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Raman spectra of beryllium to 23 GPa

H Olijnyk† and A P Jephcoat
Department of Earth Sciences, University of Oxford, Oxford OX1 3PR, UK

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Abstract. Raman spectra of Be were studied at room temperature at pressures up to 23 GPa. The transverse-optical (TO) zone-centre phonon mode of hcp Be could be observed to maximum pressure. Neither new modes nor anomalies in the pressure shift were observed in the pressure range of 8.6–14.5 GPa where a phase transition has been reported. The TO mode frequency and its pressure dependence are discussed in terms of the elastic properties of Be.

1. Introduction

Under ambient conditions Be crystallizes in the hcp lattice (Be-I). A transition into the bcc structure (Be-II) occurs slightly below the melting point at normal pressure. The pressure decrease of the hcp–bcc transition temperature suggests a hcp–bcc transition at room temperature under high pressures [1] in accordance with theoretical structure stability studies, which predict a transition to bcc below 200 GPa at 0 K [2]. X-ray diffraction studies, performed at pressures up to 28 GPa, found a slightly distorted hcp phase (Be-III) which becomes stable at pressures between 8.6 and 14.5 GPa [3]. Based on these x-ray diffraction data a smaller orthorhombic cell was also proposed for Be-III [4].

It is well known that structural phase transitions may be accompanied by phonon anomalies. In hcp metals, softening of the transverse-optical (TO) zone-centre phonon mode occurs in connection with transitions into the Sm-type phase (regular lanthanides) [5] and into the ω-phase (Zr) [6], which appears to be related to a weakening of the C_{44} elastic constant [7]. No such behaviour could be noticed for the hcp–bcc transition in Mg [8].

In this respect, it is of interest to study the behaviour of the phonon modes of Be, especially in the vicinity of the phase transition. For Be, phonon data are only available at ambient pressure from inelastic neutron scattering [9, 10] and Raman scattering [11, 12]. In the present study, we investigated Be by Raman spectroscopy at pressures up to 23 GPa, well above the pressure range where the structural transition was reported.

2. Experimental details

The Raman studies were performed on polycrystalline Be, with a purity of 99.7%, using a high-pressure diamond-anvil cell. Special care was taken in handling the Be in view of its toxicity. Raman spectra were excited with the 514.5 nm line of an Ar^+ laser focused down to 20 μm. Scattered light was analysed at an angle of 135° with respect to the incoming laser beam using a 0.6 m triple spectrograph and a liquid-nitrogen-cooled CCD multichannel

† Author to whom correspondence should be addressed.

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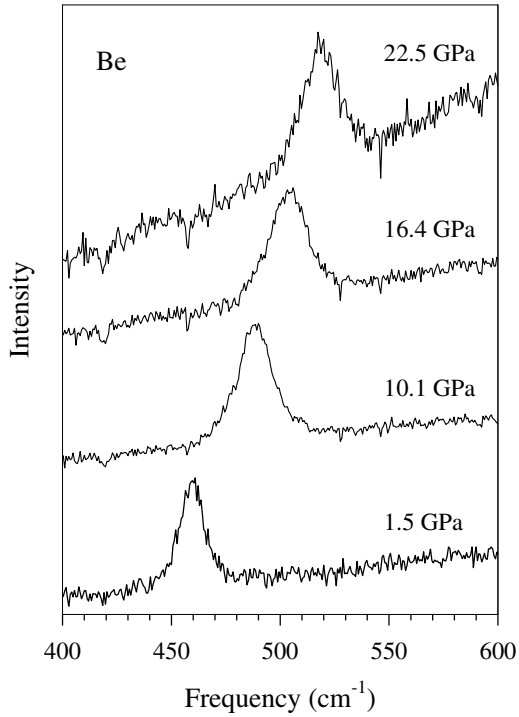

Figure 1. Raman spectra of Be at various pressures. The given uncertainties in the values for δ_0 and δ_0' represent the standard deviations of the fit and do not take into account the uncertainties in the frequency–pressure relation of the reference material Zn.

detector. Pressures were determined by the shift of the TO mode of a Zn sample [13] which was compressed together with the Be sample.

3. Results

The hcp lattice has two atoms per unit cell, which are located on sites of symmetry D_{3h}. The six normal modes of zero wavevector belong to the irreducible representations $A_{2u}+B_{1g}+E_{1u}+E_{2g}$. The B_{1g} and E_{2g} modes are the longitudinal and transverse optical modes, respectively. The doubly degenerate E_{2g} mode is Raman active.

One mode was observed in the Raman spectra of Be metal up to the maximum pressure. Typical Raman spectra of this mode at various pressures are shown in figure 1. A positive pressure shift in the investigated pressure range can be noticed (see figure 2). The frequency–pressure data are well represented by the expression

$$\nu(P)/\nu_0 = [1 - (\delta_0'/\delta_0)P]^{-\delta_0^2/\delta_0'} \tag{1}$$

where ν_0 is the mode frequency at $P = 0$, $\delta_0 = (\mathrm{d}\ln\nu/\mathrm{d}P)_{P=0}$ the logarithmic pressure coefficient and δ_0' the pressure derivative of δ for $P = 0$. These parameters are collected together in table 1.

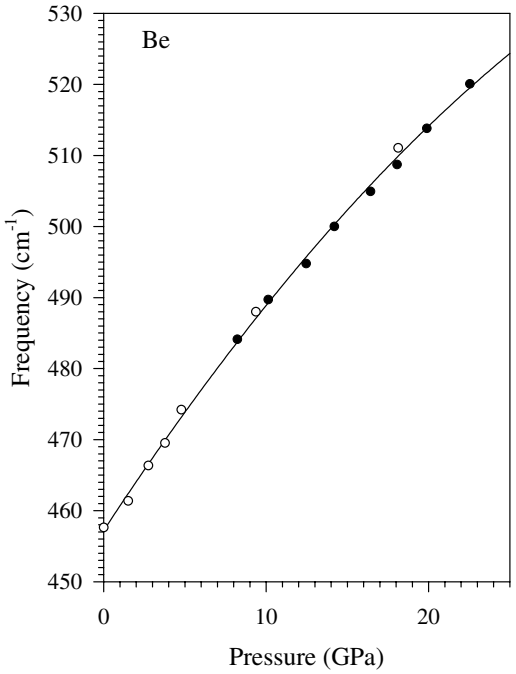

Figure 2. Pressure shift of the TO mode in Be. Full circles denote loading and open circles denote unloading.

Table 1. Pressure coefficients of the TO mode of Be.

	ν_0 (cm^{-1})	δ_0 (GPa^{-1})	δ_0' (GPa^{-2})
Be	457 ± 1	$0.008\,08 \pm 0.0004$	$-0.000\,332 \pm 0.000\,07$

4. Discussion

The hcp structure allows one Raman-active phonon mode. The frequency of the zone-centre TO phonon of hcp Be at room temperature and normal pressure from the present study is 457 cm^{-1} and compares favourably with the values obtained from inelastic neutron scattering [9, 10] and Raman scattering [11, 12]. The results of the present study—observation of the hcp TO mode to the maximum pressure of 23 GPa together with the non-occurrence of any discontinuity in the frequency–pressure curve—give no obvious evidence for a phase transition between 8.6 and 14.5 GPa. On the other hand, the TO mode might not be well suited for probing the transition to a phase whose structure seems to be a slight distortion of the original phase. The evidence for Be-III is based on the appearance of three additional diffraction lines above 14.5 GPa, which, together with the diffraction peaks of hcp, were indexed to obtain the distorted hcp or orthorhombic structure. Another interpretation, compatible with the present Raman results, is also possible. Assuming that only the new diffraction lines are characteristic for the new phase implies that hcp Be coexists with the new phase over a broad pressure range. A definite answer, regarding the structural behaviour of Be at high pressures, can only be given by a structural reinvestigation, for example using synchrotron sources with sensitive image plate techniques.

The zone-centre TO mode is a shear mode in which successive hexagonal planes beat

Table 2. Comparison between experimental and calculated (from equation (2)) C_{44} and C'_{44}.

Be	C_{44} (GPa)	C'_{44} (GPa)
Ultrasonic [16]	170.6	2.55
Ultrasonic [17]	154.9	
Present study	110	1.65

against each other and it is therefore intimately linked to the elastic shear modulus C_{44}. For many hcp metals this relation is well described by the expression [7, 14, 15]

$$\nu_{TO}(k=0) = \frac{1}{2\pi}\sqrt{\frac{4\sqrt{3}a^2C_{44}}{mc}} \tag{2}$$

where a and c are the lattice constants and m is the atomic mass. In table 2, the results for C_{44} and its pressure derivative C'_{44} calculated in this way are compared with ultrasonic data [16, 17]. The calculated C_{44} and C'_{44} are approximately 30% lower than the experimental values. Similar deviations between experimental and calculated elastic moduli data have been observed for Zn, Cd and Tl [7] which are distinguished by high elastic anisotropy. The bonding properties of Be are also highly anisotropic, which is manifested, for example, by the small c/a ratio of 1.58, which apparently decreases further under compression [3], and by an unusually small value of the elastic modulus C_{13} [16, 17], for which even negative values have been reported. The estimates of C_{44} from TO mode frequencies using equation (1) appear reasonable enough, in the case of Be, to use this relation for a semi-quantitative discussion of the compressional effects on the TO mode.

An average mode Grüneisen parameter $\gamma_i = -\mathrm{d}\ln\nu_i/\mathrm{d}\ln V$ was determined by the linear least-squares fitting of the $\ln\nu_i(P) - \ln V(P)$ values. The $V(P)$ data were taken from the high-pressure x-ray diffraction data using a Birch–Murnaghan equation of state with bulk modulus $B_0 = 128$ GPa and its pressure derivative $B'_0 = 3.5$ [3]. In figure 3 the mode Grüneisen parameter thus determined is shown as a function of the relative volume together with corresponding data for other hcp metals [13]. Be has the lowest Grüneisen parameter among the considered metals. Using expression (2) one obtains for the mode Grüneisen parameter

$$\gamma = 0.5\left(\frac{B}{B_c} - \frac{2B}{B_a} + \frac{BC'_{44}}{C_{44}}\right) \tag{3}$$

where B is the bulk modulus, B_a and B_c are the inverse linear compressibilities of the a and c axes, respectively, and C'_{44} is the pressure derivative of the elastic modulus C_{44}. Comparing the contributions of the three terms of (3) to γ for the different metals, one can note that the last term is relatively small for Be. This can be shown exemplarily for Be and Re which have comparable C_{44} values of 170 and 160.5 GPa, respectively, while the bulk modulus of Be is by more than a factor of three lower than that of Re ($B_{0Be} = 111$ GPa, $B_{0Re} = 372$ GPa) [16, 18]. Although C'_{44} of Be is 70% higher than for Re [16, 18], altogether the third term in (3) is approximately a factor of two smaller for Be than for Re. The contributions of the other two terms appear not to be significantly different between Be and Re according to the available compressibility data [3, 16–18]. The present analysis then suggests that it is an unusually high value of C_{44} relative to the bulk modulus which is responsible for the relatively low γ in Be.

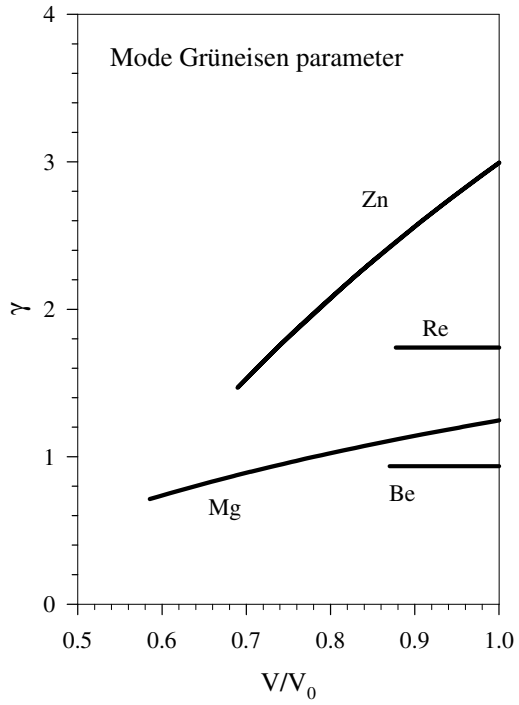

Figure 3. Experimental TO mode Grüneisen parameter against the relative volume for Be and various metals [7].

5. Conclusion

In Raman spectroscopic investigations the TO zone-centre phonon mode of hcp Be was observed to a maximum pressure of 23 GPa at room temperature. No new modes nor any discontinuity in the positive pressure shift were detected in the pressure range of 8.6–14.5 GPa, where a phase transition has been reported. The mode frequency was related to the elastic properties of Be using a simple relation derived previously from lattice dynamical force constant models. Within this formalism the relatively low mode Grüneisen parameter appears to be a consequence of an unusual high elastic modulus C_{44}.

Acknowledgment

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