the volume of the primitive unit cell, M_r is the reduced mass of the vibrating atoms and ϵ_∞ is the high-frequency dielectric constant ($\epsilon_\infty = 2.95$ for BeO). Using the LO and TO values at atmospheric pressures, we obtain $q_S^*/Z_c e = 0.56$ for the A_1 mode and 0.55 for E_1 mode. The corresponding values of γ are plotted versus $q_S^*/Z_c e$ in Fig. 3, where the rest of the data are taken from Ref. 8. As can be seen from the figure, the values of γ_i are very similar to ZnO and follow the trend noted by Mitra, Brafman, Daniels, and Crawford.[8]

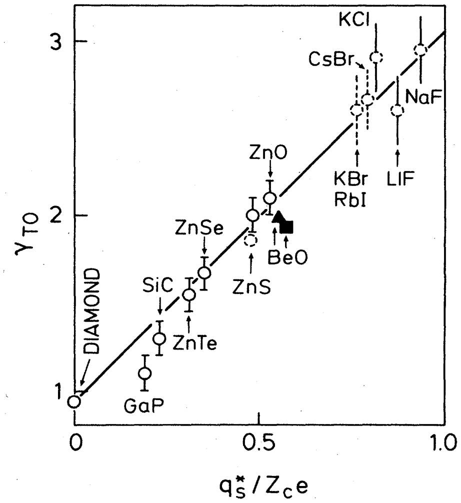

FIG. 3. The long-wavelength transverse-optic-mode Grüneisen parameter vs the Szigetti effective ionic charge per cation electrons. All the data except for BeO have been taken from Ref. 8. Δ, E_1 mode of BeO; □, A_1 mode of BeO.

Chang and Cohen from their calculations of the total energy have predicted a wurtzite to NaCl-type phase transition in BeO around 20 GPa.[10] If the phase transition occurs, one expects to see the Raman peaks of wurtzite to disappear, and in the NaCl-type phase there should be no first-order Raman peaks. Up to the highest pressure reached in the present study (20.6 GPa) the Raman peaks of the wurtzite phase are still seen, although they become quite weak in intensity at the highest pressures. Also there is no visual indication under the microscope for a phase change. From these results one is tempted to conclude that the wurtzite to NaCl-type phase transition has not occurred in BeO at pressures up to 20 GPa. However, the Raman results cannot decide the issue, for the following reason. If the phase transition is very sluggish, there will be both wurtzite and NaCl-type phases coexisting over a range of pressure and this can still give Raman peaks from the wurtzite phase. In fact such a situation has been encountered in CdS (Ref. 9) where the wurtzite Raman peaks are seen even at 4 GPa, while the wurtzite–NaCl-type phase transition is known to occur near 2.7 GPa. In any case the pressure limit of the present study is not adequate to show the presence of this transition, which is bound to be sluggish, requiring considerable overpressure to initiate the transition. Further, we feel that only high-pressure x-ray diffraction can settle this question decisively and at the present time such a study is in progress.

ACKNOWLEDGMENT

We wish to thank Dr. K. Nassau of AT&T Bell Laboratories for kindly supplying the BeO crystals for this study.

---

[*] Present address: National Technical University, Department of Physics, Zografou Campus, Athens 15773, Greece.

[†] On leave from Materials Science Laboratory, Reactor Research Center, Kalpakkan 603102, India.

[1] For a review, see B. A. Weinstein and R. Zallen, in *Light Scattering in Solids, Vol. IV,* edited by M. Cardona and G. Güntherodt, Topics in Applied Physics, Vol. 54 (Springer, Heidelberg, 1984); A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).

[2] R. Trommer, H. Müller, M. Cardona, and P. Vogel, Phys. Rev. B **21**, 4869 (1980).

[3] J. A. Sanjurjo, E. Lopez-Cruz, P. Vogl, and M. Cardona, Phys. Rev. B **28**, 4579 (1983).

[4] K. Aoki, E. Anastassakis, and M. Cardona, Phys. Rev. B **30**, 681 (1984).

[5] B. A. Weinstein, Solid State Commun. **24**, 595 (1977).

[6] W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).

[7] W. Porod, P. Vogl, and G. Bauer, J. Phys. Soc. Jpn. **49**, Suppl. A, 649 (1980).

[8] S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, Phys. Rev. **186**, 942 (1969); O. Brafman and S. S. Mitra, in *Light Scattering in Solids,* edited by M. Balkanski (Flammarion, Paris, 1971), p. 284.

[9] Umadevi Venkateswaran, M. Chandrasekar, and H. R. Chandrasekar, Phys. Rev. B **30**, 3316 (1984).

[10] K. J. Chang and M. L. Cohen, Solid State Commun. **50**, 487 (1984).

[11] K. R. Hirsch and W. B. Holzapfel, Rev. Sci. Instrum. **52**, 52 (1981).

[12] J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instum. **44**, 1 (1973).

[13] H. D. Hochheimer, H. J. Jodl, W. Henkel, and F. Boldua, Chem. Phys. Lett. **106**, 79 (1984).

[14] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. **181**, 1351 (1969).

[15] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, New York, 1954), Chap. 2.