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1999 J. Phys.: Condens. Matter 11 6589

(http://iopscience.iop.org/0953-8984/11/34/311)

J. Phys.: Condens. Matter **11** (1999) 6589–6594. Printed in the UK PII: S0953-8984(99)03732-7

Unusual broadening and splitting of the $K \approx 0$ transverse-optical phonon in hcp Mg at high pressure

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Received 26 April 1999, in final form 17 June 1999

Abstract. The transverse-optical Γ-point phonon mode was studied in the stability range of hcp Mg up to 50 GPa by Raman spectroscopy. A positive frequency shift is observed with increasing pressure in good agreement with recent theoretical studies using the pseudo-potential method. Unexpected broadening and splitting of this mode occurs under pressure. The separation increases to 20 cm^{-1} at 50 GPa. Slight structural modifications, anharmonic effects or an unusual pressure-induced dispersion around the Γ-point, not observed in other hcp metals so far, are suggested as possible explanations for the splitting.

1. Introduction

Mg, which crystallizes in the hcp structure at ambient conditions, is known to transform to the bcc structure around 50 GPa [1–3]. The formation of the high-pressure phase is intimately connected with subtle changes in the electronic structure due to sp $\rightarrow$ d electron transfer [1, 2]. In contrast to its heavier homologues Ca, Sr and Ba, which become d-like transition metals, Mg is considered as a nearly free-electron metal to about 100 GPa [4]. As a prototype for this class of simple metals Mg has been the subject of several theoretical studies and the calculated thermodynamic and elastic properties, as well as its P–T phase diagram, are in good agreement with the available experimental data [1, 2, 5–9]. Experimental high-pressure data on Mg are limited. In this paper the effect of pressure on optical phonons in Mg is reported to 50 GPa. The Raman spectroscopic data of the present study show an anomalous broadening and splitting of the TO zone-centre mode in Mg with increasing pressure not observed in other hcp metals and also not accounted for by the theoretical studies so far.

2. Experiment

Polycrystalline Mg samples of approximate thickness of 10 μm were loaded into the gasket hole of a high-pressure diamond-anvil cell. A 4:1 methanol:ethanol mixture and n-pentane were used as pressure-transmitting media. Pressures were determined by the ruby fluorescence method using the linear pressure scale [10]. Raman spectra were obtained with the 647.1 nm line of a Kr^+ laser (mainly) and the 514.5 nm line of an Ar^+ laser. The diameter of the focal spot was 10–15 μm. Scattered light was analysed at an angle of $\approx 135^\circ$ with respect to the incoming laser beam using a 0.6 m triple spectrograph and a liquid-nitrogen-cooled CCD multichannel detector.

0953-8984/99/346589+06$30.00

3. Results

The hcp lattice has two atoms per primitive 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. The bcc lattice with one atom per primitive unit cell has no optical phonon modes and therefore no Raman signals are expected in the stability field of this phase.

Raman spectra of Mg at various pressures are shown in figure 1. Starting from ambient pressure there is one Raman mode as expected for the hcp lattice. With increasing pressure this mode shifts to higher frequencies and the band gradually broadens. In the spectra above ∼15 GPa a rather broad plateau can be recognized in the peak maximum region which may be indicative of two closely located modes. The Raman signals became increasingly weak above 40 GPa and were not detectable above 50 GPa. This observation is in accordance with the onset of the transition to bcc in this pressure range and the gradual reduction of the hcp portion [3]. The peak positions were determined by fitting Voigt profiles to the Raman signals. Above 8 GPa a better description was achieved by fitting two modes to the observed Raman band. The pressure dependences of the phonon frequencies of the different high-pressure runs determined in this way are shown in figure 2. The data show a continuous increase of the mode splitting under compression which increases to about 20 cm^{-1} at the maximum pressure. The frequency of the E_{2g} phonon of hcp Mg at room temperature and normal pressure from the present study is 122.5 cm^{-1} and compares favourably with the values obtained from previous ambient-pressure Raman and inelastic neutron scattering [11–14].

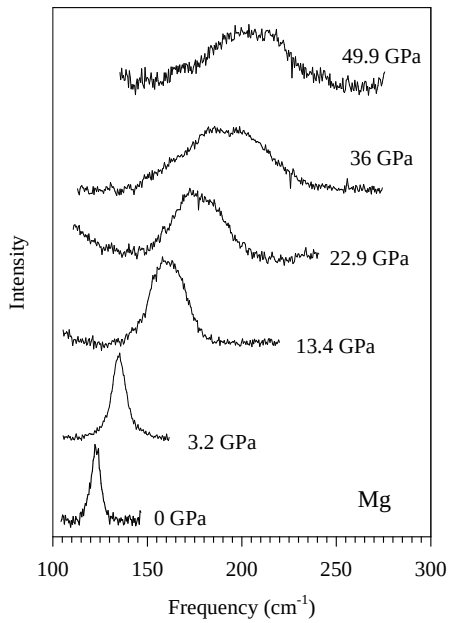

Figure 1. Raman spectra of Mg in the hcp phase at various pressures. The spectrum at 3.2 GPa was recorded in the down stroke run.

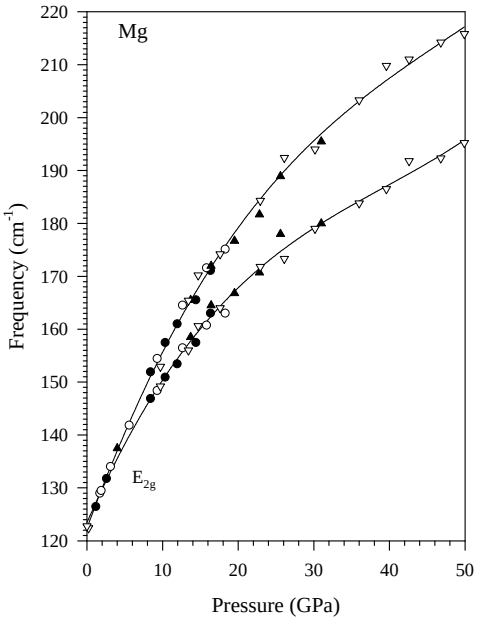

Figure 2. Pressure shift of the Raman modes of hcp Mg. The different symbols indicate different experiments. The solid circle data points were obtained by excitation with the 514.5 nm laser line. All other data were obtained by excitation with the 647.1 nm laser line. The solid lines serve as a guide for the eye.

4. Discussion

If one disregards the splitting, the observed frequency increase with pressure represents the normal pressure response of this mode, which has also been observed in the hcp phases of Zn and Si [15]. A negative pressure shift of this mode has been observed in the rare earth metals and in Zr [16], when the transition to Sm-type structure and ω-phase, repectively, is approached. In this respect the present data indicate that the hcp $\rightarrow$ bcc transition in Mg is not associated with a softening of the E_{2g} mode.

The observed broadening and splitting of this mode observed above 10 GPa is quite unusual, since at the Γ-point ($K = 0$) of the Brillouin zone in the hcp lattice there is one doubly degenerate E_{2g} mode. Also the other hcp metals investigated so far did not show this effect. One possibility could be that the known crystal structure is in error. In an early study, indications for the possible existence of a dhcp phase were found by Perez-Albuerne *et al* [17]. Though the later high-pressure x-ray diffraction study, as well as theoretical studies, confirmed the stability range of the hcp phase to 50 GPa, with the coexistence of hcp and bcc between 42 and 54 GPa [3], a subtle distortion of the hcp lattice above 10 GPa, which might not be detected due to low signal-to-background ratio in that study, cannot be excluded. Structural studies in this pressure regime taking advantage of third generation synchrotron sources and image plate techniques, which are more sensitive to subtle structural modifications, could give an answer to this question.

For Mg the generalized pseudopotential method was used to predict the pressure shift of the transverse-optic Γ-point phonon to 50 GPa in the quasiharmonic approximation [7]. Agreement with the experiment is obtained within 5 cm^{-1} over the whole pressure range, if the observed splitting is disregarded and comparison is made with the mean value of

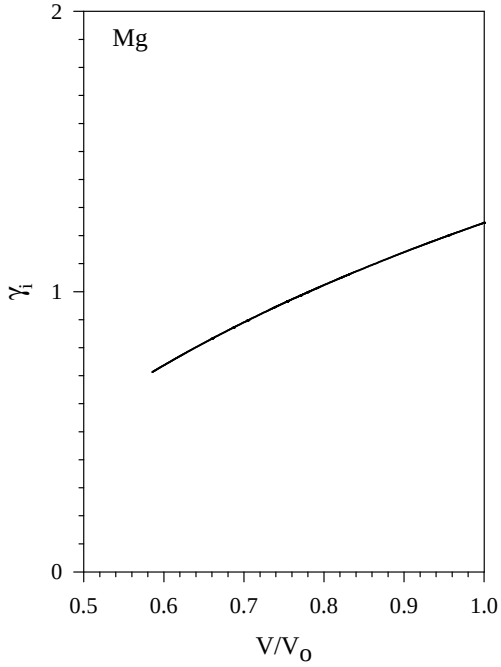

Figure 3. Volume dependence of the mode Grüneisen parameter γ.

the two components. In a recent simulation of lattice vibrations in the presence of strong anharmonicities it was demonstrated that pecularities like the symmetrically forbidden splitting of phonon branches can occur [18]. In this context it is interesting to note that evidence for anharmonic effects in Mg was provided by an investigation of the mechanism of the hcp $\rightarrow$ bcc transition using a first-principles pseudopotential method [6]. In this study the transition was described by two distortions: one corresponds to an hcp transverse phonon at the Brillouin-zone edge A, and the other characterizes the internal hexagonal angles. A strong correlation between these parameters was found near the transition, which causes strong anharmonic effects in the zone edge phonon mode. In this respect a theoretical study of the phonon frequencies, which incorporates anharmonic effects beyond the quasiharmonic approximation would be quite helpful.

One has also to consider that in Raman studies of polycrystalline samples the recorded Raman signals are not strictly restricted to zero wavevector. Due to the random orientation of the crystallites in polycrystalline samples the wavevector of the observed Raman phonons covers a maximum range Δk around the Γ-point with

$$\Delta k = 2\omega n/c \tag{1}$$

where ω is the frequency of the exciting light, n is the index of refraction of the sample and c is the speed of light [19]. The observed broadening and splitting might then indicate that along certain directions in the Brillouin zone the degeneracy or near degeneracy at ambient pressure for $K \neq 0$ in a small interval around $K = 0$ is lifted at higher compression. Wave-vector dependent phonon energies in different high-symmetry directions around the Γ-point were determined recently by single-crystal Raman scattering in hcp Os at ambient pressure [20]. For this metal a strong frequency dispersion of 4 cm^{-1} around $K = 0$ was found for certain symmetry directions.

The alcohols used as pressure transmitting media in this study are not hydrostatic above 10 GPa and the observed anomaly might be due to pressure inhomogeneities. At 15 GPa the pressure differences throughout the gasket hole (150 μm in diameter) were 0.8 GPa which increased to 3 to 4 GPa at maximum pressure. The diameter of the probed sample region is 15–20 μm, giving rise to a pressure gradient of a few tenths of a GPa in the probed sample region at maximum pressure. In a study of the E_{2g} mode of Zn with a 4:1 methanol:ethanol mixture as pressure transmitting medium, an increase of the halfwidth from 6.5 cm^{-1} at normal pressure to 9 cm^{-1} at 58 GPa was observed [21]. In a study with no pressure transmitting medium, the half width of the Zn mode increased to 15 cm^{-1} at 61 GPa [21]. For Mg in the present study at 15 GPa, where the pressure inhomogeneities are still small, the halfwidth increased rapidly to 23 cm^{-1} from 6 cm^{-1} at normal pressure. These considerations suggest that the broadening and splitting observed in Mg are not caused by pressure inhomogeneities.

The mode Grüneisen parameter $\gamma_i = -\mathrm{d}\ln\nu_i/\mathrm{d}\ln V$ was determined by fitting the $\ln\nu(P) - \ln V(P)$ values to a second order polynomial. Here the observed splitting is disregarded and the mean values of the frequencies of the two components were taken. The $V(P)$ values were obtained using a Murnaghan equation of state with bulk modulus $B_0 = 36$ GPa and its pressure derivative $B_0' = 3.11$ [22]. In figure 3 the mode Grüneisen parameter thus determined is shown as a function of volume. A decrease of γ_i from 1.25 at ambient pressure to 0.7 at 50 GPa is observed which corresponds to a decrease by approximately 40% in the investigated pressure range. These values for the mode Grüneisen parameter compare favourably with the thermodynamic Grüneisen parameters of Na and K [23]. The experimental mode Grüneisen parameter is $\approx 1/3$ lower than the calculated thermodynamic Grüneisen parameter [7] over the same compression range. Since the theoretical thermodynamic Grüneisen parameter is in good agreement with the experimental value available only for ambient pressure, it implies that some modes must exhibit a stronger frequency shift under pressure than the $K = 0$ TO mode.

5. Summary

The zone-centre transverse-optical phonon mode of hcp Mg shows unusual broadening and splitting with increasing pressure, not observed in other hcp metals and also not reproduced by theoretical studies so far. This unusual behaviour is discussed with respect to possible structural distortions of the hcp lattice, anharmonic effects or unusual dispersion in small intervals around the Γ-point. The present data indicate that further structural and lattice-dynamical studies, both experimentally and theoretically, are necessary to understand these special aspects in the behaviour of compressed Mg.

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